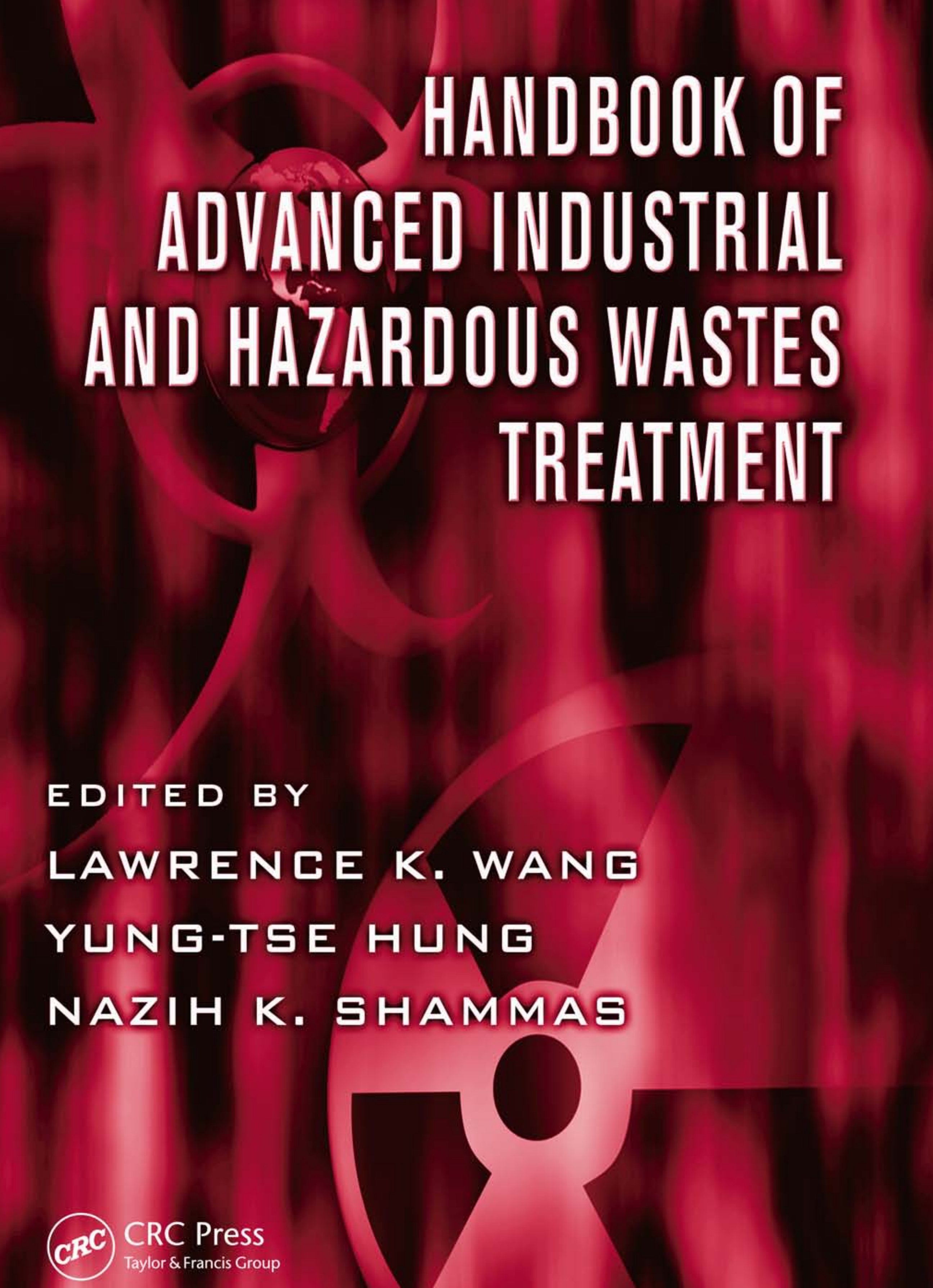

HANDBOOK OF ADVANCED INDUSTRIAL AND HAZARDOUS WASTES TREATMENT

EDITED BY

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Preface

Environmental managers, engineers, and scientists who have had experience with industrial and hazardous waste management problems have noted the need for a handbook series that is comprehensive in its scope, directly applicable to daily waste management problems of specific industries, and widely acceptable by practicing environmental professionals and educators.

Many standard industrial waste treatment and hazardous waste management texts adequately cover a few major industries, for conventional in-plant pollution control strategies, but no one book, or series of books, focuses on new developments in innovative and alternative environmental technology, design criteria, effluent standards, managerial decision methodology, and regional and global environmental conservation.

In 2004, CRC Press published the first volume in the series, *Handbook of Industrial and Hazardous Wastes Treatment.* That first handbook emphasized an in-depth presentation of environmental pollution sources, waste characteristics, control technologies, management strategies, facility innovations, process alternatives, costs, case histories, effluent standards, and future trends for each industrial and commercial operation (such as the pharmaceutical industry, oil refineries, metal plating and finishing industry, photographic processing industry, soap and detergent industry, textile industry, phosphate industry, pulp and paper mills, dairies, seafood processing factories, meat processing plants, olive oil processing plants, potato production operations, pesticide industry, livestock industry, soft drink factories, explosive chemical plants, rubber industry, timber industry, and power industry) and an in-depth presentation of methodologies, technologies, alternatives, regional effects, and global effects of each important industrial pollution control practice that may be applied to all industries (such as industrial ecology, pollution prevention, in-plant hazardous waste management, site remediation, groundwater decontamination, and stormwater management).

In a deliberate effort to complement the 2004 handbook as well as other industrial waste treatment and hazardous waste management texts, this 2010 *Handbook of Advanced Industrial and Hazardous Wastes Treatment* covers many new advances in the field of industrial and hazardous waste treatment, such as waste minimization, cleaner production, legislation and regulations for hazardous wastes, hazardous industrial wastes characteristics, soil remediation, brownfield sites restoration, bioremediation, enzymatic process, underground storage tank releases, biological treatment processes, deep-well injection, methyl tertiary-butyl ether, fuel oxygenates, evapotranspiration, landfill cover, hazardous leachate treatment, secondary flotation, solid waste treatment, and so on. This handbook also gives an in-depth presentation of hazardous industrial treatment and management technologies used in many new industries and operations that were not covered in the previous handbook, such as the aluminum forming industry, coil coating industry, nickel–chromium plating plants, porcelain enameling industry, pentachlorophenol processing facilities, pulp and paper industry, and inorganic chemical industry. Many industries are covered for the very first time.

Special efforts were made to invite experts to contribute chapters in their own areas of expertise. Since the field of industrial hazardous waste treatment is very broad, no one can claim to be an expert in all industries; collective contributions are better than a single author's presentation for a handbook of this nature.

This 2010 *Handbook of Advanced Industrial and Hazardous Wastes Treatment* and its sister book, 2004 *Handbook of Industrial and Hazardous Wastes Treatment*, are to be used together as college textbooks as well as reference books for environmental professionals. They feature the major industries and hazardous pollutants that have significant effects on the environment. Professors, students, and researchers in environmental, civil, chemical, sanitary, mechanical, and public health engineering and science will find valuable educational materials here. The extensive bibliographies for each industrial waste treatment or practice should be invaluable to environmental managers and researchers who need to trace, follow, duplicate, or improve on a specific industrial hazardous waste treatment practice.

A successful modern hazardous industrial waste treatment program for a particular industry will include not only traditional water pollution control but also air pollution control, noise control, soil conservation, site remediation, radiation protection, groundwater protection, hazardous waste management, solid waste disposal, and combined industrial–municipal waste treatment and management. In fact, it should be a holistic environmental control program. Another intention of this handbook series is to provide technical and economical information on the development of the most feasible total environmental control program that can benefit both industry and local municipalities. Frequently, the most economically feasible methodology is a combined industrial–municipal waste treatment.

Lawrence K. Wang, Massachusetts
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Editors

Lawrence K. Wang has over 25 years of experience in facility design, plant construction, operation, and management. He has expertise in water supply, air pollution control, solid waste disposal, water resources, waste treatment, hazardous waste management, and site remediation. He is a retired dean/director of both the Lenox Institute of Water Technology and Krofta Engineering Corporation, Lenox, Massachusetts, and a retired vice president of Zorex Corporation, Newtonville, New York. Dr. Wang is the author of over 700 technical papers and 24 books, and is credited with 24 U.S. patents and 5 foreign patents. He received his BSCE degree from National Cheng-Kung University, Taiwan; his MS degrees from both the Missouri University of Science and Technology, at Rolla, Missouri, and the University of Rhode Island at Kingston, Rhode Island; and his PhD degree from Rutgers University, New Brunswick, New Jersey.

Yung-Tse Hung has been a professor of civil engineering at Cleveland State University since 1981. He is a fellow of the American Society of Civil Engineers. He has taught at 16 universities in 8 countries. His primary research interests and publications have been involved with biological wastewater treatment, industrial water pollution control, industrial waste treatment, and municipal wastewater treatment. He is now credited with over 450 publications and presentations on water and wastewater treatment. Dr. Hung received his BSCE and MSCE degrees from National Cheng-Kung University, Taiwan, and his PhD degree from the University of Texas at Austin. He is the editor of the *International Journal of Environment and Waste Management*, the *International Journal of Environmental Engineering*, and the *International Journal of Environmental Engineering Science.*

Nazih K. Shammas has been an environmental expert, professor, and consultant for over 40 years. He is an ex-dean and director of the Lenox Institute of Water Technology, and advisor to the Krofta Engineering Corporation, Lenox, Massachusetts. Dr. Shammas is the author of over 250 publications and 12 books in the field of environmental engineering. He has experience in environmental planning, curriculum development, teaching and scholarly research, and expertise in water quality control, wastewater reclamation and reuse, physicochemical and biological treatment processes, and water and wastewater systems. He received his BE degree from the American University of Beirut, Lebanon; his MS from the University of North Carolina at Chapel Hill; and his PhD from the University of Michigan at Ann Arbor.

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1 Waste Minimization and Cleaner Production

Nazih K. Shammas and Lawrence K. Wang

CONTENTS

1.1 INTRODUCTION AND BACKGROUND

For many years a large part of industrial pollution control has been carried out essentially on an end-of-pipe basis, and a wide range of unit processes (physical, chemical, and biological) have been developed to service the needs of the industry. Such end-of-pipe systems range from low intensity to high intensity arrangements, from low technology to high technology, and from low cost to high cost. Most end-of-pipe systems are destructive processes in that they provide no return to the operating company in terms of increased product yield or lower operating cost, except in those circumstances where reduced charges would then apply for discharge to a municipal sewer.

It should be noted that in all cases the size (and hence cost) of end-of-pipe treatment has a direct relationship to both the volume of effluent to be treated and the concentration of pollutants contained in the discharge. For example, the size of most physicochemical reactors (balancing, neutralizing, flocculation, sedimentation, flotation, oxidation, reduction, etc.) is determined by hydraulic factors such as surface loading rate and retention time.

The size of most biological reactors is determined by pollution load, for example, kg BOD (biochemical oxygen demand) or COD (chemical oxygen demand) per kg MLVSS (mixed liquor volatile suspended solids) per day in the case of suspended growth type systems, and kg BOD or COD per m^3 of media or reactor volume in the case of fixed-film type systems.

It is evident therefore that the reduction of emissions by action at source can have a significant impact on the size and hence the cost of an end-of-pipe treatment system. On this basis, it should be established practice in industry that no capital expenditure for end-of-pipe treatment should be made until all waste reduction opportunities have been exhausted. This has not often been the case, and many treatment plants have been built that are both larger and more complicated than is necessary.

Increased environmental pressure and awareness now require industry to meet tighter environmental standards on a global basis. In many countries, such requirements generally cannot be met by using conventional end-of-pipe solutions without seriously impacting on the economic viability of the individual industries. Accordingly, much more emphasis has to be placed on waste reduction as a necessary first step to reduce to a minimum the extent of the end-of-pipe treatment to be provided. A full understanding of the nature of all wastestreams (aqueous, gaseous, or solid) and the exact circumstances by which they are generated must be developed in order to achieve cleaner production and to eliminate or minimize pollution before it arises. This is a necessity for industry today.

Waste minimization is a policy mandated by the U.S. Congress in the 1984 Hazardous and Solid Waste Amendments[1] (HSWA) to the Resource Conservation and Recovery Act (RCRA).[2,3] The U.S. Environmental Protection Agency (U.S. EPA) has established an Office of Pollution Prevention to promote waste reduction. On February 26, 1991, U.S. EPA published a pollution prevention strategy aimed at providing guidance and direction for incorporating pollution prevention into U.S. EPA programs.[4]

Pollution prevention practices have become part of the U.S. National Pollutant Discharge Elimination System (NPDES) program, working in conjunction with best management practices (BMPs) to reduce potential pollutant releases. Pollution prevention methods have been shown to reduce costs as well as pollution risks through source reduction and recycling/reuse techniques.[5]

Best management practices are inherently pollution prevention practices. Traditionally, BMPs have focused on good housekeeping measures and good management techniques intending to avoid contact between pollutants and water media as a result of leaks, spills, and improper waste disposal.

However, based on the authority granted under the regulations, BMPs may encompass the entire universe of pollution prevention, including production modifications, operational changes, materials substitution, materials and water conservation, and other such measures.[5]

U.S. EPA endorses pollution prevention as one of the best means of pollution control. In 1990, the Pollution Prevention Act[6] was enacted and set forth a national policy that "pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner."

Significant opportunities exist for industry to reduce or prevent pollution through cost-effective changes in production, operation, and raw materials use. In addition, such changes may offer industry substantial savings in reduced raw materials, pollution control, and liability costs, as well as protect the environment and reduce health and safety risks to workers. Where pollution prevention practices can be both environmentally beneficial and economically feasible, one would consider their implementation to be prudent.

Improvement in environmental performance and production efficiency in both the short and in the long term are expected to be achieved by means of the following steps[7,8]:

1. *Effective management and training.* This is the introduction of a sustained approach to pollution control and environmental management. It will be achieved as a result of senior management's commitment to
   (a) Specific objectives for overall environmental performance, including specific performance targets on a process by process basis including utilities
   (b) Cradle to grave philosophy in product design
   (c) A management structure that positively links production, pollution control, and the environment with clearly defined responsibilities and lines of communication to managing director level, supported by
      i. An initial audit of present production methods, housekeeping practices, procedures and factory support services to identify opportunities for waste reduction and optimized end-of-pipe treatment
      ii. Regular environmental audits to ensure standards are being maintained
      iii. Monitoring programs and procedures designed to continuously assess process efficiency and environmental performance
      iv. A database with relevant information and documentation on performance and on efficient use of resources and reduction of waste production
      v. Training procedures for technical and operational personnel
      vi. General environmental awareness programs at all levels within the company hierarchy.
2. *In-house process control.* This comprises the achievement of optimum efficiency in relation to production and processing methods including the introduction, where feasible, of cleaner processes (alternative technology) or processing methods (substitute materials and/or reformulations, process modifications, and equipment redesign).
3. *Good housekeeping.* This involves the rethinking of localized habitual practice and the identification and implementation of new practices and procedures.
4. *Water conservation/reuse/recycle.* In this, the aim is to achieve optimum efficiency in relation to water use, looking at the possible elimination of use, the regulation of use to only specific requirements, sequential use, or reuse and in-process recycling.
5. *Waste recovery and/or reuse.* This comprises the identification and implementation of opportunities to recover process chemicals and materials for direct reuse or for reuse elsewhere through renovation or conversion technology.

As a result of the foregoing the industrial facility will do the following:

1. Decrease costs for raw materials, energy, and waste treatment/disposal
2. Improve the working environment, thus decreasing costs associated with workers' health
3. Acquire the favorable image of a company that protects the environment
4. Create a potential for production expansion by being one step ahead of environmental regulations

The country as a whole will benefit from:

1. Decreased pollution loadings
2. Decreased consumption of raw materials and energy
3. Decreased costs associated with workers' safety and health

1.2 GOOD HOUSEKEEPING

Good housekeeping is essentially the maintenance of a clean, orderly work environment. Maintaining an orderly facility means that materials and equipment are neat and well kept to prevent releases to the environment. Maintaining a clean facility involves the expeditious remediation of releases to the environment. Together, these terms—clean and orderly—define a good housekeeping program.[5]

Maintaining good housekeeping is the heart of a facility's overall pollution control effort. Good housekeeping cultivates a positive employee attitude and contributes to the appearance of sound management principles at a facility. Some of the benefits that may result from a good housekeeping program include ease in locating materials and equipment; improved employee morale; improved manufacturing and production efficiency; lessened raw, intermediate, and final product losses due to spills, waste, or releases; fewer health and safety problems arising from poor materials and equipment management; environmental benefits resulting from reduced releases of pollution; and overall cost savings.

1.2.1 FUNCTION OF A GOOD HOUSEKEEPING PROGRAM

Good housekeeping measures can be easily and simply implemented. Some examples of commonly implemented good housekeeping measures include the orderly storage of bags, drums, and piles of chemicals; prompt cleanup of spilled liquids to prevent significant runoff to receiving waters; expeditious sweeping, vacuuming, or other cleanup of accumulations of dry chemicals to prevent them from reaching receiving waters; and proper disposal of toxic and hazardous wastes to prevent contact with and contamination of storm water runoff.

The primary impediment to a good housekeeping program is a lack of thorough organization. To overcome this obstacle, a three-step process can be used[5]:

1. Determine and designate an appropriate storage area for every material and every piece of equipment
2. Establish procedures requiring that materials and equipment be placed in or returned to their designated areas
3. Establish a schedule to check areas to detect releases and ensure that any releases are being mitigated

The first two steps act to prevent releases that would be caused by poor housekeeping. The third step acts to detect releases that have occurred as a result of poor housekeeping.

1.2.2 CREATION OF A GOOD HOUSEKEEPING PROGRAM

As with any new or modified program, the initial stages will be the greatest hurdle; ultimately, however, good housekeeping should result in savings that far outweigh the efforts associated with initiation and implementation. Generally, a good housekeeping plan should be developed in a manner that creates employee enthusiasm and thus ensures its continuing implementation. The first step in creating a good housekeeping plan is to evaluate the organization of the facility site. In most cases, a thorough release identification and assessment has already generated the needed inventory of materials and equipment and has determined their current storage, handling, and use locations. This information, together with that from further assessments, can then be used to determine if the existing location of materials and equipment is adequate in terms of space and arrangement.

Cramped spaces and those with poorly placed materials increase the potential for accidental releases due to constricted and awkward movement in these areas. A determination should be made as to whether materials can be stored in a more organized and safer manner (e.g., stacked, stored in bulk as opposed to individual containers, etc.). The proximity of materials to their place of use should also be evaluated. Equipment and materials used in a particular area should be stored nearby for convenience, but should not hinder the movement of workers or equipment. This is especially important for waste products. Where waste conveyance is not automatic, waste receptacles should be located as close as possible to the waste generation areas, thereby preventing inappropriate disposal leading to environmental releases.

Appropriately designated areas (e.g., equipment corridors, worker passageways, dry chemical storage areas) should be established throughout the facility. The effective use of labeling is an integral part of this step. Signs and adhesive labels are the primary methods used to assign areas. Many facilities have developed innovative labeling approaches, such as color coding the equipment and materials used in each particular process. Other facilities have stenciled outlines to assist in the proper positioning of equipment and materials.

Once a facility site has been organized in this manner, the next step is to ensure that employees maintain this organization. This can be accomplished through explaining organizational procedures to employees during training sessions, distributing written instructions, and, most importantly, demonstrating by example.

Support of the program must be demonstrated, particularly by responsible facility personnel. Shift supervisors and others in positions of authority should act quickly to initiate activities to rectify poor housekeeping. Generally, employees will note this dedication to the good housekeeping program and will typically begin to initiate good housekeeping activities without prompting. Although initial implementation of good housekeeping procedures may be challenging, these instructions will soon be followed by employees as standard operating procedures.

Despite good housekeeping measures, the potential for environmental releases remains. Thus, the final step in developing a good housekeeping program involves the prompt identification and mitigation of actual or potential releases. Where potential releases are noted, measures designed to prevent release can be implemented. Where actual releases are occurring, mitigation measures such as those described below may be required.

Mitigative practices are simple in theory: the immediate cleanup of an environmental release lessens chances of spreading contamination and lessens impacts due to contamination. When considering choices for mitigation methods, a facility must consider the physical state of the material released and the media to which the release occurs. Generally, the ease of implementing mitigative actions should also be considered. For example, diet, crushed stone, asphalt, concrete, or other covering may top a particular area. Consideration as to which substance would be easier to clean in the event of a release should be evaluated.

Conducting periodic inspections is an excellent method to verify the implementation of good housekeeping measures. Inspections may be especially important in the areas identified in the release identification and assessment step where releases have previously occurred.

It may not always be possible to immediately correct poor housekeeping. However, deviations should occur only in emergencies. The routines and procedures established as a part of the program should allow for adequate time to conduct good housekeeping activities.[5]

1.2.3 Good Housekeeping: What to Do

1. Integrate a recycling/reuse and conservation program in conjunction with good housekeeping. Include recycle/reuse opportunities for common industry wastes such as paper, plastic, glass, aluminum, and motor oil, as well as facility-specific substances such as chemicals, used oil, dilapidated equipment, and so on into the good housekeeping program. Provide reminders of the need for conservation measures including turning off lights and equipment when not in use, moderating heating/cooling and conserving water.
2. When reorganizing, keep pathways and walkways clear with no protruding containers.
3. Create environmental awareness by developing a regular (e.g., monthly) good housekeeping day.
4. Develop slogans and posters for publicity. Involve employees and their families by inviting suggestions for slogans and allowing children to develop the facility's good housekeeping posters.
5. Provide suggestion boxes for good housekeeping measures.
6. Develop a competitive program that may include company-wide competition or facility-wide competition. Implement an incentive program to spark employee interest (i.e., one half day off for the shift that best follows the good housekeeping program).
7. Conduct inspections to determine the implementation of good housekeeping. These may need to be conducted more frequently in areas of most concern.
8. Pursue an ongoing information exchange throughout the facility, the company, and other companies to identify beneficial good housekeeping measures.
9. Maintain necessary cleanup supplies (i.e., gloves, mops, brooms, etc.).
10. Set job performance standards that include aspects of good housekeeping.

1.3 STRATEGY FOR WASTE REDUCTION

Pollution prevention initiatives tend to progress in three separate stages, beginning with a waste audit and associated training and awareness raising, which brings forward the most easily implemented and cost-effective waste reduction measures, as described below. The strategy should be for each company to move through the first stage and get started on a long-term and sustained pollution prevention effort involving all the three stages.

A way to classify wastestreams is to consider them "intrinsic," "extrinsic," or somewhere in-between. Intrinsic wastes are inherent in the fundamental process configuration, whereas extrinsic ones are associated with the auxiliary aspects of the operation.

Intrinsic wastes are built into the original product and process design. These represent impurities present in the reactants, byproducts, coproducts, residues inherent in the process configuration, and spent materials employed as part of the process. Becoming free of intrinsic wastes requires modifying the process system itself, often significantly. Such changes tend to require a large amount of research and development, major equipment modifications, improved reaction (e.g., catalytic) or separation technology—and time.

Extrinsic wastes are more functional in nature and are not necessarily inherent to a specific process configuration. These may occur as a result of unit upsets, selection of auxiliary equipment, fugitive leaks, process shutdown, sample collection and handling, solvent selection, or waste handling practices. Extrinsic wastes can be, and often are, reduced readily through administrative controls, additional maintenance or improved maintenance procedures, simple recycling, minor materials substitution or equipment changes, operator training, managerial support, and changes in auxiliary aspects of the process.

A recent study of programs for existing facilities of several companies reveals that a pollution-prevention initiative will tend to progress in stages.[9] After a training period and an audit of the wastes in the process, the first reduction efforts emphasize the simple, obvious, and most cost-effective alternatives and are generally directed at extrinsic wastes.

1.3.1 Phase I

Phase I efforts include good housekeeping and standard operating practices, waste segregation (separating hazardous wastes from trash), simple direct recycling of materials without treatment, and the other practices noted above. Emphasis is on the operation rather than the underlying system. Activities carried out during this period usually generate a good and immediate economic return on any pollution-prevention investment (return on investment, ROI).

1.3.2 Phase II

If the program continues and additional reductions are desired, more expensive and more complex projects begin to emerge (Phase II). These are often associated with equipment modifications, process modifications and process control and may include the addition or adaptation of auxiliary equipment for simple source treatment, possibly for recycle. This phase usually has little immediate ROI, and more inclusive approaches to assessing the economics of the operation (estimating costs for waste handling, long-term liability, risk) are needed to justify the continued pollution-prevention operation.

1.3.3 Phase III

The program becomes mature (Phase III) when it starts to address the intrinsic wastes through more complex recycling and reuse activities, more fundamental changes to the process, changes in the raw material or catalysts, or reformulation of the product. Emphasis has now shifted to the process itself.

Because of the long payback required for some of these Phase III changes, they are best introduced as a new unit or process is being developed. Justifying fundamental changes to the process as part of the pollution-prevention program *per se* is particularly difficult—the first construction-cost estimate of process plants involving new technology is usually less than half of the final cost, with many projects experiencing even worse performance.

The project will progress in stages, beginning with a waste audit carried out by an audit team. The audit team consists of a waste audit expert, a sector specialist, a financial expert, an economist/marketing expert, and an expert in product life-cycle assessments. The audit team also supports the project in its different stages.

The following seven outputs will be produced by the audit team[9]:

1. Availability of material balances for selected unit process operations (Table 1.1)
2. Obvious waste reduction measures identified and implementation initiated (improved housekeeping) (Table 1.2)
3. Long-term waste reduction options identified (emphasis minimization of hazardous waste) (Table 1.3)
4. Financial and environmental evaluation of waste reduction options (Table 1.4)
5. Development and implementation started on a plan to reduce wastes and increase production efficiency (Table 1.5)
6. Recommendations for equipment modifications and/or process changes to reduce wastes (Table 1.6)
7. Opportunities identified for product reformulation (Table 1.7)

TABLE 1.1
Availability of Material Balances for Selected Unit Process Operations

Activities
Undertake audit preparatory work:
1. Introduce the audit to top management
2. Select and train waste audit team
3. Identify laboratory and other equipment resources
4. Select scope of audit
5. Collect existing site plans and process diagrams
6. Preliminary survey
Determination of raw material inputs to unit operations
Record water usage
Evaluation of waste recycling
Quantify process outputs
Quantify wastewater streams
Quantify gaseous and particulate emissions
Quantify offsite waste disposal
Assemble input and output data for unit operations
Prepare material balance

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

Measurement equipment such as flow measurement gauges, sampling equipment and effluent analysis equipment is necessary for carrying out the audits. A budget provision is made to cover one set of equipment. The equipment will remain in the custody of the industrial facility.

1.4 PLANNING FOR WASTE REDUCTION

Waste reduction should be geared towards increasing production efficiency in existing industrial plants; that is, one must know what is going on inside the factory walls. In-depth knowledge about the production is essential for the implementation of a preventive approach to environmental protection that

TABLE 1.2
Obvious Waste Reduction Measures Identified and Implementation Initiated (Improved Housekeeping)

Activities
Identify opportunities for improvements in specifications and ordering procedures for raw materials
Identify opportunities for improved materials receiving operations
Identify opportunities for improvements in materials storage
Identify opportunities for improvements in material and water transfer and handling
Identify opportunities for improved process control
Identify opportunities for improved cleaning procedures
Compile a prioritized implementation plan of the most obvious waste reduction measures identified in Table 1.3

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

TABLE 1.3
Long-Term Waste Reduction Options Identified (Emphasis Minimization of Hazardous Waste)

Activities
Based on the material balance obtained in Table 1.1 for each unit operation, locate sources of hazardous waste
Identify opportunities for increased recycling through waste segregation
Identify potential for changes in process conditions
Identify opportunities for reduced raw material use
Identify opportunities for raw material substitution

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

involves waste segregation, simple recycling, process control, equipment modifications, source treatment, complex recycling, process changes, raw material changes, and even product reformulation.

Countries need to build the technical and scientific institutional capacity to develop, absorb, and diffuse pollution prevention techniques and cleaner production processes essential for a successful program. This could be done by the following[9]:

1. Demonstrating the financial and economic advantages and environmental benefits of such a program
2. Providing technical support for the design, establishment, operation, evaluation, and monitoring of pollution prevention techniques and cleaner production processes and technologies

TABLE 1.4
Financial and Environmental Evaluation of Waste Reduction Options

Activities
Determine financial implications of audit options
Calculate annual operating cost for existing processes including waste treatment and/or disposal costs
Determine potential savings for each waste reduction option: 1. Reduced raw materials costs 2. Reduced waste treatment costs 3. Reduced waste disposal costs 4. Reduced utility costs 5. Reduced maintenance costs
Determine investment required for each waste reduction option
Determine financial attractiveness of each option and rank options
Evaluate the environmental impacts of each option: 1. Effect on volume and pollutant concentration in wastes 2. Potential cross-media effects 3. Changes in toxicity, degradability, and treatability of wastes 4. Reduced use of nonrenewable resources, including energy 5. Likelihood of unsafe incidents
Prioritize options according to financial and environmental impacts

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

TABLE 1.5
Development and Implementation Started on a Plan to Reduce Wastes and Increase Production Efficiency

Activities

Organize seminar to present the results of the waste audit and its evaluation and tangible waste reductions achieved so far to plant management and to draft waste reduction plan

Establish a monitoring program to run alongside the waste reduction plan to facilitate measurement of actual improvements

Establish an internal waste charging system (cost centres at each waste-generating location)

Establish training program for:

1. Managerial and supervisory staff
2. Technical staff
3. Plan operations

Establish a database on waste discharges, resource use, and reduction of waste production and resource consumption

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

Recognizing the need to prevent pollution and minimize waste, governments, through their environmental protection agencies, should continue their catalytic role to promote, (with industry, research organizations and other relevant institutions) the establishment of a network that will allow the transfer of environmental protection technology.

The United Nations Industrial Development Organization (UNIDO) defines "cleaner production" as "the conceptual and procedural approach to production that demands that all phases of the life-cycle of products must be addressed with the objective of the prevention or minimization of short- and long-term risks to humans and the environment. A total societal commitment is required for effecting this comprehensive approach to achieving the goal of sustainable societies."[9]

The UNIDO program links existing sources of information on low and nonwaste technologies and promotes cleaner production worldwide through four primary activities: the International

TABLE 1.6
Recommendations for Equipment Modifications and/or Process Changes to Reduce Wastes

Activities

Evaluate the following equipment and/or process changes, from the standpoint of environment and safety, which could reduce wastes:

1. Reduction in transfer distances between raw material storage and process and between individual unit operations
2. Improvements in materials handling equipment (conveyors, pumps, transfer points)
3. Improved process control (monitoring and instrumentation); more automation
4. Replacement of batch operations with continuous flow or optimized sequencing of batch operations
5. Waste segregation
6. Introduction of water reuse technology or sequential water reuse.

Determine financial implications of equipment/process modification:

1. Determine investment costs
2. Revise operating costs
3. Determine financial implications of options evaluated above

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

TABLE 1.7
Opportunities Identified for Product Reformulation

Activities
1. Undertake a detailed evaluation of the industry subsector, of which the audited facility is part, within the country or region, to determine the size and type of market for its product and supplier/customer relationships
2. Evaluate the environmental impacts of the product after it leaves the plant gate (whether as an input to subsequent industrial processing or following disposal by the consumer)
3. Identify alternative products or modified products that minimize environmental impact through enhanced recycling potential or biodegradability
4. Determine the financial implications to the plant of product reformulation or modification

Source: From UNIDO, Project Document, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

Cleaner Production Information Clearing house (ICPIC), expert working groups, a newsletter, and training activities.

UNIDO has developed a manual on waste reduction auditing[10] suitable for industrial firms. The manual contains the basic methodology that will be used when assisting any industrial facility in identifying and implementing waste minimization opportunities. However, the importance of integrating an environmental strategy into the corporate strategy must be emphasized. Waste auditing is merely a tool to discover new opportunities for improvement. Without a comprehensive environmental policy embedded in the corporate policy, there will not be a sustained effort towards cleaner production.

The UNIDO project “Demonstration of Cleaner Production Techniques”[11] demonstrates that the concept of preventing wastes at their source as opposed to end-of-pipe treatment is as applicable and profitable in developing countries as in developed countries. The experience gained as well as the demonstrations produced will be of great value in the promotion and implementation of a Cleaner Production Program.

1.5 AUDIT REVIEW

The audit review should cover five main areas: raw materials and utilities, processes and integrated source control, end-of-pipe emission control systems, final emissions and discharges, and storage and handling.[9,12,13] Risk category is usually identified as high, medium or low (H/M/L).

1.5.1 Raw Materials and Utilities

1. Are all raw materials used onsite documented in an inventory? Provide a schedule and identify the sources of raw materials.
2. Has one individual been nominated to be responsible for the maintenance of the inventory?
3. Are records kept on the quantities of raw materials used and unit costs?
4. Has an environmental assessment been carried out on all the raw materials used?
5. Has environmental assessment documentation been provided?
6. Has a risk category for each raw material used been identified?
7. Has the potential for using alternative, less damaging materials been considered?
8. Has the potential for the optimum use of raw materials through conservation of resources to minimization of losses been considered?
9. Has the potential for reuse/recycle/recovery been considered for all materials in use or likely to be introduced?
10. Are disposal requirements and implications considered before introducing any materials?

1.5.2 PROCESSES AND INTEGRATED SOURCE CONTROL

1. Are all processes used onsite documented in an inventory? Provide a schedule of processes and identify the risk category.
2. Has an individual been nominated to be responsible for the maintenance of this inventory? Identify a nominated individual and identify the risk category.
3. Has an environmental impact assessment been carried out for all unit processes? Provide details of the assessments and identify the risk category for each process.
4. Have all hazards associated with the use of process materials been identified, for example, identifying a schedule of risks? Identify a risk category on a hazard-by-hazard basis.
5. Has the potential for using alternative, less damaging processes been considered? Identify changes already introduced and identify the potential for further change.
6. Has consideration been given to the conservation of water through application of integrated source control on a process-by-process basis, for example, conservation of water, reuse of water, recycling of water?
7. Has consideration been given to the avoidance or minimization of waste through the application of integrated source control on a process-by-process basis, that is, minimization of process solution losses through redesign of working procedures or minimization of process solution losses through the application of direct recovery procedures?
8. Has consideration been given to the recovery of materials through the application of integrated source control on a process-by-process basis, for example, direct or indirect recovery of materials by sidestream treatment, process solution enhancement through sidestream removal of contaminants, conversion of waste to byproduct of value?
9. Are records kept of specific raw material usage on a process-by-process basis?

1.5.3 END-OF-PIPE EMISSION CONTROL SYSTEMS

1. Are design details and specifications for end-of-pipe emission control systems fully documented in an inventory? Provide details of all end-of-pipe control systems (for aqueous emissions, gaseous emissions, and waste). Identify the risk category.
2. Has an individual been nominated to be responsible for the maintenance of this inventory? Identify a nominated individual and identify the risk category.
3. Are end-of-pipe emission control systems monitored on a regular basis to ensure compliance with design requirements (inputs and outputs)? Provide monitoring information over the last 12 months. Identify the risk category on a system-by-system basis.
4. Have all end-of-pipe systems been regularly checked for integrity and correctness of operation? Provide reports for the last 12 months. Identify a risk category in relation to integrity on a system-by-system basis.
5. Are alternative processes available that would further reduce environmental impact on a technical and economic basis? Identify potential opportunities. Identify the risk category.

1.5.4 FINAL EMISSIONS AND DISCHARGES

1. Are all emissions and discharges documented in an inventory, for example, process effluent domestic wastewater, cooling water, stack emissions, hazardous wastes, nonhazardous wastes? Provide a schedule of emissions. Identify the risk category.
2. Has one individual been nominated responsible for the maintenance of this inventory? Identify a nominated individual. Identify the risk category.
3. Are emissions and discharges to the sewer, surface water or groundwater controlled by regulations? Provide details of the relevant regulations. Provide details of the specific emission standards required. Identify the risk category.

4. Are final emissions and discharges to the sewer, surface water, or groundwater fully quantified and characterized on an ongoing basis? Provide monitoring data on the relevant emissions and discharges for the last 12 months. Identify the risk category.
5. Do emissions and discharges to the sewer, surface water, or groundwater fully comply with relevant regulations? Provide data on the extent of compliance. Identify the risk category on an emission-by-emission basis.
6. Are emissions and discharges to atmosphere controlled by regulations? Provide details of the relevant regulations. Provide details of the specific emission standards required. Identify the risk category.
7. Are the final emissions and discharges to atmosphere fully quantified and characterized on an ongoing basis? Provide monitoring data on relevant emissions and discharges for the last 12 months.
8. Do emissions and discharges to atmosphere fully comply with relevant regulations? Provide data on the extent of compliance. Identify the risk category on an emission-by-emission basis.
9. Are emissions and discharges of waste to offsite disposal controlled by regulations? Provide details of the relevant regulations. Provide details of the specific controls and requirements. Identify the risk category.
10. Are emissions and discharges to offsite disposal fully quantified and characterized on an ongoing basis? Provide monitoring data on all disposal arrangements for the last 12 months. Identify the risk category.
11. Do emissions and discharges of waste to offsite disposal fully comply with relevant regulations? Provide data on the extent of compliance. Identify the risk category on a waste type basis.
12. Are the contractors who are responsible for disposal competent? Provide evidence. Identify the risk category.
13. Do all waste-handling procedures comply with existing legislation? Provide confirmation of compliance. Identify the risk category.
14. Are records kept of the fate of wastes produced onsite? Provide documentation for the last 12 months. Identify the risk category.
15. Are records kept on the amount of waste generated per unit of production? Provide specific waste generation data for the last 12 months. Identify the risk category.
16. Are contingency/emergency plans in place in the event of accidental emission/discharge? Provide documentary evidence. Identify the risk category.

1.5.5 STORAGE AND HANDLING

1. Does an inventory exist for all materials (raw materials, products, byproducts, and waste materials) stored onsite? Provide a schedule of materials stored onsite. Identify the risk category.
2. Have all legal requirements associated with storage and handling of materials been identified? Provide schedules of applicable legal requirements. Provide details on how the regulations are enforced. Identify the risk category.
3. Are raw process and waste materials stored in a safe and appropriate manner; for example, are bulk acids in tanks bunded with secondary containment, are flammable materials in a fire-protected, ventilated store, are powders and pellets in areas fitted with dust extraction segregation of noncompatible materials? Provide details of existing storage arrangements, inducing plans and specifications. Identify risk areas. Identify the risk category.
4. Has consideration been given to the requirements for segregation of incompatible materials? Provide details on the type of wastes stored in specific areas. Identify risk areas. Identify the risk category.
5. Are all stored materials labeled clearly and correctly? Identify a schedule of omissions. Identify the risk category.

6. Has consideration been given to the measures required to contain or monitor for spills or leaks, for example, provision of adequate bund capacity, use of sealants, provision of blind gully pots, atmospheric vapor/gas monitoring, groundwater monitoring, surface water monitoring? Provide details on existing arrangements for all storage areas, including drawings and specifications where available. Identify risk areas. Identify the risk category.
7. Has the integrity of raw material, process, and waste storage areas been checked on a regular basis, for example, ground quality monitoring, inspection of tanks, containers, bunds, and so on? Provide details and records. Identify the risk category.

1.6 CLEANER PRODUCTION

Since the late 1980s, several developed countries have made major public sector commitments to build awareness of cleaner production, also referred to as pollution prevention and waste minimization. These commitments, most notably in Denmark, the Netherlands, the U.K. and the U.S., have led the private sector to investigate and implement pollution prevention measures for existing processes and products. As a result, cleaner production is now seen in these countries as a potentially cost-effective complement to pollution abatement in meeting environmental standards.

There have been several efforts to transfer the experience of developed countries in this field to developing countries. All of these efforts are examples of technology transfer (i.e., the transfer of knowledge, skills, equipment and so on) to achieve a particular objective: the reduction of pollution intensity in the industrial sector of developing countries.

1.6.1 Barriers to Cleaner Production

National pollution control programs implemented by UNIDO aim to influence national policies on the reduction of industrial pollution in developing countries as well as to change the approach of individual entrepreneurs to this problem.[14] National environmental policies for the reduction of industrial pollution consist of discharge standards and implementation schedules based on the pollution abatement potential of end-of-pipe technologies. They do not recognize the considerable potential of source reduction for meeting discharge standards and for minimizing the costs of installing and operating pollution abatement technologies. In turn, enterprises, particularly small and medium enterprises (SMEs), are not concerned about environmental matters (or even waste minimization), and when they are confronted with government regulations respond in one of two ways.[15] Either they make no investment in end-of-pipe technology, claiming that it is impossible given their financial situation, or they install the technology to signify compliance with environmental regulations and then fail to carry out the necessary operational and maintenance activities that would actually reduce pollutants.

These national policies and entrepreneurial approaches reflect the dominant strategy for industrial environmental management in developed countries. Primary reliance on end-of-pipe pollution abatement has been the basis for industrial environmental management in most developed countries since the late 1970s. Although it has been effective in reducing pollution from major sources and in many situations was the only way to meet regulatory deadlines, end-of-pipe treatment has been an expensive approach and has not managed to reduce pollution from all sources. More recently, some developed countries, and industries in those countries, have been calling for cleaner production as the first choice for reducing pollution, including that from the industrial sector. Although a few companies recognized the importance of the preventive approach in the 1970s, only in the late 1980s did governments in a few developed countries begin to encourage its general application.

The problem for environmental management institutions and industrial establishments in developing countries (and in developed countries as well, but to a lesser extent) is that they are not aware of the potential of preventive measures, such as the reduction of excess process inputs and the utilization of nonproduct outputs to meet environmental norms. In some cases, these countries do not have information about cleaner production techniques and technologies and in other cases they do not have the professional staff that can convey the information or adapt it to a given industrial situation. In still other cases, they do not think that cleaner production techniques and technologies are appropriate for their situations, because they are heavily invested in pollution control technology.

The limited utilization of cleaner production techniques and technologies in developing countries, in spite of their significant potential for waste minimization because of old and inefficient equipment, has a number of causes[16,17]:

1. A legislative and regulatory regime that does not assign priority to cleaner production
2. Confusion over the difference between cleaner technology and end-of-pipe control
3. A lack of knowledge (or awareness) of the financial and environmental benefits of no-cost and low-cost changes, primarily good housekeeping but also small modifications to existing equipment
4. The unsuitability of some techniques and technologies for developing countries or for certain types or sizes of industry
5. The lack of information about process-specific technology options
6. A broken supply chain for many simple source-reduction technologies
7. The perception by enterprises that local environmental consulting engineers and research institutions provide inappropriate advice and information
8. A lack of technical personnel at the plant level to install and maintain techniques and technologies
9. Costs of the technology (usually not a significant constraint)
10. Cultural factors
11. The slow rate of new investment among SMEs, which lowers the rate of diffusion of new technologies

1.6.2 PROGRAM AS A RESPONSE TO BARRIERS

The Environment and Energy Branch of UNIDO and the Industry and Environment Program Activity Centre of UNEP supported pollution control programs in approximately 20 countries over a five-year period. UNIDO/UNEP played a coordinating and catalytic role in cleaner production by being a source of information on cleaner production, supporting demonstrations of cleaner production techniques and technologies, training industry and government officials, and providing policy advice on environmental management. They worked primarily with SMEs[15] in the private sector, which became the core of a network of institutions and trained local experts involved in pollution prevention activities.

The programs did several things to facilitate the transfer of technical information and technology from developed to developing countries[17]:

1. They disseminated information on cleaner production by serving as an information clearing house, publishing newsletters and holding marketing seminars in order to increase awareness.
2. They conducted sectoral and cross-sectoral in-plant demonstrations of cleaner production to show the potential of waste minimization in the country.
3. They trained in-plant personnel and consulting engineers on how to conduct waste reduction audits in order to increase the in-country capacity for such activities.
4. They prepared and distributed country-specific technical reports (a waste audit manual in the appropriate language, sector-specific guidelines and fact sheets) to allow factories interested in cleaner production to pursue relevant activities on their own.
5. They held conferences and meetings to increase awareness on the part of key policy-makers from ministries of environment and industry, environmental management agencies, and financial institutions, in the hope that they will support the adoption of appropriate institutional policies.

1.6.3 GOALS FOR CLEANER PRODUCTION PROGRAMS

1. *Demonstration.* One goal is the implementation of in-plant demonstrations that exploit the readily available source reduction measures for existing processes and products and that can inspire a small number of "innovative" enterprises to implement similar measures. Cleaner production programs in countries like the U.S. and the Netherlands[18] can be judged to have succeeded in achieving this goal, and it would probably be reasonable to assume that similar cleaner production programs initiated in developing countries, such as the NCPC program, will also succeed.
2. *Dissemination.* A second goal is the dissemination of the results of demonstration projects to a large number of plants in the industrial sector, in order to obtain a multiplier effect.
3. *Integration.* A third goal, and the one that is clearly the most significant indicator of the penetration of cleaner production techniques and technologies, is the integration of waste minimization considerations into all aspects of standard industrial practice. Only in this way will cleaner production, and for that matter any environmentally superior technology,[19] become a sustained, continuous effort to reduce the resource and pollution intensity of existing and new processes and products.

These three goals should not be seen as mutually exclusive. Each may be appropriate in a given context and form part of a continuum for measuring the success of cleaner production programs. In the short term, successful demonstration projects are necessary where there has never been a cleaner production program. In the intermediate term, dissemination of the results is necessary to stimulate enterprises to investigate and implement cleaner production measures. In the long term, integration of cleaner production into all aspects of entrepreneurial decision-making is necessary for a sustained effort.

1.7 METAL FINISHING

1.7.1 INDUSTRY PROFILE

The category of metal finishing includes manufacturers that take raw metal stock and subject it to various treatments to produce a product at, or closer to, its finished stage. Manufacturers classified as metal finishers perform similar operations that fall under a variety of standard industrial classification codes, including fabricated metal products; machinery, except electrical and electronic machinery, equipment, and supplies; transportation equipment; measuring, analyzing, and controlling instruments; photographic, medical, and optical goods; watches and clocks; and miscellaneous manufacturing industries.[5] The processes used to treat raw metal stock and, correspondingly, the wastes produced are the common link among the metal finishing category members. Some of these processes are especially amenable to BMPs; that is, implementation of BMPs is relatively easy and results in a significant reduction in the discharge of pollutants. Listed below are processes common among metal finishers and the targeted pollutants that enter wastewater streams.[5]

1. *Electroplating.* Typical wastes produced include spent process solutions containing copper, nickel, chromium, brass, bronze, zinc, tin, lead, cadmium, iron, aluminum, and compounds formed from these metals.
2. *Electroless plating.* The most common wastes produced are spent process solutions containing copper and nickel.
3. *Coating.* Depending on the coating material that is being applied, wastes of concern include spent process solutions containing hexavalent chromium, and active organic and inorganic solutions.
4. *Etching and chemical milling.* Typical solutions used in etching and milling that ultimately enter the wastestream and are of concern include chromic acid and cupric chloride.

5. *Cleaning.* Various organic and inorganic compounds enter the wastewater stream from cleaning operations.

The sources of the targeted pollutants are process solutions and raw materials that enter the wastewater stream primarily through rinsing or cleaning processes. A work piece that is removed from a process or cleaning solution is typically subjected to rinsing directly afterwards, carrying excess process contaminants, referred to as dragout, into the rinse tank. The dragout concentrates pollutants in the rinse tank, which is typically discharged into the sewer system.

Another pathway by which targeted pollutants enter the wastewater stream is through the disposal of spent batch process solutions into the sewer system. Spent solutions consist of aqueous wastes and may contain accumulated solids as well. Spent solutions are typically bled at a controlled rate into the wastewater stream. Other sources of pollutants in wastewater streams include cleanup of spills and washdown of fugitive aerosols from spray operations.

1.7.2 Effective BMPs

Numerous practices have been developed to eliminate or minimize discharges of pollutants from the metal finishing industry. Successful source reduction measures have been implemented to eliminate cyanide plating baths, as well as substitute more toxic solvents with less toxic cleaners.

In many cases, cleaning with solvents has been eliminated altogether through the use of water-based cleaning supplemented with detergents, heating, and/or agitation. Other source reduction measures have been implemented to minimize the discharges of toxic materials. For example, drain boards and splash plates have been commonly installed to prevent drips and spills. Additionally, the design of immersion racks or baskets and the positioning of parts on these racks or baskets have also been optimized to prevent trapping of solvents, acids/caustics, or plating baths.

The utilization of recycle and reuse measures has also been commonly used. Many facilities have been able to minimize water use and conserve rinsewaters and plating baths by measures including the following[20,21]:

1. Utilizing a dead rinse, resulting in the concentration of plating bath pollutants. This solution may be reused directly or further purified for reuse.
2. Conserving waters through countercurrent rinsing techniques.
3. Utilizing electrolytic recovery, customized resins, selective membranes, and adsorbents to separate metal impurities from plating baths, acid/caustic dips, and solvent cleaning operations.

These operations and measures not only extend the useful life of solutions, but also prevent or reduce the discharge of pollutants from these operations. Two industries have implemented best management practices that resulted in substantial cost savings and pollutant reductions. Emerson Electric implemented a program that resulted in savings of more than USD 910,000/yr (in terms of 2007 USD)[22] and reductions in solvents, oxygen-demanding pollutants, and metals. Best management practices implemented by a furniture manufacturer in the Netherlands resulted in a reduction in metals discharged and a decrease in water use. A detailed discussion of these programs is provided in the following paragraphs.

Emerson Electric, a manufacturer of power tools, implemented a Waste and Energy Management Program to identify opportunities for pollution prevention. An audit resulted in the following actions[5]:

1. Development of an automated electroplating system that reduced process chemical usage by 25%, process batch dumps by 20%, and wastewater treatment cost by 25%.
2. Installation of a water-based electrostatic immersion painting system to replace a solvent-based painting system. The water-based system resulted in a waste solvent reduction of more than 95%.

3. Installation of an ultrafiltration system that recovers 30 kg/d (65 lb/d) of waste oil and purifies 1135 kg/d (2500 lb/d) of alkaline cleaning solution for reuse, which resulted in a reduction of 5-day biochemical oxygen demand (BOD_5) loadings to the treatment system of 200 kg/month (370 lb/month). This avoided the need for installation of additional treatment.
4. Installation of an alkaline and detergent and steam degreasing system, which resulted in a reduction in waste solvents by 80%.

In addition to the reduction of pollutants, Emerson realized annual costs savings of USD 835,000 (in terms of 2007 USD)[22] in reduced raw material use, USD 2900 in reduced water use, and USD 68,500 in reduced waste disposal.

A furniture manufacturer in the Netherlands reduced metals in its effluent by switching to cyanide-free baths, allowing for longer drip times, using spray rinsing, reusing water, and implementing a closed cooling system. These best management practices, complemented by the installation of treatment technology, reduced metals in the effluent from 945 to 37 kg/yr. Water use also decreased from 330,000 to 20,000 m^3/yr.

1.7.3 Waste Minimization in Electroplating

The Michigan Department of Environmental Quality recommended the following procedures for waste minimization in the electroplating industry[23]:

1. Slow line to an 8 s count for removal from baths, which drastically reduces the dragout and in turn reduces waste in rinsewater. Rinsewater flow can now be reduced and ultimately the amount of sludge generated can be reduced.
2. Hold the rack for a 10 s count over the bath, during which time the majority of drips will fall. By doing this you will reduce waste in rinsewater.
3. Put drip catchers between the baths to catch and return any solution to the bath. This will also eliminate most of the buildup between the baths and ultimately reduce the cleanup time and waste generated.
4. Use the rinse bath water again in a different area. For example, if there is a line with a chromic acid etch bath followed by counter-flow rinse baths and a neutralizer bath followed by counter-flow rinse baths, use the dirtiest rinse after the neutralizer bath and pipe it to the rinse baths after the chromic acid tank. This saves water and reduces sludge.
5. Spraying or aerating the rinses uses less water and does a better job. Also, counter-flow rinses will save water.
6. Assess wastewater treatment chemicals, and replace the chemicals that create large volumes of sludge with chemicals that do not.
7. If there is a three-bath rinse after a metal bath, leave the first rinse as a dead bath and use as make-up for the metal bath.
8. Cost out a dryer for the sludge to reduce the volume of sludge.
9. Look at metal recovery online and either reuse or sell it as scrap.
10. Look at sending your waste to a smelter who recovers metals from dried sludge. Separate wastewater treatments may be needed for metal separation.

1.8 PRIMARY METALS

1.8.1 Industry Profile

Primary metal industries include facilities involved in smelting and refining of metals from ore, pig, or scrap; rolling, drawing, extruding, and alloying metals; manufacturing castings, nails, spikes, insulated wire, and cable; and production of coke. Major subcategories include blast furnaces, steel works, rolling and finishing mills; iron and steel foundries; primary and secondary smelters and refiners of nonferrous metals such as copper, lead, zinc, aluminum, tin, and nickel; establishments engaged in rolling, drawing, and extruding nonferrous metals; and facilities involved in nonferrous castings and related fabricating operations. The main processes common to metal forming operations and the wastes that are typically generated are discussed in the following[5]:

1. *Sintering.* This process agglomerates iron-bearing materials (generally fines) with iron ore, limestone, and finely divided fuel such as coke breeze. The fine particles consist of mill scale from hot rolling operations and dust generated from basic oxygen furnaces, open hearth furnaces, electric arc furnaces, and blast furnaces. These raw materials are placed on a traveling grate of a sinter machine. The surface of the raw materials is ignited by a gas and burned. As the bed burns, carbon dioxide, cyanides, sulfur compounds, chlorides, fluorides, and oil and grease are released as gas. Sinter may be cooled by air or a water spray at the discharge end of the machine, where it is then crushed, screened, and collected for feeding into blast furnaces. Wastewater results from sinter cooling operations and air scrubbing devices that utilize water.
2. *Iron making.* Molten iron is produced for steel making in blast furnaces using coke, iron ore, and limestone. Blast furnace operations use water for noncontact cooling of the furnace, stoves, and ancillary facilities and to clean and cool the furnace top gases. Other water, such as floor drains and drip legs, contribute a lesser portion of the process wastewaters.
3. *Steel making.* Steel is an iron alloy containing less than 1% carbon. Raw materials needed to produce steel include hot metal, pig iron, steel scrap, limestone, burned lime, dolomite fluorspar, and iron ores. In steel-making operations, the furnace charge is melted and refined by oxidizing certain constituents, particularly carbon, in the molten bath, to specified levels. Processes include the open hearth furnace, the electric hearth furnace, the electric arc furnace, and the basic oxygen furnace, all of which generate fumes, smoke, and waste gases. Wastewaters are generated when semiwet or wet gas collection systems are used to cleanse the furnace off gases. Particulates and toxic metals in the gases constitute the main source of pollutants in process wastewaters.
4. *Casting operations.* This subcategory includes both ingot casting and continuous casting processes. Casting refers to the procedure of turning molten metal into a specified shape. Molten metal is distributed into an oscillating, water-cooled mold, where solidification takes place. As the metal solidifies into the mold, the cast product is typically cooled using water, which is subsequently discharged.
5. *Forming operations.* Forming is achieved by passing metal through cylindrical rollers, which apply pressure and reduce the thickness of the metal. Rolling reduces ingots to slabs or blooms. Secondary operations reduce slabs or blooms to billets, plates, shapes, strips, and other forms. Cooling and lubricating compounds are used to protect the rolls, prevent adhesion, and aid in maintaining the desired temperature. Hot rolling generates wastewaters laden with toxic organic compounds, suspended solids, metals, and oil and grease. Cold rolling operations, occurring at temperatures below the recrystallization point of the metal, require more lubrication. The lubricants used in cold rolling include more concentrated oil–water mixtures, mineral oil, kerosene-based lubricants (neat oils), or graphite-based lubricants, which are typically recycled to reduce oil use and pollutant discharges. Subsequent operations may include drawing or extrusion to manufacture tube, wire, or die casting operations. In these operations, similar pollutants are discharged. Contaminated wet scrubber wastewaters may also be generated from extrusion processes but to a lesser degree than in iron- and steel-making and sintering operations.

6. *Acid pickling.* Steel products are immersed in heated acid solutions to remove surface scale during pickling operations. This generates wastewater from three sources:
   - (a) Rinsewater used to clean the product after immersion in pickling solution
   - (b) Spent pickling solution or liquor
   - (c) Wastewater from wet fume scrubbers

   The first source accounts for the largest volume of wastewater but the second source is very acidic and contains high concentrations of iron and heavy metals.
7. *Alkaline cleaning.* This process is used when vegetable, mineral, and animal fats and oils must be removed from the metal surface prior to further processing. Large-scale production or situations where a cleaner product is required may use electrolytic cleaning. The alkaline cleaning bath typically contains a solution of water, carbonates, alkaline silicates, phosphates, and sometimes wetting agents to aid cleaning. Alkaline cleaning results in the discharge of wastewaters from the cleaning solution tank, and subsequent rinsing steps. Potential contaminants include dissolved metals, solids, and oils.

1.8.2 EFFECTIVE BMPS

Primary metals manufacturing operations have experienced source reduction and recycle/reuse benefits similar to those available to metal finishing operations, including conserving waters through countercurrent rinsing techniques, and utilizing electrolytic recovery, customized resins, selective membranes, and adsorbents to separate metal impurities from acid/caustic dips and rinsewaters to thereby allow for recycle and reuse.

Some very unique opportunities are also exclusively available to the primary metals industry. For example, the use of dry air control devices and dry cast quench operations have been adopted at some facilities to avoid the generation of contaminated wastewater. Additionally, many facilities are finding markets for byproducts (e.g., sulfides resulting from nonferrous smelting operations can be converted to sulfuric acid and subsequently sold) which avoids the need to discharge these contaminants.[24,25]

California Steel Industries, Inc., located in Fontana, CA, reclaimed wastes to increase profits and address water use issues. The facility, a steel mill, is situated in an area that does not have a ready supply of process water. Also, the offsite recycling facility used to dispose of spent process pickle liquor was soon to become unavailable. As a result of these concerns, the company constructed an onsite recycling facility designed to recover ferrous chloride for resale and to reuse water and hydrogen chloride for use in steel processing operations. Environmental benefits include the recovery and resale of 20 to 25 t/d of ferrous chloride, 13,440 L/d of hydrogen chloride, and 49,200 L/d of water. In addition, corporate liability was minimized because spent liquor was no longer sent to a disposal facility.

1.9 CASE STUDIES

1.9.1 RECYCLING ZINC IN VISCOSE RAYON PLANTS BY TWO-STAGE PRECIPITATION

1.9.1.1 The Significance

Over 22.7 million kg (50 million lb) of zinc sulfate are used annually in the U.S. for the manufacture of approximately 454 million kg (one billion lb) of viscose rayon. Zinc is used as a regeneration retardant in the acid spinning bath. Because it is not consumed in any of the viscose reactions, these 22.7 million kg (50 million lb) of zinc represent process losses, through dragout by the filaments to the subsequent wash streams, filter backwashing, splashes, leaks, and the washing of equipment.[14]

The effects of zinc as a pollutant are well documented. Concentrations as low as 1.0 mg/L have been shown to be harmful to fish. In addition, there is some evidence indicating that zinc has a synergistic property when associated with copper.

Although it has been known that zinc can be precipitated from acid wastestreams by the use of lime, the resultant sludge has been of low zinc assay, contaminated with other compounds, and with very poor settling characteristics. In commercial operations, the sludge presented a disposal problem and recovery of zinc suitable for recycle was impossible.

In a U.S. EPA demonstration grant with the American Enka Company, a process for precipitating a dense sludge with high zinc assay was proven. The zinc in the sludge was recovered and recycled to the rayon manufacturing plant. This recycling of zinc was shown to have no ill effects on the rayon yarn.

There are ten viscose rayon manufacturing plants in the U.S., all of which are believed to use zinc sulfate in their spinning bath. This process greatly enhances the economics of removing this source of zinc pollution, allowing neutralization of the acid stream and recovery of the zinc while generating a good profit for industrial yarns and at a moderate cost for textile yarns.

1.9.1.2 The New Process

The key to this zinc recovery process is a two-stage precipitation,[26] with the second precipitation taking place under careful pH control, using sodium hydroxide in contact with circulating slurry of zinc hydroxide crystals. All of the zinc precipitates in the second step, most of the impurities in the first.

The elements of the process are as follows. Acid and alkaline wastestreams are collected in a neutralization tank. Here sufficient lime is added to raise the pH to 6.0. At this point, no zinc hydroxide will precipitate but a portion of the iron, calcium sulfate, and other impurities will form a light precipitate. With a coagulant aid, the mixture is sent to a clarifier where a clear overflow containing the dissolved zinc is obtained.

This clear overflow is contacted in a reactor with a circulating stream of previously precipitated sludge containing zinc hydroxide. The pH is raised subsequently to 9.5 to 10.0 with sodium hydroxide. The bulk of the zinc precipitates onto the existing crystals in the circulating slurry. At steady-state conditions, the withdrawal rate of the circulating slurry stream is made equivalent to that of the zinc being added. This dense sludge is then settled. The settled sludge of 4 to 7% zinc assay is converted back to zinc sulfate with sulfuric acid and sent back to the spinning bath. If desired, the sludge can be filtered or centrifuged to 18% solids before dissolving with acid.

The zinc content of the overflow water from the densator-reactor is set by the pH–solubility relationship of zinc in water and results in a zinc content of 0.5 to 1 mg/L at pH = 10. Once the precipitated zinc is removed from the wastewater, the pH can be readjusted to a lower value.

1.9.1.3 The Economics

The conventional technique for removing zinc from the spinning acid wastestream has been direct lime precipitation to ~pH 10, with no zinc recovery. The economics of this approach are compared to the American Enka zinc recycle process.

The economics of recovery are a very strong function of the amount of zinc used in the preparation of the yarn and the ratio of acid to zinc in the spinning bath. In manufacturing industrial yarns and tire cords, it is common to use 4.5 to 7.5 kg of zinc per 100 kg of yarn. This high concentration of zinc makes recovery extremely attractive. Textile yarns use less zinc, and although recovery is still the most economic solution, it offers less of a return. These two cases are presented as extremes, with many plants falling between the two values.

The use of two-stage precipitation combined with zinc recycle offers a saving of 2007 USD 498,000 over neutralization for a plant producing industrial yarns and a saving of USD 88,400 for textile yarns. Many plants produce a mix of the two and the results would therefore fall between these values. The costs associated with the more extensive sludge handling and storage in neutralization and precipitation only are not included. The cost of installing the complete neutralization and zinc recycle system would have negligible economic impact on the rayon industry, running from USD 1.14/100 kg profit to a USD 0.37/100 kg cost compared to selling prices of USD 86 to 100/100 kg of staple, USD 200 to 230/100 kg of tire yam, and USD 290 to 430/100 kg of filament. Zinc oxide manufacturers face the loss of the bulk of a 22.7 million kg (50 million lb/yr) market as this product is reused rather than wasted.[14]

1.9.1.4 Areas of Application

This technology, with only small modifications to conform to local plant conditions, could have immediate application in any viscose rayon plant with soluble zinc in the plant wastestream. The techniques of initially precipitating the impurities, which would prohibit zinc recycle as well as the use of a sludge recirculation process to obtain a dense sludge, are excellent examples of good process engineering being applied to a waste problem.

In a broader sense this technology could have application to any wastestream containing soluble zinc in a form that can be precipitated by lime or caustic addition. The possibility of recycling the precipitated zinc would depend upon the nature of the process considered and may require further work. Examples of other areas that produce zinc-containing wastes are groundwood pulp, metal plating, zinc refining, and recirculating water systems.

1.9.2 POLLUTION ABATEMENT IN A COPPER WIRE MILL

1.9.2.1 The Significance

All wire drawing operations require cleaning of the metal surfaces before drawing to prevent surface impurities from being pulled into the drawn wire. This cleaning or "pickling" is usually accomplished by the use of sulfuric or hydrochloric acid. To maintain good pickling activity the solution must be replaced when it reaches a minimum concentration. This depleted pickling solution is then a waste disposal problem.

The metal must also be washed free of pickling solution. The resulting rinsewaters contain metal salts. Because of the low concentration of these contaminants the rinses are difficult to treat economically.

In the case of the production of copper wire, additional complications are present because of the chemical reduction of cupric oxide to a cuprous oxide coating, which cannot be removed by sulfuric acid. This coating has normally been treated by a "secondary pickle" of chromic acid–sulfuric acid, chromic acid–ammonium bifluoride mixtures, or by nitric acid. All of these techniques produce additional pollutants. Each of the three to four drawing steps required to produce fine copper wire from copper rod requires these pickling and rinse steps.

The waste from such an operation, if treated by conventional precipitation techniques without an examination of the manufacturing process itself, would impose a severe cost on the manufacturing operation and produce large amounts of sludge for disposal.

In a U.S. EPA demonstration grant, the Volco Brass and Copper Company, of Kenilworth, NJ, with Lancy Laboratories as consultants, demonstrated that water consumption could be reduced by 90% from 757,000 L/d to 75,700 L/d (200,000 gal/d to 20,000 gal/d) by chemical rinsing and water reuse. The sulfuric acid pickle was regenerated and high purity metallic copper recovered by continuous electrolysis,[27,28] thereby eliminating the dumping of spent pickle liquor. Hydrogen peroxide was proven to be an improved secondary pickle and the chromates and fluorides previously used were eliminated. Total solids leaving the plant in the rinsewaters were reduced from 1136 kg/d (2500 lb/d) to less than 45 kg/d (100 lb/d). Metal losses in the effluent were reduced to less than 0.45 kg/d (1 lb/d) compared to the previous 273 to 318 kg/d (600 to 700 lb/d). A comparison of the effluent quality before and after the process modification is shown in Table 1.8.[14]

TABLE 1.8
Comparison of Effluent Quality before and after Process Modification

Parameter	Old Quality	New Quality
Water usage (L/min)	570	38
pH	3.8	7.5–8.5
Total Cr (mg/L)	90	0
Zn (mg/L)	200	1
Cu (mg/L)	100	1
Suspended solids (mg/L)	30	20
Dissolved solids (mg/L)	1500	800

Source: From UNIDO, *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.

1.9.2.2 The New Process

The pollution control system that is integrated into the manufacturing process consists of three basic steps:

1. The regeneration and copper recovery system for the primary pickle bath
2. The chemical rinse system
3. The use of hydrogen peroxide plus proprietary additives for the secondary pickle.

Figure 1.1 illustrates the final process. Block A shows the work flow through the new system. After the hot sulfuric acid pickle and the secondary pickle of 2.5% hydrogen peroxide in sulfuric acid, the work passes through a chemical rinse step that neutralizes the acid dragout. It also precipitates any copper salts by reduction of cupric (Cu^{2+}) ions to cuprous (Cu^{+}) ions, which are insoluble at the pH of the chemical rinse. The work then goes to a cold rinse using city water, a hot rinse using deionized water, and finally a lubricant bath prior to the drawing operation.

Block B shows the electrolytic copper recovery cell, which recovers metallic copper and regenerates sulfuric acid from the metal salts in the hot sulfuric acid pickle solution. It was originally felt that trace metals (zinc, tin, lead) would interfere with the recovery of pure copper. By controlling current density at 50 to 100 A/m^2, however, pure copper can be recovered while maintaining the copper concentration in the pickle bath at 15 g/L.

The secondary pickle reservoir is also shown in Block B. Copper sulfate accumulates in this bath and eventually crystallizes out. These crystals can be recovered and sold as a copper-rich sludge or added to the electrolytic copper recovery loop.

The chemical rinse reservoir is maintained at the proper pH and composition by the addition of caustic, sodium carbonate, and a reducing agent, in this case hydrazine. The sludge draw off along with the flow from the floor spill neutralization first goes to a sludge filter to recover salvage copper sludge and then to a final sump for discharge.

The rinse flows go to a pH adjustment tank, a settling tank, and finally to the rinsewater sump, where the bulk of the flow is recirculated to the first water rinse tank.

1.9.2.3 The Economics

The economics for this project are presented in comparison to the previous operating situation with essentially no waste treatment, and to estimated costs if a conventional precipitation and neutralization waste treatment system had been installed without modifying the manufacturing process itself.

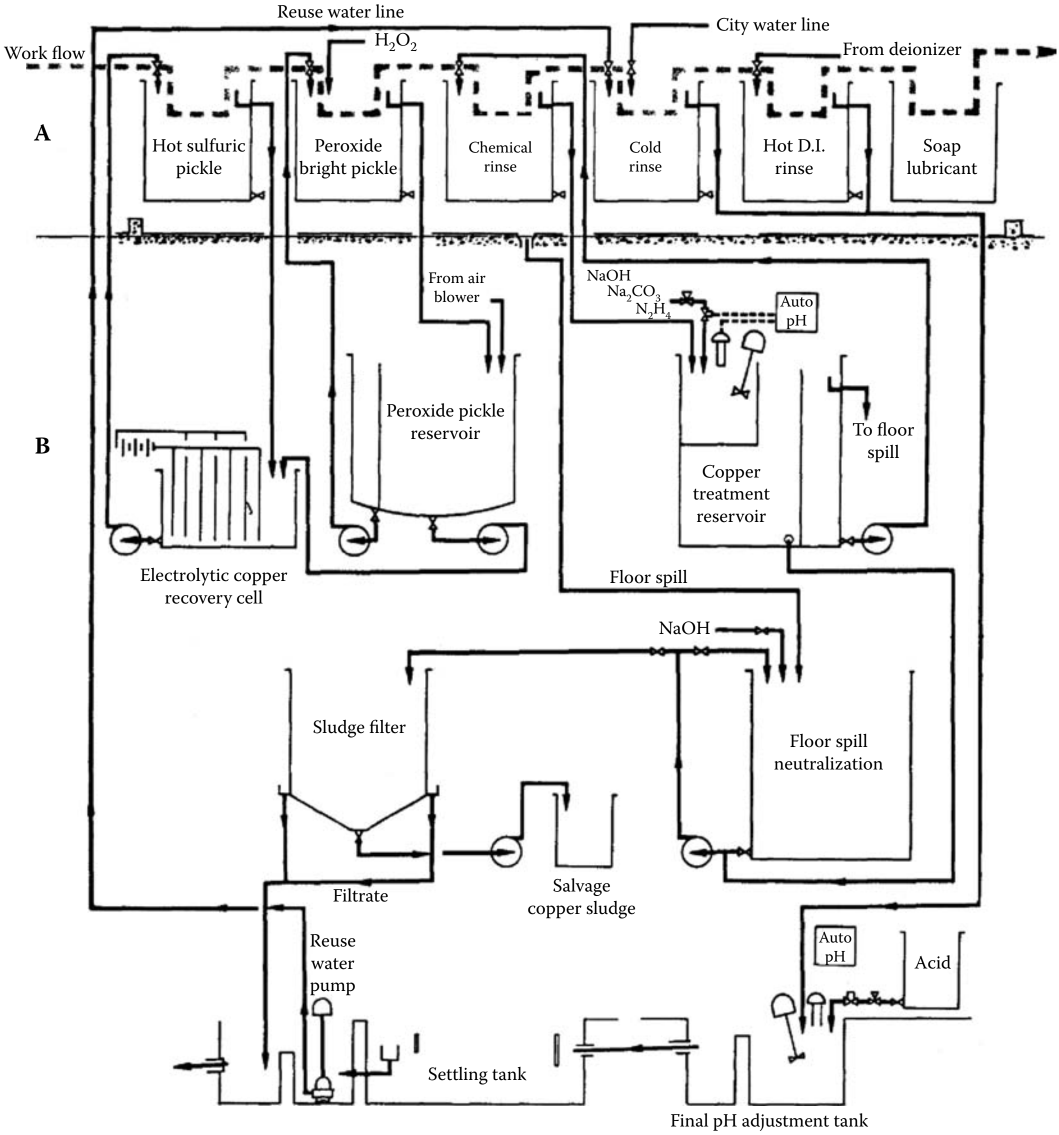

FIGURE 1.1 Illustration of the final copper recovery process. DI, deionized water.

The approach taken for this project gave a major reduction in pollutants, including sludge, at a slight profit, whereas the isolated installation of a waste treatment system would have resulted in a major cost to the company.

Several changes were made in the plant operation simultaneously with the installation of the pollution abatement system resulting in a total of 2007 USD 130,000 annual savings cost in the drawing operation. The credit of 2007 USD 39,000 annually for increased die life taken for this project is an estimate by the Volco staff.[14]

1.9.2.4 Areas of Application

This process is currently being used at five other installations manufacturing copper and copper-alloy products. The chemical rinse technique is applicable to electroplating operations and has gained wide acceptance there. Any facility utilizing a fluoride–chromate bright pickle should consider the use of a hydrogen peroxide–sulfuric acid mixture as an alternative to treatment.

1.9.3 GAS-PHASE HEAT TREATMENT OF METALS

Chartered Metal Industries Toolroom in Singapore produces a wide range of standard and customized products to support manufacturers in the metal industries. Their production includes high-volume, batch-run precision parts, prototype components, subassemblies, tooling, fixtures, and gauges.

The hardening, carburizing, and nitrocarburizing of steel are heat treatment processes usually carried out in baths of molten salts, such as nitrites, nitrates, carbonates, cyanides, chlorides, or caustics. The combination of chemicals and high temperature means that there are risks of explosion, burns, and poisoning. Environmental problems arise from the resulting vapors and the removal, transport, and disposal of the toxic salts. Disposal of cyanide salt costs 2007 USD 4300/t. Neutralization[27] of quench water, oil, cleaning water and washing water should be carried out before discharge to the sewer, but is not always carried out. Off-gases can be cleaned by passing the exhaust gases through a chemical scrubber, although this also is not always done.

1.9.3.1 Cleaner Production

The new process avoids these problems by gas-phase treatment using a fluidized bed of alumina particles (Figure 1.2). A mixture of air, ammonia, nitrogen, natural gas, pg (liquefied petroleum gas), and other gases are used as the fluidizing gas to carry out the heat treatment. The bed is heated by electricity or gas and quenching is also carried out in a fluidized bed.[14]

Fluidized beds have been used for some years in a variety of roles: heat exchange, gas absorption, chemical reaction, and combustion. In this case the mixture of gases produces the fluidizing

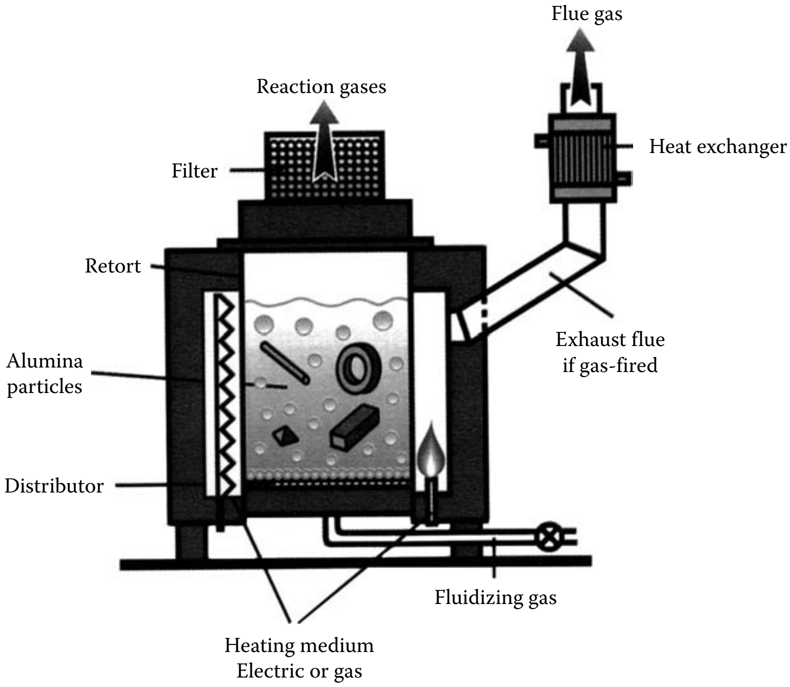

FIGURE 1.2 Fluidized bed. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

atmosphere for heat treatment of the material immersed in the fluidized bed. Hydrocarbon gases are used for carburizing, ammonia for nitriding, and nitrogen for neutral hardening. The hot exhaust gases are used for heat exchange.

1.9.3.2 Advantages

The most obvious advantages are the reduction in effluents and the improved working atmosphere. The safety aspects have also been improved to a very large extent and the quality of the product in many cases is superior to that produced by the older methods. All forms of heat treatment are amenable to fluidized bed techniques, but austempering is the most cost effective, in spite of the nitrate bath method being less troublesome than other traditional methods.

1.9.3.3 Economic Benefits

The installation consists of four fluid beds (Figure 1.2) used to replace their existing salt bath lines.[14]

	Cost Saving in 2007 USD
Energy	47,000 USD/yr
Salt & maintenance	66,000 USD/yr
Total	113,000 USD/yr
Capital investment	234,000 USD
Payback	2 yr

1.9.4 NEW TECHNOLOGY: GALVANIZING OF STEEL

Galvanizing is an antirust treatment for steel. The traditional technique consists of chemically pretreating the steel surface, then immersing it in 10 to 16 m long baths of molten zinc at 450°C (Figure 1.3). The process involves large quantities of expensive materials, which increases the cost of the finished steel. In addition there are significant quantities of waste arising from the chemical and zinc baths. There is also the problem of fumes from these operations.

1.9.4.1 Cleaner Production

The company's objective was to galvanize steel products of constant cross-section, such as reinforcing and structural steel, tubes, wire, and so on, on a more compact production line, using up to two to three times less zinc, with reduced energy consumption and the suppression of all forms of pollution.

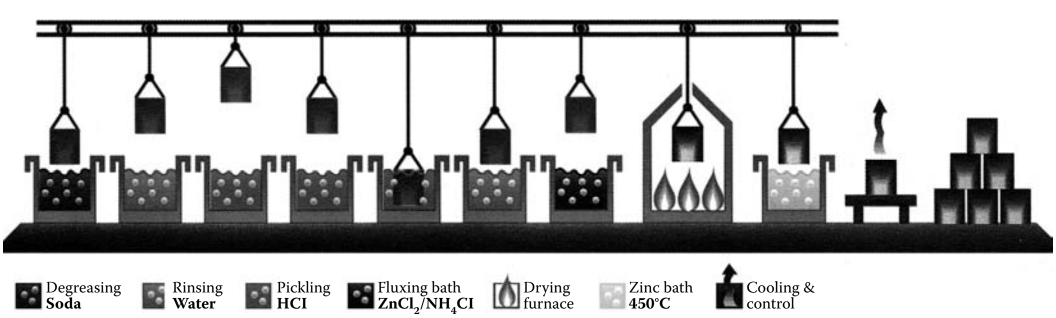

FIGURE 1.3 Sketch of a classical hot dip. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

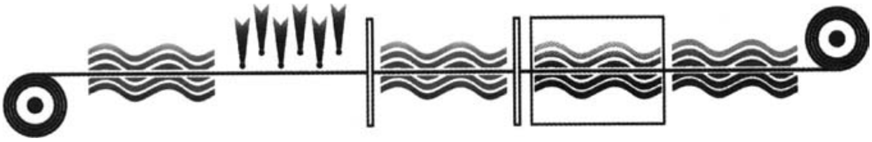

FIGURE 1.4 Sketch of the prototype line. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

The raw steel is fed in automatically. The process can be operated continuously or in batches, depending on the material to be coated. The surface preparation is performed by controlled shot blasting (Figure 1.4). The steel is heated by induction and enters the coating chamber through a window profiled to match the cross-section of the steel. The zinc is melted in an inert atmosphere by an electric furnace and flows into the galvanizing unit. The liquid zinc is held in suspension by an electromagnetic field. The speed of the production line is controlled by computer. Measuring the thickness of the coating using electromagnetic methods allows precise control of the process.[14]

The first stage of the project was to develop the technology for coilable material, that is, wire and thin rod. The company later developed the technology to handle rigid steel.

The technology that enabled the cleaner production included induction heating to melt the zinc, the use of an electromagnetic field to control the distribution of the molten zinc, and computer control of the process.

1.9.4.2 Advantages

These include the following:

1. Total suppression of conventional plating waste
2. A smaller inventory of zinc
3. Better control of the quality and thickness of the zinc coating
4. Reduced labor requirements
5. Reduced maintenance
6. Safer working conditions

1.9.4.3 Economic Benefits

Capital cost was reduced by two-thirds compared to a traditional dip-coating process. The lower operating costs resulted in the coating process comprising 18% of the steel cost, compared to 60% with traditional methods. The payback period was three years for replacing existing plant.[14]

1.9.5 Waste Reduction in Electroplating

FSM Sosnowiec manufactures automobile lamps, door locks, and window winders for the Polish-manufactured Fiat cars. The lamp bodies are made of zinc–aluminum alloy and then copper–nickel–chromium plated. The door locks and window winders are made of steel and then zinc plated. The wastestreams contain cyanide and the heavy metals chromium (VI), copper, zinc, and nickel. The company carries out the traditional treatments of detoxification, neutralization, and dewatering.[29]

1.9.5.1 Cleaner Production

A pollution prevention audit was carried out to reduce environmental pollution, improve working conditions, and improve efficiency. One of the results was that low concentration plating and pacifying is now being introduced. All of the rinsing systems have been modified so that some of the circulating (overflow) rinses have been changed to static rinses. A similar system has been installed for nickel and cyanide. The final rinse tank in each rinsing sequence has been equipped with ion exchange columns, which permit water recycling and raw materials recovery.

1.9.5.2 Advantages

These include the following:

1. A decrease in both water and raw materials consumption
2. A reduction in both wastestream quantities as follows[14]:
    (a) Chromic acid, 80%
    (b) Copper, 95%
    (c) Cyanide, 80%
    (d) Nickel, 98%
    (e) Zinc, 96%
    (f) Wastewater, 93%
3. Purification of the wastewater to the following levels:
    (a) Chromium, 0.1 mg/L
    (b) Copper, 0.1 mg/L
    (c) Nickel, 1.0 mg/L
    (d) Cyanide, 2.0 mg/L
    (e) Zinc, 0.9 mg/L

1.9.5.3 Economic Benefits

	Cost Saving in 2007 USD/yr
Total savings	251,000 USD/yr
Capital investment	47,000 USD
Payback period	2 months

1.9.6 WASTE REDUCTION IN STEELWORK PAINTING

The Ostrowiec Steelworks of Poland consists of eleven departments; the main production departments are steelworks processing, steel construction, machinery building, and the foundry. The manufacture of steel products is carried out using production-line methods. The final operations required for almost all products are surface treatment and painting. In the machinery-building department these operations are carried out with shot-blasting machines and manually operated spray booths. The original painting method was air-atomized spraying, which has the lowest transfer efficiency of the coating methods and yields large quantities of waste.

1.9.6.1 Cleaner Production

A pollution prevention audit was carried out to improve the environment and efficiency and working conditions in the painting areas.[30] The objective of this program was to reduce the quantity of wastes and costs of painting by a combination of improvements to the technology and good housekeeping. The overall aim was to improve the quality of coating, to reduce the amount of paint raw material and to reduce the quantities of wastes.

The existing painting method was compared with two more advanced painting technologies. The transfer efficiencies for the different methods are as follows:

1. Air-atomized spray (conventional), 30 to 50%
2. Airless spray, 65 to 70%
3. Pressure-atomized electrostatic spray, 85 to 90%

In conventional spraying, compressed air is used both to atomize the paint and to carry it to the surface to be painted (Figure 1.5). With airless spraying the paint is pumped under high pressure to a small jet where the high velocity is sufficient to induce atomization. The lack of any expanding compressed air stream eliminates unwanted spray mist, reduces the loss of paint by overspray, and most of the paint adheres to the work surface (Figure 1.6). With pressure-atomized electrostatic spray, paint is delivered at high pressure as before, but it is fed to an insulated nozzle. An electrostatic charge of about 100kV is applied to this nozzle. The charging of the paint particles assists the atomization and causes them to repel each other. Additionally, the charged paint moves along the field lines to the earthed work piece. As the electrostatic field lines envelop the object the paint particles cannot fly straight past, but "wrap" themselves uniformly around the surface. It is this effect that gives the high paint efficiency and reduces waste (Figure 1.7). Note that electrostatic hand spray guns require a small mains transformer and a much reduced current to avoid accidental electrical shock. Comparison of raw material consumption and waste quantities of the different methods are as follows[14]:

	Air-Atomized Spray	Airless Spray	Pressure-Atomized Electrostatic Spray
Paints (m^3)	8.0	6.8	5.6
Solvents (m^3)	6.5	1.6	1.6
Wastes (kg)	2400	1400	500

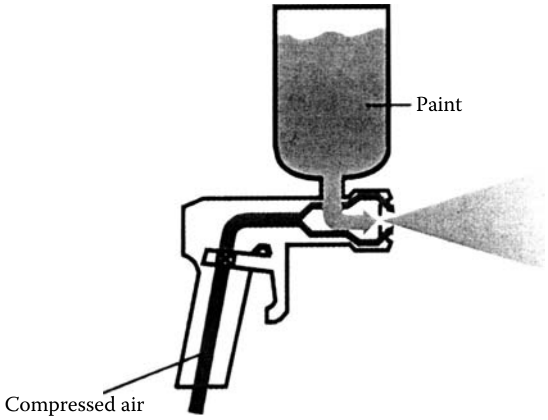

FIGURE 1.5 Air atomized paint spraying.

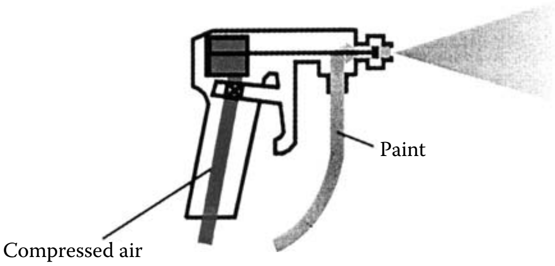

FIGURE 1.6 Airless or high pressure paint spraying. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

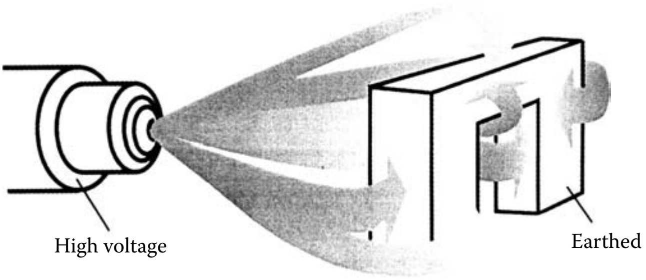

FIGURE 1.7 "Wrap around" effect of electrostatic paint spraying. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

1.9.6.2 Advantages

These include the following:

1. Reduction of high disposal costs
2. Reduced running costs
3. Decreased financial liability by generating a smaller quantity of hazardous wastes
4. Improved public perception and acceptance in the business community
5. Reductions in the effluent concentrations of about 45% for sludge and 75% for organic solvents

1.9.6.3 Economic Benefits

The cost savings in 2007 USD for airless spray and pressure-atomized electrostatic spray are as follows[14]:

	Airless Spray	Pressure-Atomized Electrostatic Spray
Total savings (USD/yr)	50,000	51,200
Capital investment (USD)	6,200	17,000
Payback (months)	1.5	4

1.9.7 RECOVERY OF COPPER FROM PRINTED CIRCUIT BOARD ETCHANT

Praegitzer Industries Inc., founded in 1981, is a leading designer and manufacturer of advanced circuit boards. The company employs 500 people in three locations.

In the manufacture of printed circuit boards, the unwanted copper is etched away by acid solutions of cupric chloride (Equation 1.1). As the copper dissolves, the effectiveness of the solution tails and it must be regenerated. The traditional way of doing this is to oxidize the cuprous ion produced with acidified hydrogen peroxide. During the process the volume of solution increases steadily and the copper in the surplus liquor is precipitated as copper oxide and usually landfilled.

In the etching process:

$$\mathrm{Cu} + \mathrm{CuCl_2} \rightarrow 2\mathrm{CuCl} \tag{1.1}$$

1.9.7.1 Cleaner Production

The original proposal for recovering the copper in high-quality form came from the U.K. Electricity Research Council. Using an electrolytic technique involving a divided cell (Figure 1.8), simultaneous

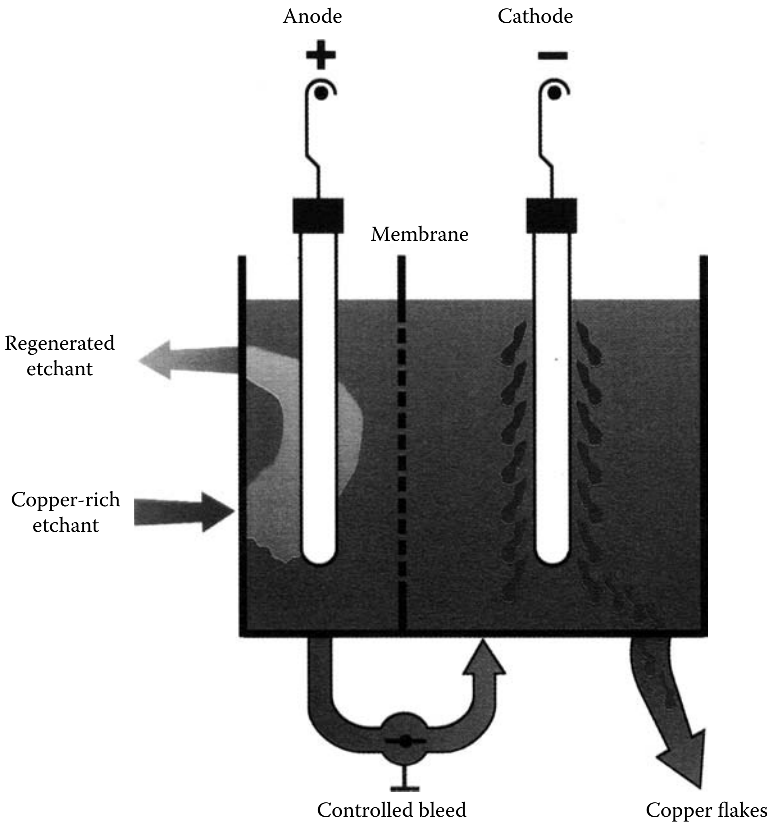

FIGURE 1.8 Electrolytic process. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

regeneration of the etching solution and recovery of the unwanted copper is possible. A special membrane allows hydrogen and chloride ions through, but not the copper. The copper is transferred via a bleed valve and recovered at the cathode as pure flakes (Equation 1.2).

In the electrolytic process:

$$2CuCl \rightarrow CuCl_2 + Cu \tag{1.2}$$

This process was enabled by the development of a suitable cell-dividing material; a process development where the excess etchant is pumped to the recovery circuit and the copper is obtained in a recoverable form.

1.9.7.2 Advantages

These include the following:

1. Improvement in the quality of the circuit boards
2. Elimination of virtually all the disposal costs
3. Maintenance of the etching solution at its optimum composition
4. Recovery of the copper in a high-value form
5. No hazardous chemicals need to be handled

1.9.7.3 Economic Benefits

Based on 50 t of copper recovered per year, the cost saving in 2007 USD is as follows[14]:

Copper (USD/yr)	65,000
Materials (USD/yr)	104,000
Disposal (USD/yr)	32,500
Total (USD/yr)	500
Capital investment (USD)	286,000
Payback	17 months

1.9.8 CHROME RECOVERY AND RECYCLING IN THE LEATHER INDUSTRY

The Greek and Dutch governments have a framework of bilateral collaboration in the field of environmental protection. One result of this has been that clean technology has been applied in a full-scale cooperative R&D project between the two countries at the Germanakos tannery. The project was carried out with the support of the Commission of the European Communities.

The Germanakos SA tannery near Athens in Greece was founded in 1978. Today it produces good quality upper leather from cattle hides, processing 2200 t/yr and with an annual turnover of 2007 USD 11 million and a staff[14] of 65.

Tanning is a chemical process that converts putrescible hides and skins into a stable material. Vegetable, mineral, and other tanning agents may be used—either separately or in combination—to produce leather with different qualities and properties. Trivalent chromium (Cr^{3+}) is the major tanning agent, because it produces modern, thin, light leather suitable for shoe uppers, clothing, and upholstery. However, recent limits for discharge to the environment have limited chromium discharge to levels as low as 2 mg/L in wastewaters.

1.9.8.1 Cleaner Production

The technology developed involves the recovery of chromium from the spent tannery liquors and its reuse.

Tanning of hides is carried out with basic chromium sulfate, $Cr(OH)SO_4$, at a pH of 3.5 to 4.0. After tanning the solution is discharged by gravity to a collection pit. The liquor is sieved during this transfer to remove particles and fibers that have come from the hides. The liquor is then pumped to the treatment tank and a calculated quantity of magnesium oxide is added with stirring until the pH reaches at least 8. The stirrer is switched off and the chromium precipitates as a compact sludge of $Cr(OH)_3$. After settling the clear liquid is decanted off. The remaining sludge is dissolved by adding a calculated quantity of concentrated sulfuric acid (H_2SO_4) until a pH of 2.5 is reached. The liquor now contains $Cr(OH)SO_4$ and is pumped back to a storage tank for reuse (Figure 1.9).

In conventional chrome tanning processes 20 to 40% of the chrome used is discharged into wastewaters. In the new process 95 to 98% of the waste Cr^{3+} can be recycled.

1.9.8.2 Advantages

These include the following:

1. Very little change to production process
2. More consistent product quality
3. Easier monitoring of the amounts of water and process chemicals used
4. Much reduced chromium content in the effluent waters.

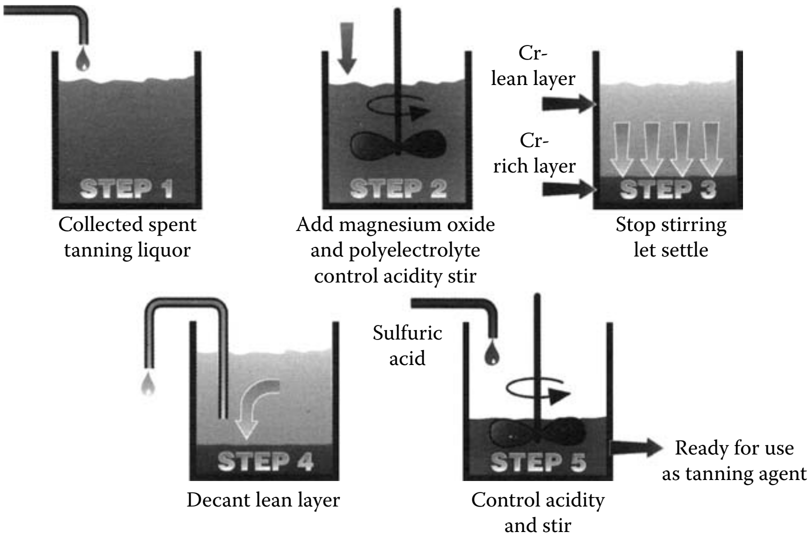

FIGURE 1.9 Five-step batch process for chromium recycling. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

1.9.8.3 Economic Benefits

For the Germanakos tannery, which has a chrome recycling capacity of 12 m^3/d, the approximate costs were as follows[14]:

	Cost Saving in 2007 USD
Savings (USD/yr)	95,880
Operating cost (USD/yr)	39,260
Total net savings (USD/yr)	56,620
Capital investment (USD)	52,000
Payback	11 months

Savings can be made with any plant processing more than 1.7 m^3/d.

1.9.9 Minimization of Organic Solvents in Degreasing and Painting of Metals

Thorn Jarnkonst of Sweden produces lighting fixtures from aluminum or steel sheets for indoor and outdoor use. The production amounts to 750,000 units. They employ about 650 people. In 1988 the company merged with Thorn EMI, the main branch being located in England.

Metal working, degreasing, and painting are the main phases in this production process. The degreasing of the metal sections has been carried out in the past by using the volatile organic compound trichloroethylene, which is a pollutant and an environmental hazard.

The painting plant consisted of an automatic liquid lacquer line, with different colors using different organic solvents. The air pollution and the accumulated remaining products were a considerable problem, both within the plant and externally.

When the company planned to expand production the local authorities ordered the company to reduce its current air emissions. As a result the company intended to install equipment to capture the trichloroethylene and incinerate the solvents from the painting plant.[31] However, an independent research organization, by carrying out a pollution prevention audit, suggested an alternative approach having environmental benefits.

1.9.9.1 Cleaner Production

The pollution prevention audit started with an analysis of the material flow in the degreasing process. It was shown that by better housekeeping, the need for trichloroethylene degreasing could be reduced by 50%, but this has now been cut to zero. The cutting of aluminum sheets required cutting fluids, which were difficult to remove without the use of chlorinated solvents. A change to biodegradable cutting oils allowed an alkaline degreasing procedure in place of the previous trichloroethylene method.

The degreasing is carried out in a new piece of equipment in the form of a totally enclosed tunnel, 30 m long. The metal products are suspended from an overhead conveyor and then pass through five zones where they are sprayed with various liquids (Figure 1.10). The stages carried out are degreasing, water rinse, iron phosphating to aid the adherence of the paint, water rinse, a deionized water rinse, and drying. The liquid runs off the metal items into tanks below, where it is recirculated back to the spray nozzles.

Electrostatic powder painting uses polymer-based paints that do not have any solvent in their formulation. A long-term problem was changing to a different color of paint. This is now accomplished by changing the whole module with containers of different colors. The company has now installed a new electrostatic powder painting line having 12 automatic powder guns. The paint is positively charged relative to the metal items. Now only 5% of the colors have organic solvents and are used only for the painting of short production runs in special colors or for retouching of the automatically sprayed items where necessary. Manual spraying is carried out in a ventilated booth fitted with two electrostatic guns.

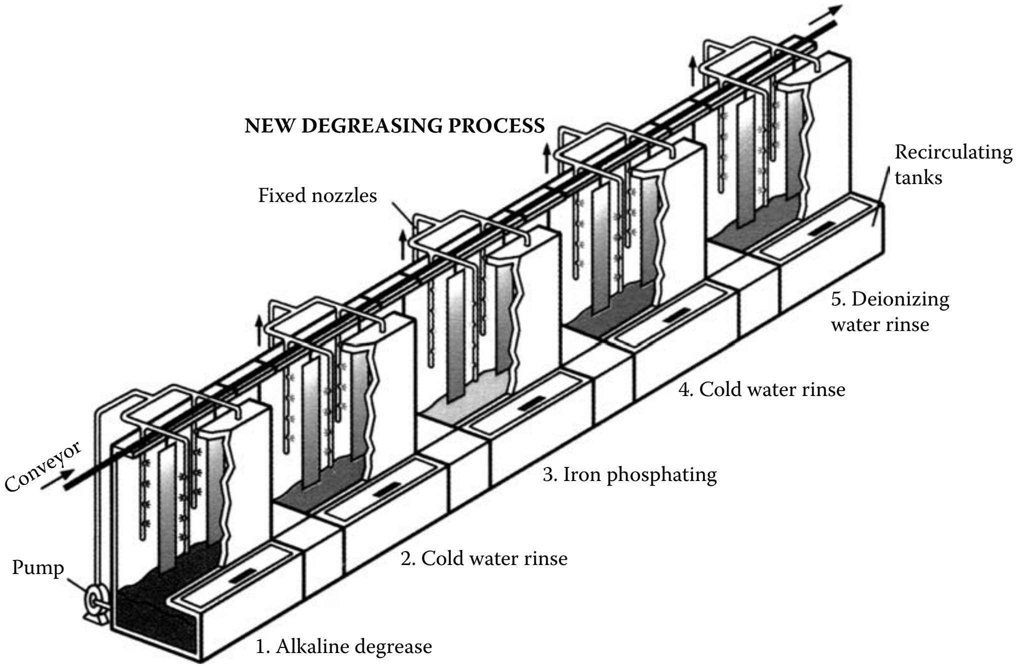

FIGURE 1.10 Schematic of the new degreasing process. (From Wang, L.K. et al. *Case Studies of Cleaner Production and Site Remediation*, Training Manual DTT-5-4-95, United Nations Industrial Development Organization, Industrial Sectors and Environment Division, Vienna, Austria, April 1995.)

1.9.9.2 Advantages

These include the following:

1. Changed degreasing techniques:
    (a) The environmental advantages that have been achieved are external and also within the workplace.
    (b) The company more than adequately meets the demands from the authorities.
    (c) The water purification plant, which is also used for other process baths, can be used for alkaline degreasing too and results in little additional water pollution from the degrease stage.
2. Changed painting techniques:
    (a) There is a large reduction in the discharge of organic solvents.
    (b) Hazardous waste is reduced.
    (c) There is an improved work environment.
    (d) Production has been enabled to expand without conflicting with environmental demands.

1.9.9.3 Economic Benefits

The alkaline degrease turned out to be USD 32,800 cheaper a year than the trichloroethylene degrease and did not require the installation of recovery equipment.

The powder painting techniques have led to considerably lower working costs. The following costs for solvent painting have disappeared with the use of powder painting.[14]

	Cost Savings in 2007 USD
Paint (USD/yr)	268,000
Cleaning (USD/yr)	81,000
Disposal (USD/yr)	61,000
Pumping (USD/yr)	43,000
Labor (USD/yr)	146,000
Total (USD/yr)	599,000
Capital investment (USD)	559,000
Payback	11 months

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2 Waste Treatment in the Iron and Steel Manufacturing Industry

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Yung-Tse Hung, and Lawrence K. Wang

CONTENTS

2.1 INTRODUCTION

The iron and steel industry is currently on an upsurge because of strong global and local demands. It plays a critical role in the infrastructural and overall economic development of a country. The versatility of steel can be understood from its wide range of applications in the construction, transportation, and process industries. There has been a remarkable growth in world crude steel production, from 189 million metric tons in 1950 to 1244 million metric tons in 2006 (International Iron and Steel Institute, IISI). However, the steel production process is an energy-, raw-material, and labor-intensive process, accounting for major environmental releases.[1–7]

Environmental regulations have always had a profound effect on all stages of manufacturing and forming processes of the iron and steel industry. Taking into consideration the high cost of new equipment and the relatively long lead time required to bring them into the industry, any change in production method or product takes place at a slow pace. The installation of major pieces of new steel-making equipment may cost millions of dollars and require additional retrofitting of other equipment.[8–16] However, in spite of the competition from substitute materials, which forces steelmakers to invest in cost-saving and quality-enhancing technologies, it has always remained a challenge for the industry to develop and maintain cleaner yet efficient steel-making processes. It may therefore be expected that in the long run it would be likely for the steel industry to take up simplified and continuous manufacturing technologies that reduce the capital costs for new plant construction and allow smaller plants to operate efficiently.

2.2 INDUSTRIAL PROCESSES IN THE IRON AND STEEL INDUSTRY

Steel is an alloy of iron, usually containing less than 1% carbon. The process of steel production occurs in several sequential steps. The basic oxygen furnace (BOF) and the electric arc furnace (EAF) are two types of technology in use today for steel making. Although these technologies use different input materials, the output from both furnace types is in the form of molten steel that is further processed into steel mill products. The BOF input materials include molten iron, scrap, and oxygen. In the EAF, the input materials are electricity and scrap. BOFs are typically used for high tonnage production of carbon steels, and EAFs are used to produce carbon steels, low-tonnage alloy, and specialty steels. During the manufacturing of steel using a BOF, coke making and iron making precede steel making; however these steps are not needed for steel making with an EAF. Coke, which acts as a fuel and carbon source, is produced by heating coal in the absence of oxygen at high temperatures in coke ovens. Pig iron is produced by heating the coke, iron ore, and limestone in a blast furnace. In the BOF, molten iron from the blast furnace is combined with flux and scrap steel, followed by the injection of high-purity oxygen. In an EAF process, the input material consist primarily of scrap steel, which is melted and refined by passing an electric current from electrodes through the scrap. The molten steel from either process is formed into ingots or slabs and rolled into finished products. Rolling operations may require reheating, rolling, cleaning, and coating the steel. The process of coke making, iron making, steel making, and subsequent forming and finishing operations is collectively referred to as fully integrated production. Figure 2.1 presents a detailed flowsheet of the iron and steel manufacturing process. This chapter describes the various processes involved in steel making, the sources and types of wastes generated from these manufacturing processes, and the technical advancement necessary for pollution prevention and economic operation of the iron and steel plant.[17–20]

2.3 COKE MAKING

2.3.1 PROCESS DESCRIPTION

Coke is a residue obtained after heating coal to very high temperatures (1650 to 2200°F) in the absence of oxygen, and removing all its volatile components.[14] It is further used as a reductant for

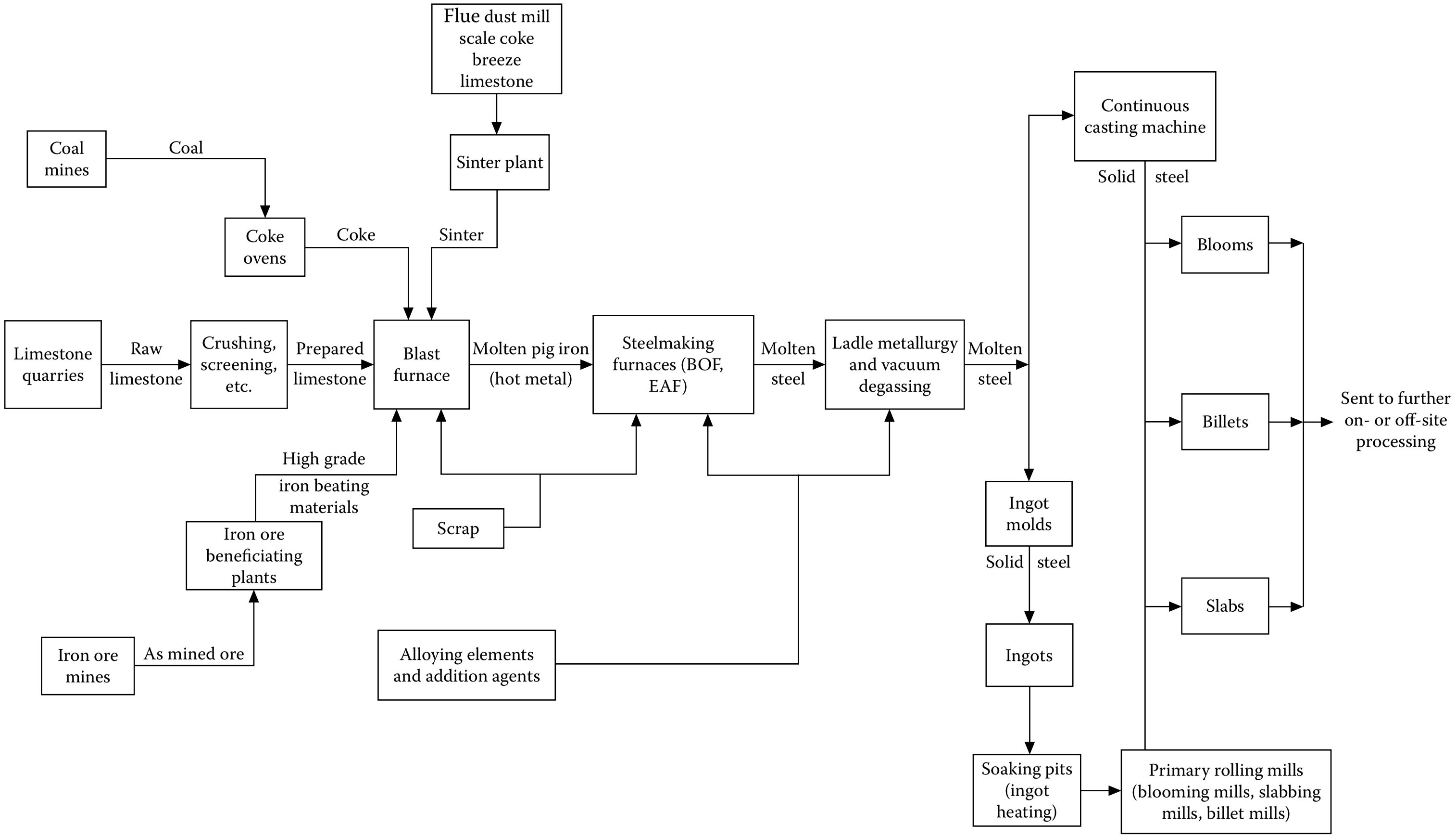

FIGURE 2.1 Iron and steel manufacturing process overview. (From U.S. EPA, Development Document for the Proposed Effluent Limitations Guidelines and Standards for the Iron and Steel Manufacturing Point Source Category, EPA-821-B-00-011, U.S. EPA, Washington, DC, 2000.)

blast furnace iron making, having good permeability that allows the free flow of gases within the furnace shaft. Nearly 1.3 to 1.35 t of bituminous (coking) coal is required for the production of 1 t of coke.[1] The U.S. integrated iron and steel industry uses the byproduct process for the manufacture of almost all coke. Byproduct coke ovens allow the collection of volatile material emitted during the coking process. Coking is carried out in brick ovens called batteries, which consist of coking chambers, heating flues, and regenerative chambers. The coking chambers are located alternatively with heating chambers, with the regenerative chambers located underneath. Pulverized coal is charged into the oven through the openings provided at the top. The necessary heat for distillation of the volatile components is supplied by the external combustion of recovered coke oven gas, blast furnace gas, and natural gas through flues located between the ovens.

Finally, the coke produced is removed through doors on either end of the oven and pushed out into a quenching car to be transported to a quenching tower, where it is sprayed onto the coke mass to cool it. The coke is sized and sent to the blast furnace or for storage. The "foul" gas obtained during the coking operation is processed to recover byproducts such as tar, light oils, ammonia, and naphthalene. Foul gas cleaning involves the spraying of weak ammonia, which condenses some tar and ammonia from the gas. The remaining gas is cooled by passing through a condenser and is then compressed by an exhauster. Any remaining coal tar is removed by a tar extractor, either by impingement against a metal surface or collection by an electrostatic precipitator.

Ammonia is removed by passing the gas through a saturator, where ammonia reacts with sulfuric acid to form ammonium sulfate, which is crystallized and removed. In the Phosam process ammonia is scrubbed directly from coke oven gas with phosphoric acid and then stripped.[19] The gas is further cooled to condense naphthalene. The light oils are removed in an absorption tower and subsequently refined. The last cleaning step is the removal of hydrogen sulfide in a scrubbing tower. The purified gas may be used as fuel for the coke ovens or in other plant combustion processes. However, the nonrecovery process for byproduct gas may also be used, in which the unpurified gas is burned within the process rather than being recovered. The energy recovered in the form of heat from the waste gases is passed through a waste heat boiler to generate steam for electricity production or process use. Figure 2.2 gives a flow diagram of the coke-making process and Table 2.1 provides the inputs and outputs of the coke-making process. Table 2.2 gives an overview of the key environmental and energy facts of coke making.

2.3.2 SOURCES OF PROCESS WASTES

2.3.2.1 Emissions

The process of coke making emits particulate matters, volatile organic compounds (VOCs), carbon monoxide, and other pollutants. The various sources of emissions include the following:

1. Fugitive particulate emissions during material handling (coal preparation)
2. Significant emissions of particulate matter and VOCs due to oven charging
3. VOC emissions from distillation within the oven during the coking cycle from leaks in the doors, charge lids, and offtake caps
4. Particulate emissions due to pushing of coke from the oven into the quench car
5. Particulate from the coke mass during coke quenching
6. Trace organic compounds and dissolved solids from the quench water entrained in the steam plume rising from the tower
7. Emissions from the underfire or combustion stack due to combustion of gas in the coke oven flues
8. VOC emissions from the processing steps for separating ammonia, coke oven gas, tar, phenol, light oils, and pyridine from the foul gas

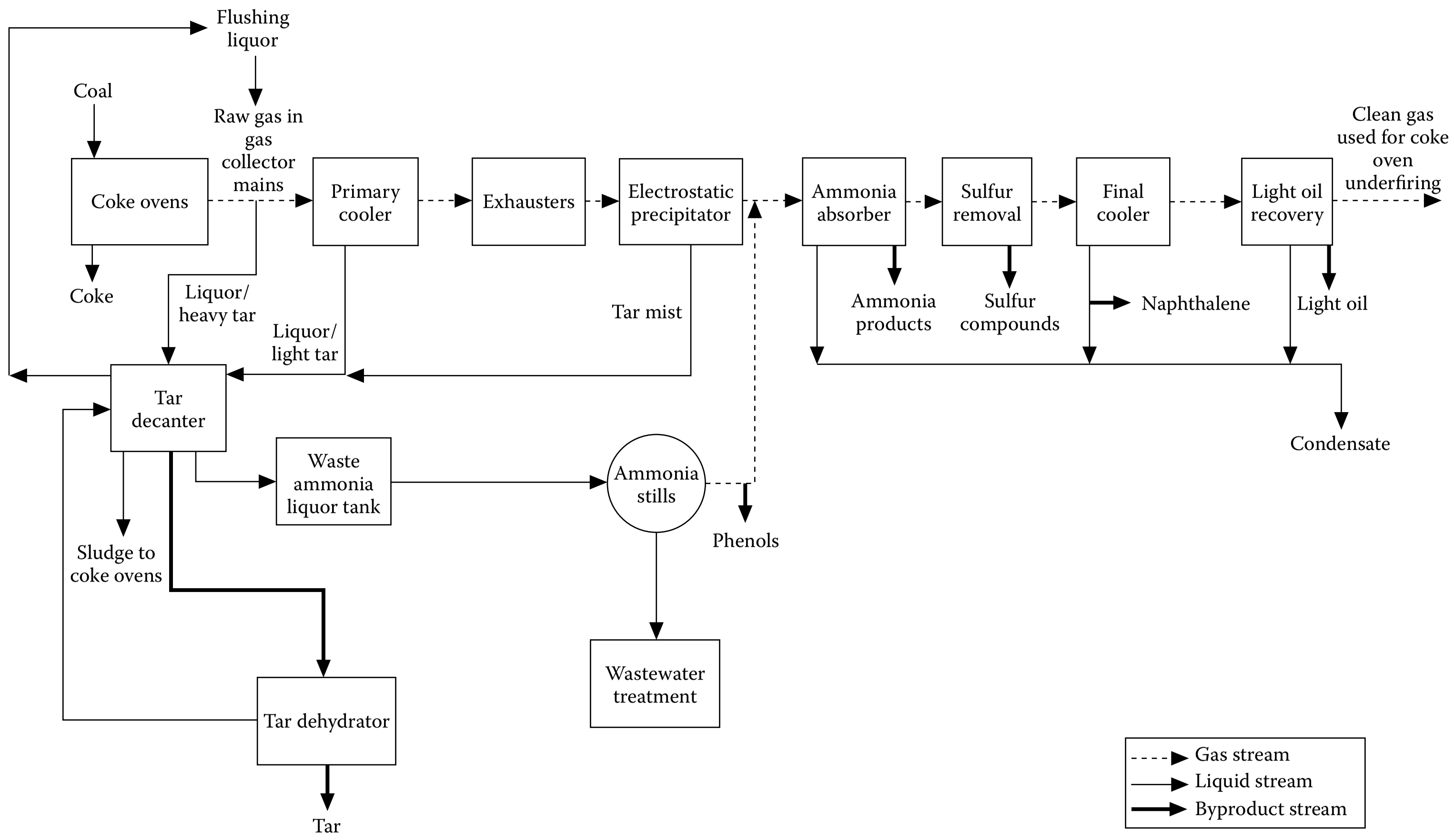

FIGURE 2.2 Coke-making flow diagram. (From U.S. EPA, Development Document for Final Effluent Limitations Guidelines and Standards for the Iron and Steel Manufacturing Point Source Category, EPA-821-R-02-004, U.S. EPA, Washington, DC, 2002.)

TABLE 2.1
Inputs and Outputs of the Coke-Making Process

Inputs	Outputs
Coal	Coke
Heat (from coke oven gas, blast furnace gas, natural gas)	Coke oven gas and byproducts including coal tar, light oil, and ammonia liquor
Electricity	Ammonia, phenol, cyanide, and hydrogen sulfide
Water	Charging, pushing, and quenching emissions
	Products of combustion (SO_2, NO_x, CO, particulate)
	Oil (K143 and K144)
	Ammonia still lime sludge (K060)
	Decanter tank tar sludge (K087)
	Tar residues (K141, K142)
	Benzene releases in byproduct recovery operations
	Naphthalene residues generated in the final cooling tower
	Sulfur and sulfur compounds recovered from coke oven gas
	Wastewater from cleaning and cooling (contains zinc, ammonia still lime, decanter tank tar, or tar distillation residues)
	Air pollution control (APC) dust

Source: From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.

2.3.2.2 Effluents

The major consumption of water in coke plants is for cooling purposes in a variety of cooling and condensing operations. For the coke quenching operation alone, about 120 to 900 gal of water are required per ton of coke.[1] The various sources of process wastewater include the following:

1. Excess ammonia liquor from the primary cooler tar decanter
2. Barometric condenser wastewater from the crystallizer, the final coolers, light oil recovery operations, ammonia still operation, coke oven gas condensates, desulfurization processes, and air pollution control operations

TABLE 2.2
Overview of Key Environmental and Energy Facts for Coke-Making

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
3.4×10^6 Btu per ton of coke produced	Major pollutants: particulate, VOCs, CO	Largest sources: waste ammonia liquor, ammonia distillation, crude light oil recovery	Major byproducts: tar, light oils, ammonia, naphthalene
	Largest sources: coke handling, charging, pushing, quenching	Typical wastewater volume: 100 gal/t of coke	Hazardous wastes: 7 RCRA-listed wastes (K060, K087, K141 to K145) Largest source: coke oven gas cleaning

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

About 100 gal of process wastewater is typically generated from 1 t of coke produced.[15] These wastewaters from byproduct coke making contain high levels of oil and grease, ammonia nitrogen, sulfides, cyanides, thiocyanates, phenols, benzenes, toluene, xylene, other aromatic volatile components, and polynuclear aromatic compounds. They may also contain toxic metals such as antimony, arsenic, selenium, and zinc. Water-to-air transfer of pollutants may take place due to the escape of volatile pollutants from open equalization and storage tanks and other wastewater treatment systems in the plant.

2.3.2.3 Hazardous Wastes

There are seven Resource Conservation and Recovery Act (RCRA) listed hazardous wastes associated with coke making, as listed below:

1. K060: ammonia still lime sludge
2. K087: decanter tank tar sludge
3. K141: process residues from coal tar recovery operations
4. K142: tar storage tank residues
5. K143: process residues from the recovery of light oil
6. K144: wastewater sump residues from light oil refining
7. K145: residues from naphthalene collection and recovery operations

Process residues from coal tar recovery (K141) are generated when the uncondensed gas from the coke oven collecting main enter the primary cooler. The condensates from the primary cooler flow into the tar collecting sump and discharged to the flushing liquor decanter. Tar storage tank residues (K142) are the residuals of the crude coal tar. These residues are recycled to the oven or landfilled. Residues from light oil processing units (K143) are built up in the oil scrubber and oil stripping still over time. Resin is also accumulated due to cleaning of the wash oil used in the light oil recovery process is resin. The residue from either a wash oil purifier or a wash oil decanter called wash oil muck is removed and recycled to the coke oven, reclaimed offsite, or used as blast furnace or boiler fuel. Wastewater sump residues (K144) accumulated in the bottom of a sump allowing oil and water to separate during light oil recovery are either recycled to the oven or landfilled offsite. Residues from naphthalene collection and recovery (K145) at the bottom of a skimmer sump where naphthalene is mechanically skimmed off the surface or in the hot and cold sumps used for collecting, or surge vessels, and on the surfaces of the cooling tower are recycled to the decanter or sometimes to the oven.

2.3.3 TREATMENT TECHNIQUES

Various pollution control equipment are needed to trap the fine particles of coke generated during charging, pushing, loading, and transporting operations. This solid waste, comprising fine particles, should be properly landfilled. For effective control of charging emissions, goosenecks and collecting main passages should be cleaned frequently to prevent obstructions. Emissions due to the combustion of gas in the coke oven are controlled by conventional gas cleaning equipment such as electrostatic precipitators and fabric filters. In fulfillment of requirements under the National Emission Standards for Hazardous Air Pollutants (NESHAPs) rule, existing coke ovens need to provide coke byproduct plants with inert gas blanketing systems for eliminating 95 to 98% of benzene emissions and preventing emissions of other VOCs as well.[6]

Conventional wastewater treatment techniques consist of physical/chemical treatments, including oil separation, dissolved gas flotation, and ammonia distillation (for removal of free cyanides, free sulfides, and ammonia) followed by biological treatment (for organics removal) and residual ammonia nitrification. Almost all residuals from coke-making operations are either recovered as crude byproducts (e.g., as crude coal tar, crude light oil, ammonium sulfate, or other sulfur compounds) and sold or recycled to the coke ovens for recovery of carbon values (e.g., coal tar decanter sludge, coke plant wastewater treatment sludge).[15] The constituents of concern and their average measured concentrations for K141 through K145 are presented in Table 2.3.

2.4 IRONMAKING

2.4.1 Process Description

In the blast furnace iron-making process, iron ore is reduced by removing oxygen, followed by melting of the resulting iron. Agglomeration processes such as pelletization and sintering help in producing coarse particles of suitable sized iron ore for easy charging into the blast furnace. In pelletization, an unbaked "green" pellet is formed from iron ore concentrate combined with a binder. These green pellets are hardened by heat treatment in an oxidizing furnace. Pelletizing is usually done at the mine site. Sintering is a crucial process in the steel mill, using natural fine iron-bearing materials as well as those recovered from ore handling and other iron and steel operations, for example, ore fines from screening operations, water treatment plant sludges, and air pollution control dusts, and fusing them into porous sinters suitable for charging to blast furnaces. In sintering, both iron ore fines and other iron-bearing materials (iron-bearing scale, dusts, and slag) are thoroughly mixed with fluxes (lime or dolomite) and approximately 5% of a finely divided fuel, such as coke breeze or anthracite.[20]

The mix is loaded onto a traveling grate called sinter strand, which is in the form of a shallow trough with small holes in the bottom. The bed of materials on the grate is ignited by passing under an ignition burner fired with natural gas and air. As the grate moves slowly towards the discharge end, windboxes on the underside of the strand pull down the combustion gases through the material bed into a duct to gas cleaning equipment. As the coke fines burn in the bed, the generated heat sinters the fine particles. The temperature of the bed reaches around 1300 to 1480°C. Average production rates of 22 to 43 metric tons/m^2/d of grate area are expected, depending upon the characteristics of the ore materials and the sintering conditions.[13]

The fused sinter mass is cooled, crushed, screened, and sent to be charged, along with the ore, to the blast furnace. Approximately 2.5 t of raw materials, including water and fuel, are required to

TABLE 2.3

Constituents of Concern and Average Measured Concentrations for Wastes K141 through K145[a]

Constituent	K141 (Process Residues from Coal Tar Recovery)	K142 (Tar Storage Tank Residues)	K143 (Residues from Light Oil Processing)	K144 (Wastewater Treatment Sludges from Light Oil Refining)	K145 (Residues from Naphthalene Collection and Recovery)
Benzene	3850	260	1600	3000	1000
Benz (a) anthracene	7850	6600	69	68	22
Benzo (a) pyrene	8450	6500	34	65	7
Benzo (b) fluoranthene	5450	7500	59	75	26
Chrysene	7950	6000	59	6	22
Dibenz (a,h) anthracene	1750	1000	38	15	1
Indeno (1,2,3-cd) pyrene	6140	2900	40	37	4
Naphthalene	95,000	55,000	52,000	27,000	140,000

Source: From U.S. EPA, Federal Register, Part III, U.S. EPA, Washington, DC, August 18, 1992.

[a] Concentrations measured in mg/kg.

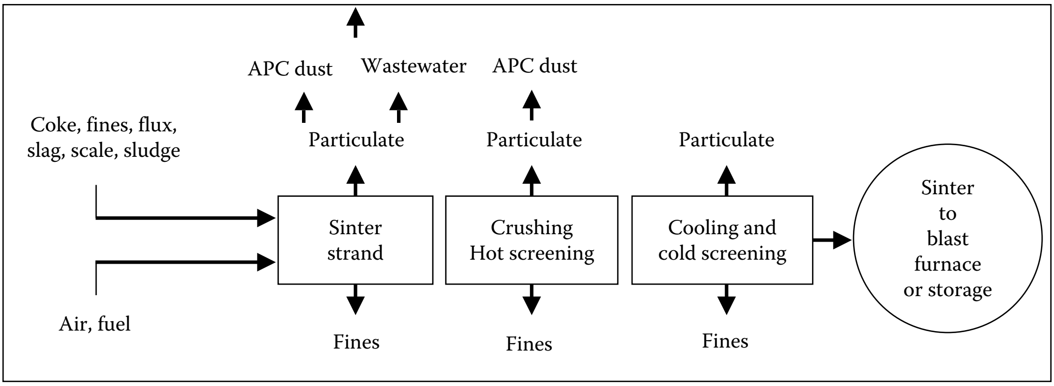

FIGURE 2.3 Sintering flow diagram. (From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.)

produce 1 t of sinter product.[16] Figures 2.3 and 2.4 illustrate the sintering and blast furnace iron-making processes, respectively. Blast furnaces are used to produce pig iron, which represents about three-quarters of the charge to basic oxygen steel-making furnaces. The chemical composition of pig iron typically comprises the following[1]:

1. Carbon (4.0 to 4.5%)
2. Silicon (0.3 to 1.5%)

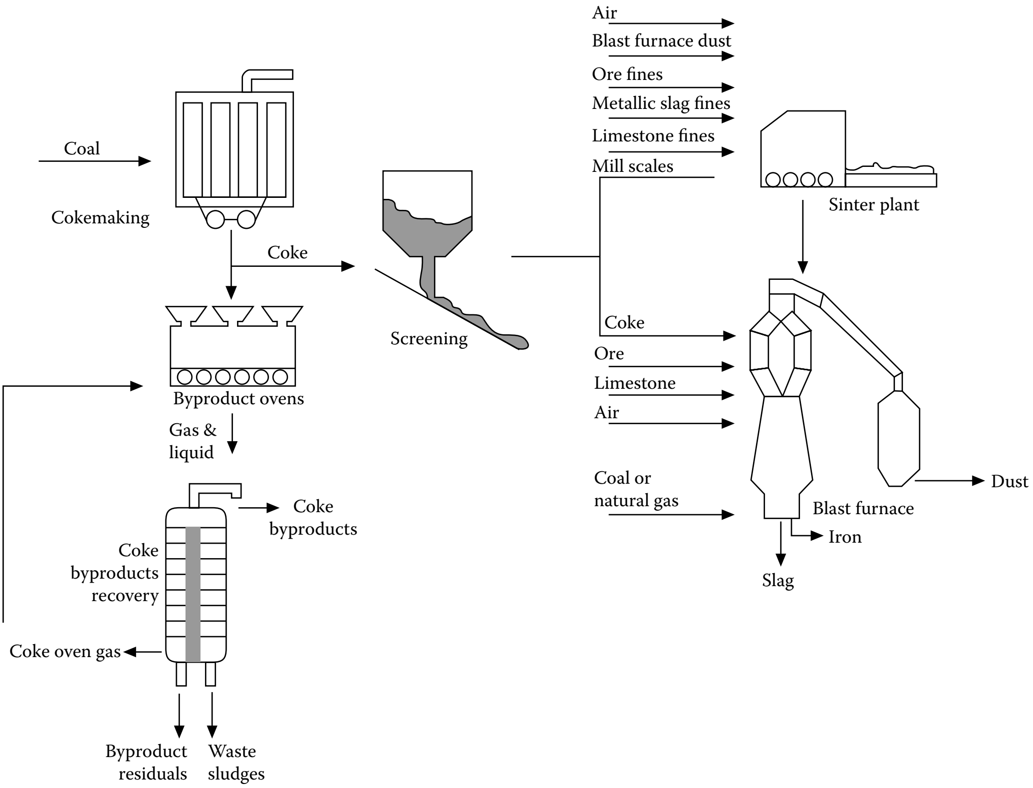

FIGURE 2.4 Flow diagram of the iron-making operation. (From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.)

3. Manganese (0.25 to 2.2%)
4. Phosphorus (0.04 to 0.20%)
5. Sulfur before desulfurization (0.03 to 0.8%)
6. Iron (>90%)

Iron ore, coke, flux (limestone and dolomite), and sinter are fed into the top of the blast furnace; heated air augmented with gaseous, liquid, or powdered fuel is injected into its base. As the charge materials descend, the reducing gas (containing carbon monoxide) generated by the burning coke flows upward, converting the iron oxide (FeO) in the ore to iron (Fe). The coke also provides the structural support for the unmelted burden materials. The combustion of the coke generates sufficient heat to melt the iron, which accumulates in the bottom of the furnace (hearth). The major function of the flux is to combine with unwanted impurities, that is, ash in the coke and gangue in the ores, to make a drainable fluid slag. Unreacted reducing gas (blast furnace gas) is collected at the top, cleaned, and used as a fuel. The molten iron called the "hot metal" is tapped into refractory-lined cars for transport to the basic oxygen furnace. The iron may be processed at desulfurization stations to minimize sulfur compounds before charging in the basic oxygen furnace. Molten slag, which floats on top of the molten iron, is also tapped and processed for sale as a byproduct. The production of one net ton of iron requires approximately 1.5 to 1.7 t of ore or other iron-bearing material, 0.35 to 0.55 t of coke, 0.25 t of limestone or dolomite, and 1.6 to 2.0 t of air.[1,16] The inputs and outputs of the iron-making operation are shown in Table 2.4, with a brief overview of key environmental and energy facts of sintering and iron making in Table 2.5 and Table 2.6, respectively.

2.4.2 SOURCES OF PROCESS WASTE

2.4.2.1 Emissions

Emissions from sinter plants are generated from raw material handling, windbox exhaust, sinter discharge (associated sinter crushers and hot screens), and from the cooler and cold screen. The primary source of particulate emissions, mainly irons oxides, magnesium oxide, sulfur oxides, carbonaceous compounds, aliphatic hydrocarbons, and chlorides, are due to the windbox exhaust. Contaminants such as fluorides, ammonia, and arsenic may also be present. At the discharge end,

TABLE 2.4
Inputs and Outputs of the Iron-Making Operation

Inputs	Outputs
Iron ore (primarily as pellets)	Molten iron
Coke (coal)	Slag
Sinter	Blast furnace gas
Limestone	Residual sulfur dioxide or hydrogen sulfide
Heated air (from coke oven gas, blast furnace gas, natural gas, fuel oil)	Air pollution control (APC) dust and/or waste treatment plant sludge
Electricity	Process wastewater
Natural gas	Kish
Coal	
Oxygen	
Water	

Source: From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.

TABLE 2.5
Overview of Key Environmental and Energy Facts: Sintering

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
1.55×10^6 Btu per ton of sinter	Largest source: windbox	Largest source: wet air pollution control devices	Dust/sludge
	Particulate: iron and sulfur oxides, carbonaceous compounds, aliphatic hydrocarbons, chlorides	Typical wastewater volume: 120 gal/t of sinter	No RCRA-listed hazardous wastes

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

emissions are mainly iron and calcium oxides. A wide variety of organic and heavy metal hazardous air pollutants (HAPs) may be released during sinter operations from the coal/coke on the sinter grate and iron, respectively. The heavy metal HAPs include cadmium, chromium, lead, manganese, and nickel. Total HAPs releases from individual sinter manufacturing operations may exceed 10 t/yr.[6] The typical components of the dust generated during sintering practice include iron, carbon, sulfur, Fe_2O_3, SiO_2, Al_2O_3, CaO, and MgO.

Large quantities of carbon monoxide and sulfur dioxide are also emitted during iron making. The primary source of blast furnace particulate emissions is due to the contact of molten iron and slag with the air above their surface during casting (removal of the molten iron and slag from the furnace). Emissions are also generated by drilling and plugging the taphole, which is an opening at the base of the furnace to allow iron and slag to flow out into runners that lead to transport ladles. Heavy emissions result from the use of an oxygen lance to open a clogged taphole. Another potential source of emissions is the blast furnace top. No serious emission problem is created if charging is through a sealed system. However, minor emissions may occur during charging from imperfect bell seals in the double bell system. Occasionally, a cavity may form in the blast furnace charge, causing a collapse of part of the charge above it. The resulting pressure surge in the furnace opens a relief valve to the atmosphere to prevent damage to the furnace by the high pressure created and is referred to as a "slip."[14]

During hot metal desulfurization, used to remove or alter sulfur compounds in the hot metal, the exhaust gases are found to bear particulate matter. Emissions may also result from slag handling. Sulfur dioxide is formed when the sulfur in the slag is exposed to air. The presence of moisture can

TABLE 2.6
Overview of Key Environmental and Energy Facts: Blast Furnace Iron Making

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
16.1×10^6 Btu per ton of iron (gross)	Largest source: removal of iron and slag from furnace (casting)	Largest source: gas cooling water and scrubber water for gas cleaning	Total generation (t/yr) Slag: 14×10^6 Dust/sludge: ~1.1×10^6
12.1×10^6 Btu per ton of iron (net)	Particulate: iron oxides, MgO, carbonaceous compounds	Typical water flows: 6000 gal/t of iron	Reuse: near 100% (slag); ~40% (dust/sludge)

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

result in the formation of hydrogen sulfide. Most sulfur emissions associated with slag handling result from quenching operations. It has been reported that highly toxic polychlorinated dibenzofurans (PCDFs) are dominant in the stack flue gases of sinter plants.[20]

2.4.2.2 Effluents

In an integrated mill, the blast furnace is one of the largest water users. Its main use is for noncontact cooling of various parts of the furnace and auxiliaries. Additional water is used for furnace moisture control, dust control, and slag granulation. Contact water use is primarily associated with blast furnace gas-cleaning operations for recovering the fuel value of the off gas. Nearly all of the wastewater generated from blast furnace operations is direct contact water from the gas coolers and high-energy scrubbers used to clean the blast furnace gas. Typical water requirements are 6000 gal/t of iron.[15]

Water in a sintering plant is mainly used for controlling the moisture content of the presinter mix, for dust control, and sinter product cooling. Wastewaters are generated from wet air pollution control devices, that is, electrostatic precipitator or wet venturi-type scrubber technology on the windbox and discharge ends of the sinter machines. Applied flows for wet air pollution control devices are typically 1000 gal/t, with discharge rates of 50 to 100 gal/t for the better controlled plants.[1] The principal pollutants of wastewater generated from blast furnace operations include total suspended solids, ammonia nitrogen, cyanides, phenolic compounds, copper, lead, nickel, zinc, selenium, arsenic, chromium, and cadmium.

2.4.2.3 Byproducts

The primary byproducts generated during the production of molten iron include blast furnace gas, slag, air pollution control dust (flue dust varying in size from about 6 mm to only a few microns), and waste treatment plant sludge (blast furnace filter cake). The blast furnace gas or top gas is a heated, dust-laden, combustible gas that can be used as a fuel throughout the plant. Water treatment plant sludge is generated as a result of wet-scrubbing systems containing relatively high levels of zinc and lead. This sludge needs to be treated before recycling as feedstock to the sinter plant or blast furnace to maintain an acceptable level of zinc and lead in the furnace. Between 2.0 and 3.0 net tons of this gas are generated for each ton of pig iron produced.[1] Blast furnace gas contains about 40% carbon monoxide and carbon dioxide combined. The dust and sludge are composed of oxides of iron, calcium, silicon, magnesium, manganese, and aluminum. Blast furnace slag comprises about 20 to 40% of molten iron production by weight. Lower grade ores yield higher slag fractions, sometimes as high as 500 to 1000 lb of slag for each ton of pig iron produced.[1]

2.4.3 TREATMENT TECHNIQUES

During the use of oil-bearing mill scale as a revert material, the VOC emissions that are generated are evaporated off the sinter strand into the windbox prior to incineration. Cyclone cleaners followed by a dry or wet electrostatic precipitator, high pressure drop wet scrubber, or baghouse are used to control the sinter strand windbox emissions. Crusher and hot screen emissions, which are the next largest emission source, are usually controlled by hooding and a baghouse or scrubber. Baghouses are used to capture particulates generated during conveyor transport and loading or unloading of sinter plant feedstocks and product. The air pollution control dust that is collected by the baghouses is either recycled as feedstock to the sinter plant or landfilled. The iron making process is the highest-emitting process among those considered, responsible for approximately 40% of total emissions for both criteria pollutants and CO_2.[1] Nitrogen oxide (NO_x) emitted from sinter plants is controlled by selective catalytic reduction (SCR) using NH_3. V_2O_5/TiO_2-based catalysts are considered to be state of the art for this application.[20] Casting emissions are controlled by evacuation through retrofitted capture hoods to a gas cleaner, or by flame suppression techniques. Emissions controlled by hoods and an evacuation system are usually vented to a baghouse. In hot metal desulfurization, exhaust gases are discharged through a series of baghouses to control airborne particulate matter. Emissions from the blast furnace are controlled by a wet venture scrubber or another control device.[1,14]

Wastewater treatment comprises sedimentation for removal of heavy solids, recycle of clarifiers or thickener overflows, and metals precipitation treatment for blowdowns. Standard treatment includes sedimentation in thickeners or clarifiers, cooling with mechanical draft cooling towers, and high-rate recycle. Low-volume blowdowns (<70 gal/t) are either consumed in slag cooling at furnaces with adjacent slag pits, or treated in conventional metals precipitation systems. A few mills practice alkaline chlorination to treat ammonia nitrogen, cyanides, and phenolic compounds.[15]

About 60% of the particulate is removed from the blast furnace gas stream by dry cyclonic vortex separation (i.e., dust catcher) of the heavy particles (flue dust). Fine particulates are subsequently removed in a two-stage cleaning operation consisting of a wet scrubber (primary cleaner), which removes about 90% of the remaining particulate, and a high-energy venturi impact scrubber or electrostatic precipitator (secondary cleaner), which removes up to 90% of the particulate eluding the primary cleaner. During the two-stage blast furnace gas cleaning process the fine particles removed by the gas washer become entrained in a liquid–solid stream that continues on to the treatment plant for settling and solids separation. The concentrated sludge can be dewatered further by mechanical filtration.[1]

At some plants the blast furnace dust is recycled as feedstock to the sinter plant. At plants without sintering operations, blast furnace dust is sometimes mixed with other byproduct residues, briquetted, and recycled back to the blast furnace. In other plants, the dust is landfilled or stockpiled.[1] Several techniques are available for removing the zinc and lead. The majority of blast furnace sludge is land disposed as solid waste or stockpiled. Because of the similarity between wastewater sludges generated by sinter plants and blast furnaces, these streams are commingled and cotreated.[1] The blast furnace slag is cooled and processed to be reused for various applications such as onsite in-land reclamation and landfill construction.

2.5 STEEL MAKING

2.5.1 Basic Oxygen Furnace Process

2.5.1.1 Process Description

The basic oxygen furnace steel-making process refines a charge of molten pig iron and ambient scrap into steel using very high purity oxygen. This results in a reduction of the carbon content of less than 1% for steel from "hot metal" containing about 4% carbon. Other elements in the hot metal such as silicon, phosphorus, sulfur, and manganese, are transferred to a slag phase. The basic raw materials required to make steel in the oxygen steel-making process include:

1. Hot metal (pig iron) from the blast furnace
2. Steel scrap (20 to 35%)
3. Other metallic iron sources (e.g., DRI, ore, oxides)
4. Fluxes (e.g., lime)

After the hot metal and scrap are charged, oxygen is injected into the BOF. The fluxes are then added to control sulfur and phosphorus and prevent erosion of the furnace refractory lining. The principle active ingredients from the fluxes are CaO (from burnt lime) and MgO (from dolomitic lime). Burnt lime consumption ranges from 40 to 100 lb/net ton of steel produced, while dolomitic lime requirements range from 30 to 80 lb/ton.[1] The energy required to raise the fluxes, scrap, and hot metal to steel-making temperatures is provided by oxidation of various elements in the charge materials, particularly iron, silicon, carbon, and manganese. No external heat source is needed, as the temperature increase caused by the oxidation reactions is countered by the addition of scrap and other coolants. During processing, the carbon in the iron is oxidized and released as CO (about 90%) and CO_2 (about 10%). These gaseous oxides exit the furnace carrying small amounts of iron oxide and lime dust. BOFs are classified according to the location of oxygen injection:

1. *Top blown.* Oxygen is injected above the hot metal bath by means of a retractable, water-cooled lance.
2. *Bottom blown.* Oxygen is injected under the molten metal bath, usually carrying pulverized additives.
3. *Combination blown.* Oxygen is injected both above and below the bath.

Bottom stirring is accomplished by the introduction of inert gas under the bath. Silicon, manganese, iron, and phosphorus form oxides that combine with the fluxes to create a liquid slag floating on top of the steel bath, removing sulfur and phosphorus from the metal. At the end of the cycle, raw steel is tapped into a ladle where it is deoxidized and alloying elements are added to adjust the composition to final levels, or to concentrations suitable for further ladle treatment processes. Figure 2.5 illustrates BOF steel-making and Table 2.7 below gives the inputs and outputs of the steel-making operation. An overview of key environmental and energy facts of steel making is presented in Table 2.8.

2.5.1.2 Sources of Process Waste

Emissions

The most significant emissions from BOF steel-making occur during the oxygen blow period. The predominant compounds emitted are iron oxides (including FeO and Fe_2O_3), although heavy metals are also present. Tapping emissions include iron oxides, sulfur oxides, and other metallic oxides, depending on the grade of scrap used. Hot metal transfer emissions are mostly iron oxides.[6,14] The particulate-laden combustion gases and fume (a very fine iron oxide containing high and variable amounts of zinc) released during oxygen blow periods are removed from the furnace by evacuation through a large collection main. The BOF gas, consisting mainly of CO, leaves the BOF at a temperature of between 1600 to 1800°C. Most of the hazardous air pollutants (HAPs) generated in the BOF are heavy metals, including cadmium, chromium, lead, manganese, and nickel.[1] Standard

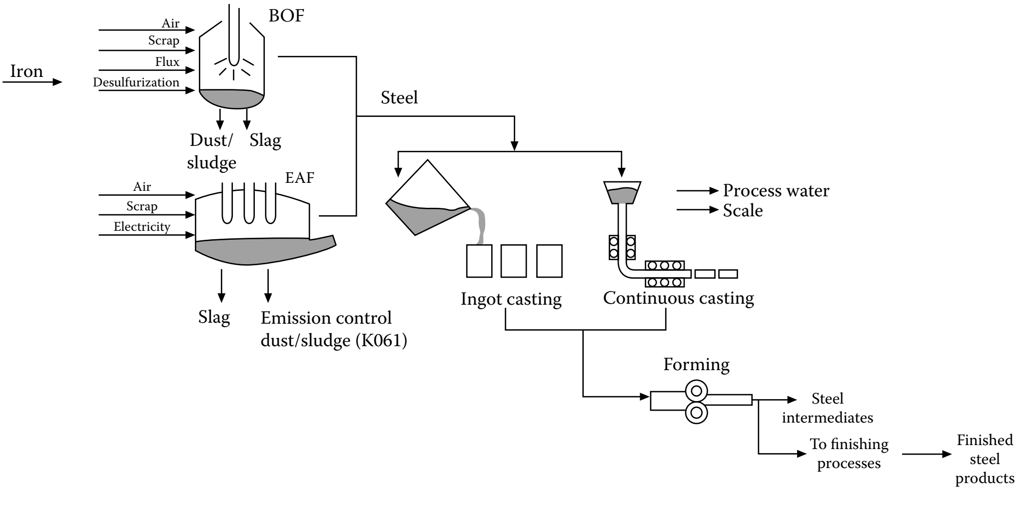

FIGURE 2.5 Flow diagram of steel-making process. (From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.)

TABLE 2.7
Inputs and Outputs of the Steel-Making Operation

Inputs	Outputs
Molten iron	Molten steel
Metal scrap	Air pollution control (APC) dust and sludge
Other metallic iron sources	Metal dusts (consisting of iron particulate, zinc, and other metals associated with the scrap, and flux)
Ore	Slag
Iron oxide materials and waste oxides	Kish
Oxygen	Carbon monoxide and carbon dioxide
Alloy materials (e.g., aluminum, manganese, chromium, nickel)	Nitrogen oxides and ozone
Fluxes (e.g., lime)	
Electricity and natural gas for auxiliary processes	
Nitrogen	
Argon	
Water	

Source: From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.

treatment of BOF-generated effluents consists of sedimentation in clarifiers or thickeners and recycle of at least 90% of the applied water. Blowdown treatment consists of metals precipitation.

Effluents

Water is mainly used for cooling in the vessel hood, ductwork, trunnion, and oxygen lance. Both closed-loop and evaporative systems are used for component cooling. The gases and submicron fumes that are released during BOF steelmaking are quenched with water to reduce their temperature and volume prior to being treated in air pollution control systems. The three major off-gas control systems result in the generation of wastewater streams containing total suspended solids and metals (primarily lead and zinc, but also arsenic, cadmium, copper, chromium, and selenium). In the open combustion and suppressed combustion systems, about 1100 and 1000 gal of water per ton of steel are used, respectively.[15]

Byproducts

BOF steel-making byproducts include BOF slag, air pollution control (APC) dust, and water treatment plant (WTP) sludge. BOF slag is composed of calcium silicates and ferrites combined with

TABLE 2.8
Overview of Key Environmental and Energy Facts: Steel Making

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
0.9×10^6 Btu per net ton of raw steel	Largest source: oxygen blow	Largest source: BOF off-gas control systems	Total generation (t/yr) Slag: 6.0×10^6 Dust: 0.3×10^6 Sludge: 1.3×10^6
	Particulate: iron oxides, heavy metals, fluorides	Typical water flows: 1000 gal/t	Reuse: less than 50%

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

fused oxides of iron, aluminum, manganese, calcium, and magnesium. After removing the molten BOF slag from the furnace, it is cooled and processed to recover the high metallic portions (iron and manganese) for use in the sinter plant or blast furnaces. The remaining nonferrous fraction is crushed and sized for reuse either within the steel works or externally. Owing to the difference in composition of BOF slag compared with blast furnace slag, the oxides present in BOF slag can result in volume expansion of up to 10% when hydrated. Hence its use is more limited than blast furnace slag. BOF slag outputs are approximately 20% by weight of the steel output.[1] Entrained steel in the slag is typically recovered and returned to the furnace. A typical BOF slag composition is as follows:

1. CaO, 48%
2. FeO, 26%
3. SiO_2, 12%
4. MgO, 6 to 7%
5. MnO, 5%
6. Al_2O_3, 1 to 2%
7. P_2O_5, 1%

The marketable slag makes up about 10 to 15% of the steel output, or 210 to 300 lb/t of steel.[1] BOF dust and sludge generated during the cleaning of gases emitted from the BOF represent two of the three largest-volume wastes typically land disposed by the iron and steel industry.

2.5.1.3 Treatment Techniques

The hot BOF gases are typically treated by one of three air pollution control methods:

1. *Semiwet.* Water is added for conditioning furnace off-gas temperature and humidity prior to processing the gas in electrostatic precipitators or baghouses.
2. *Wet—open combustion.* Excess air is admitted to the off-gas collection system, allowing combustion of carbon monoxide prior to high-energy wet scrubbing for air pollution control.
3. *Wet—suppressed combustion.* Excess air is not admitted to the off-gas collection system prior to high-energy wet scrubbing for air pollution control, thus suppressing combustion of carbon monoxide.[15]

Charging and tapping emissions are controlled by a variety of evacuation systems and operating practices. Charging hoods, tapside enclosures, and full furnace enclosures are used in the industry to capture these emissions and send them to either the primary hood gas cleaner or a second gas cleaner.[15,16] Pollution prevention opportunities for the reduction of heavy metals at the BOF are limited as heavy metals are an inherent part of the iron ore material stream, so the higher the iron production, the greater will be the use of the ore.

The cleaning of BOF gas is done by quenching the mixture of gas and particulate with water in the collection main to reduce the temperature. This quenching process removes the larger particles from the gas stream and entrains them in the water system. After settling in the classifier, these coarse solids can be easily dewatered via a long sloping screw conveyor or reciprocating rake and deposited in bins or hoppers. These solids are referred to as classifier sludge. The fine particulate matter remaining in the gas stream is forced through venturi scrubbers, where it is entrained in a wastewater stream and sent to thickener/flocculation tanks for settling and solids removal. This underflow slurry can be dewatered using mechanical filtration. In dry cleaning systems, the particulate matter collected in the electrostatic precipitator or baghouse is managed as a dust.[1]

The rising cost of scrap and waste disposal, the scarcity of onsite landfill space, and potential environmental liabilities make it an economic necessity to recover iron units from dust and sludge. However, recycling to the blast furnace raises the hot metal phosphorus content to undesirable levels.

Also, the increasing use of galvanized scrap could increase dust and sludge zinc content. Zinc is known to form a circuit in the furnace, resulting in extra coke consumption and also increasing the risk of scaffolding.[7] The quantity of zinc that can be charged to the blast furnace lies between 0.2 and 0.9 lb/t of hot metal.[1] BOF dust and sludge that is not recycled is usually landfilled.

2.5.2 ELECTRIC ARC FURNACE

2.5.2.1 Process Description

Electric arc steel-making furnaces produce carbon and alloy steels from scrap metal along with variable quantities of direct reduced iron (DRI), hot briquetted iron, and cold pig iron. Hot metal may also be added if available. The charge is melted in cylindrical, refractory-lined electric arc furnaces (EAFs) equipped with carbon electrodes (one for DC furnaces, three for AC furnaces). During charging, the roof is removed to place scrap metal and other iron-bearing materials into the furnace. Alloying agents and fluxes are added through doors on the side of the furnace. The electrodes are lowered into the furnace to about an inch above the metal and current is applied, generating heat to melt the scrap. Modern electric arc furnaces use an increasing amount of chemical energy to supplement the melting process. The chemical energy contribution is derived by burning elements or compounds in an exothermic manner. Sources that provide chemical energy include[3]:

1. Oxy-fuel burners and oxygen lancing
2. Charge carbon
3. Foaming carbon
4. Exothermic constituents in scrap
5. Exothermic constituents in alternate iron sources

Oxy-fuel burners are used to introduce combinations of natural gas, oil, or even coal into the furnace to displace electricity use. The reaction of carbon with oxygen within the bath to produce CO results in a significant energy input into the process. The injection of a carbon source also promotes the formation of a foamy slag, which retains energy that is transferred to the bath. The generation of the CO within the bath is necessary to flush out dissolved gases (nitrogen and hydrogen) in the steel, as well as flush oxide inclusions from the steel into the slag.[1] Some EAFs use ferromanganese as a catalyst in the melt to add energy and help stabilize the melt. The efficiency of manganese combustion can be between 90 and 100%.[3] Residence time in the furnace for a 100% scrap charge ranges from about 45 min to several hours.[1] When the charge is fully molten it is refined to remove unwanted materials (e.g., phosphorus, sulfur, aluminum, silicon, manganese, and carbon), tapped from the tilted furnace, and sent for secondary treatment prior to casting. Because scrap metal rather than molten iron is the primary material charged, EAF steel producers avoid the coke-making and iron-making process steps. Figure 2.5 illustrates electric arc furnace steel making and the Table 2.9 gives its major inputs and outputs. An overview of key environmental and energy facts of electric arc furnace process of steel making is presented in Table 2.10.

2.5.2.2 Sources of Process Waste

Emissions

All phases of the EAF operation result in primary or secondary emissions. Primary emissions include those produced during EAF melting and refining operations, whereas secondary emissions are from charging, tapping, and escape of fumes. The major constituents in EAF emissions are particulate matter and gases (carbon monoxide, SO_x, and NO_x). Carbon monoxide is produced in large quantities in the EAF from oxygen lancing and slag foaming activities as well as from the use of pig iron or DRI in the charge. Large amounts of CO and hydrogen are generated at the start of meltdown

TABLE 2.9
Inputs and Outputs of the Steel-Making Operation (EAF)

Inputs	Outputs
Scrap metal	Molten steel
Direct reduced iron	Slag
Hot briquetted iron	Carbon monoxide
Cold pig iron	Nitrogen oxides and ozone
Hot metal	EAF emission control dust and sludge (K061)
Alloy materials (e.g., aluminum, manganese, chromium, nickel)	
Fluxes (e.g., lime)	
Electricity	
Oxygen	
Nitrogen	
Natural gas	
Oil	
Coal or other carbon source	
Water	

Source: From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.

as oil, grease, and other combustible materials evolve from the surface of the scrap. In the presence of sufficient oxygen these compounds will burn to emit more of CO_2. NO_x is formed in furnace operations when nitrogen passes through the arc between electrodes and also during burner use in EAFs. Levels of about 36 to 90 g of NO_x per ton of steel have been reported.[1]

The organic compounds present in scrap mixes are burned off as VOCs in the furnace or destroyed by preheating followed by afterburning. However, in the absence of sufficient oxygen these hydrocarbon compounds enter the off-gas system. Iron and zinc oxide are the predominant particulate constituents emitted during melting, and nitrogen oxides and ozone are generated in minor amounts. During the refining process small amounts of calcium oxide may also be emitted from the slag. Melting emissions account for about 90% of total EAF emissions. The remaining 10% of emissions are generated during charging and tapping. Iron oxides and oxides from the fluxes are the primary constituents of the slag handling emissions. During tapping, iron oxide is the major particulate compound emitted.[14]

TABLE 2.10
Overview of Key Environmental and Energy Facts: Electric Arc Furnace Steel Making

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
5.2 to 5.6 × 10^6 Btu per net ton of raw steel	Largest sources: melting and refining	Largest source: wet/semiwet air cleaning systems	EAF slag: 50–75% reused
	Particulate: iron oxide (melting); calcium oxide (refining)		K061: EAF dust/sludge Major components: Fe, Zn, Cr, and their oxides Total generation: ~900,000 t/yr

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

Effluents

Although the significant water requirement in EAFs is for noncontact cooling purpose, few furnaces also discharge significant process wastewater. Most electric arc furnaces are operated with dry air cleaning systems with no process wastewater discharges. Other noncontact water applications include water-cooled ductwork, roof, sidewalls, doors, lances, panels, cables, and arms. These systems usually incorporate evaporative cooling towers or closed cooling loops.[1] A small number of wet and semiwet air cleaning systems are also in use.

The pollutants of concern are the same as in wet basic oxygen furnaces, but the concentration of metals (primarily lead and zinc, but also arsenic, cadmium, copper, chromium, and selenium) in wastewater is higher because of the higher percentage of scrap charged. Wastewater treatment operations are similar to those for the wet basic oxygen furnaces, including sedimentation in clarifiers or thickeners and recycle of the water.[14]

Byproducts

The two major byproducts generated during EAF steel making are slag and dust. As a result of the oxidation of phosphorus, silicon, manganese, carbon, and other materials during melting, a slag containing some of these oxidation products is formed on top of the molten metal. Electric arc furnaces produce between 110 and 420 lb of slag for every ton of molten steel made, with an average value of about 230 lb/t.[1] EAF dust is made up of the particulate matter and gases produced during the EAF process. The particulate matter removed from emissions in a dry system is referred to as EAF dust and the particulate matter removed by a wet system is the EAF sludge.

Hazardous wastes

The dust (or sludge) removed from EAF emissions is a listed hazardous waste, K061. The primary component is iron or iron oxides; a typical EAF dust contains 24% iron by weight. In cases where lower grades of scrap are used (generally for carbon steel production), EAF dust can contain large amounts of zinc and lead (as high as 44% ZnO and 4% PbO). Similarly, stainless steel production yields dust with high percentages of chromium and nickel oxides (as high as 12% Cr_2O_3 and 3% NiO). EAF dust also contains cadmium in concentrations on the order of about 0.1% by weight. Other possible EAF dust components include other metals and flux.[1]

The primary leachable hazardous constituents of EAF emission control dust/sludge are lead, cadmium, and hexavalent chromium. Generally, 20 to 40 lb of EAF dust per ton of steel are generated, depending on the mill's specific operating practices, with an average of about 35 lb/t of steel melted.[1] Table 2.11 shows the typical ranges of concentration of each of these elements in EAF dust.

2.5.2.3 Treatment Techniques

Primary emissions are controlled using a direct evacuation system, whereas the secondary emissions are controlled by canopy hoods or auxiliary tapping hoods. A direct evacuation system (DES) consisting of ductwork attached to a separate hole in the furnace roof draws emissions to a gas cleaner, thereby helping to control CO, NO_x, VOC, and particulate emissions. The canopy hood is mainly useful for capturing emissions during charging and tapping. Particulate collection is achieved with a baghouse, or scrubbers and electrostatic precipitators as required. Particulate matter removed from EAF emissions using these cleaning methods is a hazardous waste called "EAF dust."

Cooled and solidified slag is crushed and screened to recover metallics for recycle or reuse and the lower metallic aggregate is used in construction applications. The slag produced in EAFs is either reused or landfilled. EAF dust is conveyed into a gas cleaning system.[1]

The treatment options available for the 14 elements antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, vanadium, and zinc are as follows[15]:

1. Transporting the dust to an offsite processor for thermal treatment and removal of zinc, chemical fixation, glassification, or fertilizer manufacture

TABLE 2.11
Concentration of 14 Regulated Elements in Electric Arc Furnace Dust

Element	Total Concentration (mg/kg)
Antimony	5.0–294.0
Arsenic	10.2–400.0
Barium	24–400
Beryllium	<0.5–8.1
Cadmium	1.4–4,988
Chromium	<0.05–106,000
Lead	1.3–139,000
Mercury	<0.001–41
Nickel	<10–22,000
Selenium	0.07–600
Silver	2.5–71.0
Thallium	0.8–50.0
Vanadium	24–475
Zinc	3900–32,000

Source: From U.S. EPA, Final BDAT Background Document for K061, U.S. EPA, Washington, DC, August 1988.

2. Onsite processing by agglomerating or briquetting and directly recycling back through the EAF (to concentrate the zinc content)
3. Onsite processing in a separate processing facility to glassify or vitrify the heavy metal content
4. Onsite processing using hydrometallurgical or pyrometallurgical processes to upgrade the zinc values to zinc oxide or metallic zinc

In this process EAF dust, other zinc-bearing wastes, recycled materials, coke or coal, lime, and silica are mixed and fed to a rotary furnace. The zinc and other volatile nonferrous metals in the feed are entrained in the furnace off-gas and are carried from the furnace to an external dust collection system. The resulting oxide (zinc calcine) is a crude zinc-bearing product that is further refined at zinc smelters. A byproduct of the process is a nonhazardous, iron-rich slag that can be used in road construction. Solidification technologies change the physical form of the waste to produce a solid structure in which the contaminant is mechanically trapped.

Technologies for onsite recycling of the dust back into an EAF (e.g., briquetting, pelletizing, and pneumatic injection) are still being developed. They have the potential to recover some of the iron oxide values in the dust while concentrating the zinc values. Concentrating the zinc values reduces final recycling costs because smaller quantities of dust will be shipped offsite, and the resulting dust has a higher zinc concentration (improving the cost efficiency of subsequent zinc recovery treatment).

2.6 REFINING AND CASTING

2.6.1 Process Description

Ladle metallurgical furnace (LMF) processes are used to refine molten steel from the BOF or EAF prior to ingot or continuous casting. These processes include the following steps:

1. *Reheating.* Arc reheating or oxygen injection is used to adjust the temperature of steel to levels needed for uninterrupted sequential casting.

2. *Refining*. The first step in refining is deoxidation of the steel with ferromanganese, ferrosilicon, silicomanganese, and aluminum. The second step is desulfurization, which is required for steel grade, which requires low sulfur content. The third step involves addition of ferroalloys and fluxes to the molten steel. The fourth step involves inclusion modification in which the steel in the ladle is stirred by argon gas bubbling to obtain a homogeneous bath temperature, composition and the removal of nonmetallic inclusions. Inclusions responsible for clogging nozzles during the continuous casting process may be removed by calcium treatment.[1]
3. *Degassing*. In vacuum degassing, molten steel is subjected to a vacuum for composition and temperature control, deoxidation, degassing (hydrogen removal), decarburization, and the removal of impurities. While the molten steel is under vacuum, elements that have a relatively higher vapor pressure (such as manganese and zinc) volatilize and exit with the gases.[14] The argon–oxygen decarburization (AOD) is the predominant method used for the manufacture of stainless steel.[1]

In continuous casting, the molten steel is solidified into a semifinished shape (i.e., billet, bloom, or slab) for subsequent rolling in the finishing mill. Continuous casting eliminates the need for conventional processes like the ingot teeming process and directly casting steel into semifinished shapes.[14] The continuous process has higher yields, quality, and productivity compared with the ingot process, as well as higher energy efficiency.[1] The molten steel is delivered in ladles and poured into a reservoir or tundish, from which it is released into the molds of the casting machine. As it descends through the molds, the metal is cooled and emerges with a hardened outer shell. As the semifinished shapes proceed on the runout table, the center also solidifies, providing the semifinished shape.[14]

In ingot casting, the molten steel is teemed into ingot molds followed by cooling and stripping the ingots out of the molds. The ingots are then heated to a uniform temperature in soaking pits to prepare them for rolling. The heated ingots are removed from the pits and rolled into slabs, blooms, or billets. Figure 2.6 illustrates the refining and casting processes, Table 2.12 gives the major inputs

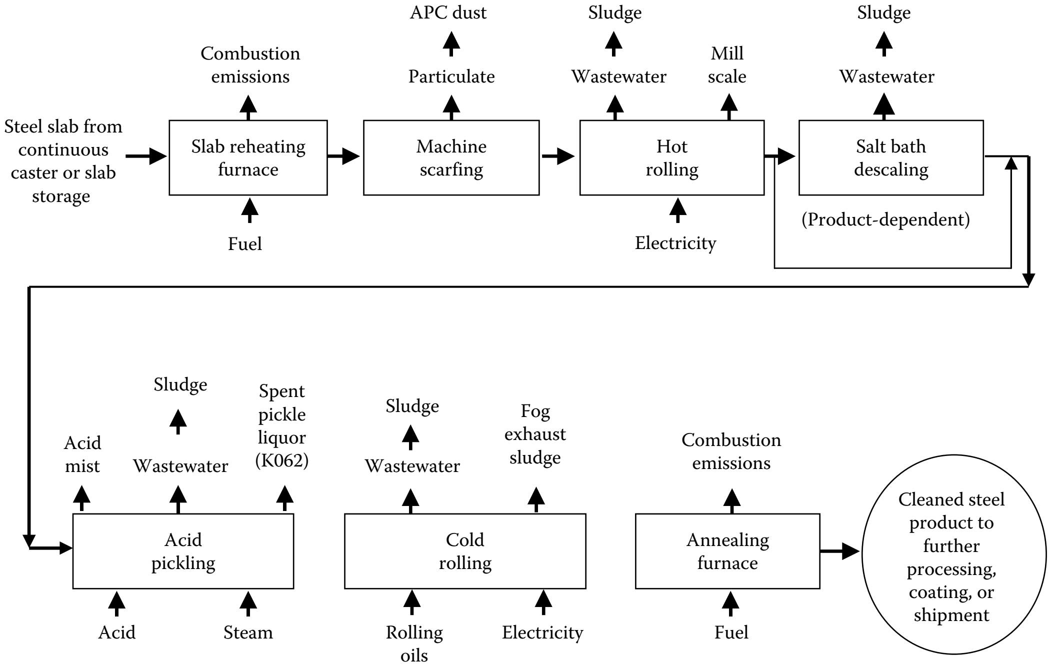

FIGURE 2.6 Refining and casting flow diagram. (From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.)

TABLE 2.12
Inputs and Outputs of the Refining and Casting Process

Inputs	Outputs
Molten steel	Semifinished steel shapes
Alloying elements	Process wastewater
Deoxidants	Scale
Fluxes	Sludge
Fuel (natural gas, coke oven gas, blast furnace gas)	Waste oil and grease
Electricity	Air pollution control (APC) dust
Oxygen	
Argon	
Water	

Source: From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.

and outputs of the process, and Table 2.13 presents an overview of the key environmental and energy facts of refining and casting.

2.6.2 SOURCES OF PROCESS WASTE

2.6.2.1 Emissions

During ingot casting, particulate emissions are produced during the teeming of molten steel into ingot molds. The major emissions include iron and other oxides (FeO, Fe_2O_3, SiO_2, CaO, and MgO). These emissions are controlled by side draft hoods that are vented to a baghouse.[1] Operational changes in ingot casting such as bottom pouring instead of top pouring can reduce total emissions. Bottom pouring exposes much less of the molten steel to the atmosphere than top pouring, thereby reducing the formation of particulate.[6]

TABLE 2.13
Overview of Key Environmental and Energy Facts: Refining and Casting

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
Energy use per ton of cast steel: ingot casting[a], 2.78×10^6 Btu	Largest source: teeming into molds	Sources: vacuum degassing, continuous casting cooling water	Mill scale, sludge
Continuous casting, 0.29×10^6 Btu	Particulate: iron and other oxides	Typical wastewater volume per ton of steel Degassing: 25 gal Continuous casting: <25 gal	

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

[a] Includes soaking pits.

2.6.2.2 Effluent

Among all the refining processes, only vacuum degassing uses process water and generates effluent streams. Vacuum degassing involves direct contact between gases removed from the steel and condenser water. The principal pollutants contained in the effluent are low levels of total suspended solids (TSS) and metals (particularly lead and zinc, but also chromium, copper, and selenium) that volatilize from the steel. Applied water rates for vacuum degassing are typically around 1250 gal/t of steel; with discharge rates of 25 gal/t achieved through high-rate recycle.[15]

Water use in the continuous casting process may be categorized as primary, secondary, and auxiliary. The primary cooling process is a closed-loop, nonevaporative, noncontact cooling of the molten steel shell in the mold (or molds on a multistrand machine) employed to obtain high surface and strand quality. Secondary or spray cooling occurs as the strand moves out of the mold with contact water sprays covering its surface. Auxiliary cooling is noncontact cooling of the casting equipment. Direct contact water cooling system is also used for flume flushing to transport mill scale from the caster runout table.[1]

Applied water rates for the contact systems are typically about 3600 gal/t of cast product; discharge rates for the better controlled casters are less than 25 gal/t. The principal pollutants are total suspended solids, oil, and grease, and low levels of particulate metals.[15]

2.6.2.3 Byproducts

In comparison to the iron-making and steel-making process, wastes generation from refining processes are very small, including solid wastes from the ladle metallurgy facility, argon bubbling APC dust and nozzle blockages. The major byproducts of continuous casting are scale and sludge.

2.6.3 TREATMENT TECHNIQUES

Certain refining processes, including ladle metallurgy, generate particulate emissions. These emissions are typically collected in baghouses as air pollution control dust. Standard treatment for vacuum degassing wastewater includes processing the total recirculating flow or a portion of the flow in clarifiers for TSS removal, cooling with mechanical draft cooling towers, and high-rate recycle. Blowdowns are usually cotreated with steel-making or continuous casting wastewaters for metals removal.[15] Cooling wastewater treatment includes settling basins (scale pits) for scale recovery, oil skimmers, mixed- or single-media filtration, and high-rate recycle.[15]

The air pollution control dusts from refining are nonhazardous and may be processed, recycled, or landfilled. Scale settling basins are provided for periodic collection of scale generated during casting and subsequently wash off from the steel. Fine-grained solids that do not settle out in the scale settling basins are removed by settling, flocculation/clarification processes, or by filtration, depending on the level of water treatment required and the degree of water recycle practiced. The scale is usually recycled and reused within the mill for sintering. Scale may also be landfilled or even charged to an electric arc furnace. Sludge generated during continuous casting is processed and recycled onsite or landfilled.[1]

2.7 FORMING AND FINISHING

2.7.1 PROCESS OVERVIEW

In forming operations the ingots, slabs, billets, and blooms obtained after casting are further processed to produce strip, sheets, plate, bar, rod, or other structural shapes through various hot forming and sometimes cold forming operations, depending on the final product. In hot forming operations, preheated (typically in the range of 1800°F), solidified steel is reduced in cross-section through a series of forming steps by applying mechanical pressure through work rolls to produce semifinished shapes for further hot or cold rolling, or finished shapes. The hot forming mills can be grouped into one of the following four types[18]:

1. Primary mills
2. Section mills
3. Flat mills (plate, hot strip, and sheet)
4. Pipe and tube mills (seamless and butt-weld)

Preheating of steel helps the slabs to undergo a surface preparation step called “scarfing,” which removes defects prior to entering the rolling mill by removing a thin layer of the steel surface through localized melting and oxidation. Surface scale is removed from the heated slab by a scale breaker and water sprays prior to its entry into this mill.

Finishing processes clean the surface of the semifinished, hot-rolled steel products before forming or cold rolling or coating operations. Mill scale, rust, oxides, oil, grease, and soil are chemically removed from the surface of the steel using solvent cleaners, pressurized water, air blasting, abrasives, alkaline agents, salt baths, or acid pickling. Salt bath descaling is a finishing process that uses the physical and chemical properties of molten salt baths to remove heavy scale from the surface of selected stainless and high-alloy steels in subsequent water quenching steps. The two salt bath descaling operations are[1]:

1. *Oxidizing* (*or Kolene*®). This removes scale using molten salt baths other than those containing sodium hydride.
2. *Reducing* (*or Hydride*®). This removes scale using molten salt baths containing sodium hydride.

These two salt bath *descaling processes* may be either batch or continuous and are conducted prior to combination acid pickling (hydrofluoric and nitric acids). Descaling may also be performed using an electrolytic solution of sodium sulfate. The other mechanical descaling operation known as blast cleaning uses abrasives such as sand, steel, or iron grit to clean the steel surface. A compressed air blast cleaning apparatus or rotary-type blasting cleaning machine is used to bring the abrasives in contact with the steel.[18]

The acid pickling process chemically removes oxides and scale from the surface of the steel by the action of water solutions of inorganic acids. It is widely used because of its comparatively low operating costs and ease of operation. Carbon steel is usually pickled with hydrochloric acid; stainless steels are pickled with sulfuric, hydrochloric, nitric, and hydrofluoric acids.[18] The pickling process uses various organic chemicals to inhibit the acid from attacking the base metal. Wetting agents may be used for effective contact of the acid solution with the metal surface. The pickling bath ends with the steel being passed through one or more rinse operations. Alkaline cleaners may also be used to remove mineral oils, grease, and animal fats and oil (used in some rolling solutions) from the steel surface prior to cold rolling. Common alkaline cleaning agents include caustic soda, soda ash, alkaline silicates, and phosphates.[18]

Steel that has been hot-rolled and pickled may be cold-rolled immediately at ambient temperatures before further oxidation can occur. This is done to impart the desired mechanical and surface properties in the steel, and for cold working of the pipe and tube. The two main types of cold mill products are cold-rolled sheets/coils for sale or for further processing in galvanizing and coatings lines, and cold-rolled coils for subsequent tinning.[1]

Cold rolling hardens the steel, which must then be heated in an annealing furnace to make it more ductile. The annealing process involves heating the strip to about 1300°F in an inert atmosphere to prevent oxidation, and then allowing it to cool such that the crystal structure of the steel changes.[1] In batch annealing, gas burners are used to indirectly heat stacked coils, whereas in continuous annealing the coils are unwound and passed through an extended furnace. After the steel has undergone the annealing process, it is run through a temper mill to produce the desired flatness, metallurgical properties, and surface finish.

Steel-coating operations, such as hot coating and electroplating, improve resistance to corrosion and improve appearance. Hot coating operations involve immersing precleaned steel into molten baths of zinc, zinc/aluminum alloy, aluminum, chromium, lead, antimony, tin/lead alloy, and zinc/nickel alloy. Electroplated steel production uses electrodes to deposit a metal coating (zinc, chromium, tin, nickel, brass, cobalt, copper, nickel/tin alloy, zinc/nickel alloy, and zinc/iron/aluminum alloy) onto the surface of the steel. Figure 2.7 illustrates the forming and finishing processes and Table 2.14

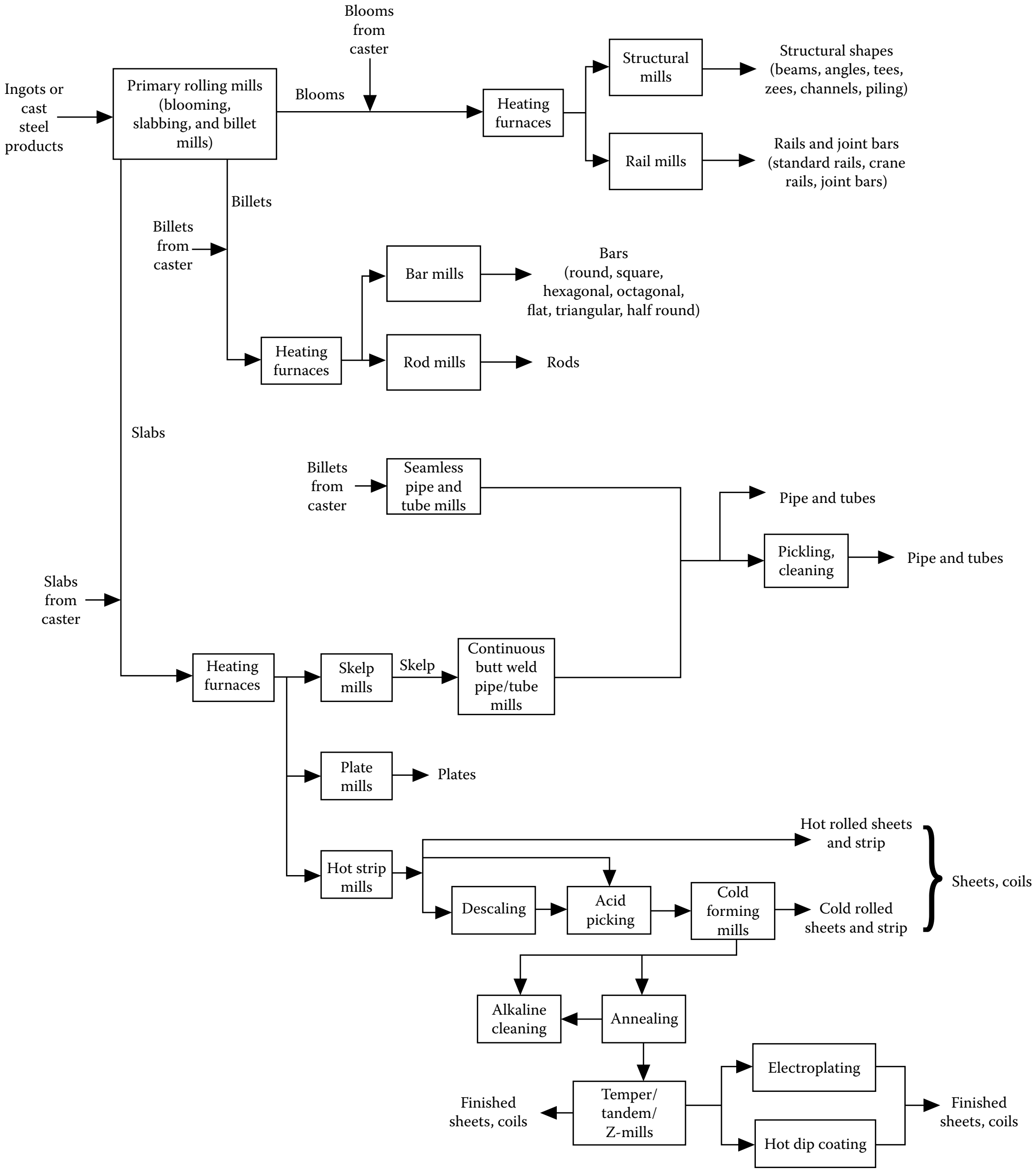

FIGURE 2.7 Forming and finishing flow diagram (sheet production). (From U.S. EPA, Development Document for Final Effluent Limitations Guidelines and Standards for the Iron and Steel Manufacturing Point Source Category, EPA-821-R-02-004, U.S. EPA, Washington, DC, 2002.)

TABLE 2.14
Inputs and Outputs for Steel Sheet

Inputs	Outputs
Semifinished steel shapes (slabs, billets, blooms)	Cleaned steel products (e.g., sheets, plates, bars, pipe)
Process cooling, rinsing, and cleaning water	Process wastewater containing mill scale, oils, other pollutants, and low levels of metals
Pickling acids	Wastewater sludge
Molten salts	Air pollution control (APC) dust
Alkaline cleaners	Spent pickle liquor (K062)
Fuel	Spent pickle liquor rinse water sludge
Electricity	
Oxygen	
Nitrogen	
Hydrogen	

Source: From U.S. EPA, Profile of the Iron and Steel Industry, EPA 310-R-95-005, U.S. EPA, Washington, DC, 1995.

gives the major inputs and outputs for steel sheet, a typical steel product. The key environmental and energy facts of forming and finishing are presented in Table 2.15.

2.7.2 SOURCES OF PROCESS WASTE

2.7.2.1 Emissions

Significant emissions from forming and finishing are limited to operations like reheat furnaces, scarfing, and pickling. Emissions from reheat furnaces include products of combustion, most of which are well controlled. Hand- or machine-scarfing of semifinished steel results in the release of a fine iron oxide fume. The major pollutants emitted during scarfing are iron and other oxides (FeO, Fe_2O_3, SiO_2, CaO, and MgO). Acid mists arise from the hot acid baths used in acid pickling operations. Emissions from teeming and handscarfing are localized and usually uncontrolled.[16] Hydrogen chloride (from hydrochloric acid pickling) is the primary hazardous air pollutant associated with pickling, with emissions from surface pickling typically over 10 t/yr/facility.[6]

2.7.2.2 Effluents

In hot rolling operations, wastewater is generated from direct cooling of mill stand work rolls, descaling of steel prior to rolling, maintenance of steel surface cleanliness and transportation of scale to scale pits. In finishing operations (i.e., pickling, cold reduction, annealing, temper, cleaner, and coating lines), water and sources of wastewater are rinsewater, pickle liquor, and wet air pollution control (WAPC) devices.[19] Water use and discharge rates from hot forming operations vary greatly depending upon the type of hot forming mill and the shapes produced. Applied process water rates typically range from 1500 gal/t for specialty plate mills to more than 6000 gal/t for hot strip mills. Discharge rates can approach zero for mills equipped with high-rate recycle systems.[15]

Typical process wastewaters from finishing operations include rinses and spent concentrates from alkaline cleaners, pickling solutions, plating solutions, and electrochemical treating solutions. Salt bath descaling wastewaters originate from quenching and rinsing operations conducted after processing in the molten salt baths. The principal pollutants in these effluents are TSS, cyanides, dissolved iron, hexavalent and trivalent chromium, and nickel. Wastewater flows normally range

TABLE 2.15
Overview of Key Environmental and Energy Facts: Forming and Finishing

Energy	Emissions	Effluents	Byproducts/Hazardous Wastes
Energy use per net ton of product	Largest sources: machine scarfing, hydrochloric acid pickling (acid mists), reheat furnace (NO_x)	Largest sources: direct cooling and descaling	Mill scale Total generation: 3.7×10^6 t/yr
Reheat furnace: 1.6×10^6 Btu average; 1.4×10^6 Btu for modern furnaces	Particulate: iron and other oxides	Typical wastewater volumes (gal/t)	Reuse: most recycled
Hot rolling: 0.8×10^6 Btu	Typical acid mist generation: >10 tons/yr per facility	Hot forming: 0 to >6000	Rolling sludge Total generation: about 1.0×10^6 t/yr Reuse: minimal
Acid pickling: 1.2×10^6 Btu		Descaling: 300 to 1800	K062, Spent pickle liquor Hazardous components: lead, nickel, chromium
Cold rolling: 0.7×10^6 Btu		Pickling: 70 to 1000	Total generation: about 6 million t/yr Reuse: some recycled
Cleaning/annealing: 1.0×10^6 Btu			

Source: From Energetics, Inc., Energy and Environmental Profile of the U.S. Iron and Steel Industry, DOE/EE-0229, U.S. Department of Energy, Washington, DC, 2000.

from 300 to 1800 gal/t, and are cotreated with wastewaters from other finishing operations.[15] Acid pickling discharge water flows for the different pickling processes are as follows:

1. Between 280 and 1020 gal/t for hydrochloric acid processes
2. Between 90 and 500 gal/t for sulfuric acid processes, and up to 1500 gal/t for combination acid processes.[1]

Pickling done before coating may use a mildly acidic bath; such spent liquor is not considered hazardous. Waste pickle liquor flows typically range between 10 and 20 gal/t of pickled product. Rinsewater flows may range from less than 70 gal/t for bar products to more than 1000 gal/t for certain flat-rolled products. The principal pollutants in rinsewater include TSS, dissolved iron, and metals. For carbon steel operations, the principal metals are lead and zinc; for specialty and stainless steels the metals include chromium and nickel.[15]

Spent pickle liquor in the acid pickling wastewaters is listed as hazardous waste K062, regulated under RCRA, as it contains considerable residual acidity and high concentrations of dissolved iron salts.[2] Exhausted pickling baths are mainly composed of nitrate (150 to 180 g/L), fluoride (60 to 80 g/L), iron (III) (30 to 45 g/L), chromium (III) (5 to 10 g/L), and nickel (II) (3 to 5 g/L).

Process wastewater from cold forming operations results from using synthetic or animal-fat based rolling solutions. The rolling solutions may be treated and recycled at the mill, used on a once-through basis, or a combination of the two. The principal pollutants are TSS, oil and grease (emulsified), and the metals lead and zinc for carbon steels and chromium and nickel for specialty and stainless steels. Chromium may also be a contaminant from cold rolling of carbon steels resulting from wear on chromium-plated work rolls. Toxic organic pollutants including naphthalene, other polynuclear aromatic compounds, and chlorinated solvents have been found in cold rolling wastewaters. Process wastewater discharge rates may range from less than 10 gal/t for mills with recirculated rolling solutions to more than 400 gal/t for mills with direct application of rolling solutions.[15]

2.7.2.3 Byproducts

The main byproducts associated with forming and finishing are scales (typically iron oxides), an oily sludge that results from lubricating the rolls (water treatment plant sludges), and air pollution control dusts associated with treating effluents and cleaning exhaust gases. Coarse scale is separated from the sludge and collected in scale pits. The sludge, which is produced from the treatment of mill scale pit overflows, consists of oils, greases, and fine-grained solids that are collected in settling basins or other separation equipment. This sludge cannot typically be added to the sinter plant because of opacity problems. A number of sludge treating processes are used to de-oil fine sludges to as low as 0.1% at a reasonable cost. However, most oily sludge (containing more than 3% oil) is landfilled rather than recycled. The quantities of scale generated vary, but tend to range between 10 and 80 lb/t for nonoily scale and 4 to 60 lb/t for oily scale. Scale is usually sold or recycled and reused within the plant (usually for sintering), although recycling the oily scale without first deoiling it may cause problems with the opacity of the gaseous stream emitted from the plant or other operational problems. Another byproduct associated with cold rolling is fog exhaust sludge generated from the mist or fog produced during cold rolling. Fog exhaust systems are utilized to allow continuous observation of the strip during processing. Airborne particulates combine with steam and oil mist generated during cold rolling and are discharged to a settling chamber. The settled material is a sludge that is generally landfilled.[1]

2.7.2.4 Hazardous Wastes

Spent pickle liquor is considered a hazardous waste (K062) because it contains considerable residual acidity and high concentrations of dissolved iron salts. For example, spent pickle liquor and waste acid from the production of stainless steel is considered hazardous. The hazardous constituents in K062 are lead, nickel, and hexavalent chromium. Waste pickle liquor sludge generated by lime stabilization of spent pickle liquor is not considered hazardous unless it exhibits one or more of the characteristics of hazardous waste. An estimated 6 million tons of spent pickle liquor are generated annually in the U.S.[1]

2.7.3 TREATMENT TECHNIQUES

Control techniques for removal of acid mists from the exhausted air include packed towers and wet scrubbers. Wet scrubbing has been identified as the control technology achieving Maximum Achievable Control Technology (MACT) standards. Machine scarfing operations generally use an electrostatic precipitator or water spray chamber for control; most hand scarfing operations are uncontrolled.[16] High removal efficiencies (>95%) can be achieved for hydrochloric and sulfuric acids, whereas the efficiency is lower in the case of hydrofluoric acid systems used in stainless steel pickling. About half of spent pickle liquor is managed for recovery of iron, chromium, and nickel.[14] Metals recovery treatment options include a high temperature metals recovery (HTMR) facility or processing onsite using chemical precipitation or other techniques. Spent pickle liquor may be sold as treatment aids for municipal and centralized wastewater treatment systems or as a replacement for ferric chloride solution used in the manufacture of fine ferric oxide powder. This waste can also be discharged or landfilled in a nonhazardous waste landfill once it is neutralized with lime and "delisted," or it can be injected into deep wells. U.S. EPA estimates that 40% of mills using sulfuric acid treat and then dispose of the wastes to receiving bodies of water. Another 45% have the spent liquor hauled offsite by private contractors, who treat the waste with lime stabilization or other methods, and then dispose of it in landfills or lagoons. The remaining 15% of mills use deep water injection, discharge the waste to a publicly owned treatment works (POTW), or engage in acid recovery. It has been estimated that approximately 80% of spent pickle liquor industry-wide is either recycled through acid regeneration plants or used in municipal wastewater treatment.[1]

The principal pollutants are total suspended solids, oil, and grease. Low levels of metals, that is, chromium, copper, lead, nickel, and zinc, are found in particulate form. Cooling and descaling water is normally discharged from the mill into scale pits where the heavier solid particles settle out. The semicleaned water is typically sent on to a treatment plant containing straining devices, solids removal, and/or deep bed filtration to remove fine particulate. Wastewater treatment may also include the collection of fine mill scale, grease, hydraulic fluids, and rolling oils. The process water is then either recycled back to the mill and/or discharged. Descaling wastewaters are usually cotreated with wastewaters from other finishing operations (e.g., combination acid pickling or cold rolling).[15]

In-process controls for acid pickling include countercurrent rinsing, use of indirect heating versus direct steam sparging for acid solutions, and recycle and reuse of fume scrubber blowdown. Some steel mills are equipped with acid recovery or regeneration systems for spent sulfuric and hydrochloric acids, respectively. After elementary neutralization, which raises the pH above 2.0, rinsewaters are usually cotreated with wastewaters from cold rolling, alkaline cleaning, hot coating, and electroplating operations.[15] Conventional treatment of cold rolling wastewaters includes chemical emulsion breaking, dissolved gas flotation for gross oil removal, and cotreatment with other finishing wastewaters for removal of toxic metal dissipated by a system of flood lubrication.[15]

Lubricants applied to the product being rolled must serve the dual purpose of lubricating and cooling. The water treatment plant sludge for cold rolling therefore contains more oil and grease, which are recovered for subsequent reuse (e.g., as a fuel) or recycle rather than for disposal. Solid waste generation in finishing facilities typically consists of central treatment plant (CTP) sludge. This metallic sludge, which contains fine-grained iron oxide, can be further dewatered by mechanical filtration or by use of sludge drying beds. The dewatered sludge is typically landfilled. The treatment of finishing facility effluents also generates both insoluble and soluble oils, which can be processed and sold for reuse.[1]

2.8 POLLUTION PREVENTION MEASURES

The iron and steel industry needs to opt for technologies that help to either prevent or reduce the generation and discharge of process wastes. The various preventive measures to be adopted for reducing the environmental impacts are as follows:

1. Reduction of dust emissions at furnaces by covering iron runners and using nitrogen blankets during tapping of the blast furnace
2. Use of pneumatic transport, enclosed conveyor belts or self-closing conveyor belts, wind barriers and other dust suppression measures to reduce the formation of fugitive dust
3. Use of low-NO_x burners to reduce NO_x emissions from burning fuel in ancillary operations; use of dry SO_x and dust removal systems in flue gases
4. Recycling of iron-rich materials such as iron ore fines, pollution control dust, and scale in a sinter plant
5. Recovery of thermal energy in the gas from the blast furnace before using it as a fuel; increasing fuel efficiency and reducing emissions by improving blast furnace charge distribution; recovery of energy from sinter coolers and exhaust gases
6. Use of a continuous process for casting steel to reduce energy consumption
7. Wastewater minimization

The processes used in manufacturing steel products use a significant amount of water, and wastewater minimization is necessary both in terms of water use and pollutant discharge loadings. These technologies achieve these reductions by retarding pollutant buildup and improving water quality to allow greater reuse; reducing the volume of wastewater treated and discharged; prolonging process bath life, enabling sites to spend less on process bath makeup and reducing bath treatment and disposal costs; and improving treated effluent quality by enhanced wastewater treatment.[19] The various types of water minimization techniques are given in the following sections.

2.8.1 High-Rate Recycle

High-rate recycle systems consist of a water recirculation loop that recycles 95% or more of the water from a process for reuse. They are used for product cooling, cleaning, and air pollution control, in operations like blast furnace iron making, sintering, basic oxygen furnace steel making, vacuum degassing, continuous casting and hot forming operations. However, during the recycling operation a portion of the water is discharged to prevent concentration buildup of contaminants within the system. These blowdown streams are either treated at an end-of-pipe treatment system or discharged to surface water or publicly owned treatment works (POTWs). The high-rate recycle consists of solids removal devices, cooling devices, and water softening technologies to improve water quality prior to reuse. Improvement in the water quality helps to increase recycle rates significantly. This in turn decreases the pollutant loading, blowdown discharges rates, and the amount of fresh water added as makeup.

2.8.2 Countercurrent Cascade Rinsing

Countercurrent cascade rinsing involves a series of consecutive rinse tanks in which water flows from one tank to another in the direction opposite to that of the product flow. Fresh water flows into the rinse tank located farthest from the process tank and overflows to the rinse tanks closer to the process tank. Over a certain period of time, the first rinse becomes contaminated with dragout solution and reaches a stable concentration much lower than the process solution. The second rinse stabilizes at a lower concentration, which enables less rinsewater to be used compared to a one-rinse tank. The greater the number of countercurrent cascade rinse tanks, the less will be the amount of rinsewater needed to adequately remove the process solution. This differs from a single, once-through rinse tank where the rinsewater is discharged without any recycle or reuse. Countercurrent cascade rinsing is used in steel finishing operations, including acid pickling, alkaline cleaning, electroplating, and hot dip coating, as the steel needs to be relatively contaminant-free for processing. However, such systems have a higher capital cost compared to once-through rinsing systems and require more space. Also, the relatively low flow rate through the rinse tanks require the use of air or mechanical agitation for dragout removal.

2.8.3 Acid Reuse, Recycle, and Recovery Systems

Acid reuse, recycle, and recovery systems are extensively used in the acid pickling industry. Typical industrial acid reuse and recovery systems include the following:

1. *Fume scrubber water recycle.* The steel finishing industry uses fume scrubbers to capture acid gases from pickling tanks. Scrubber water, which may contain a dilute caustic solution, is neutralized and recirculated continuously to adsorb the acid. Makeup water is added to replace water lost through evaporation and water that is blown down to end-of-pipe metals treatment.
2. *Hydrochloric acid regeneration.* This process is used to treat the spent pickle liquor containing free hydrochloric acid, ferrous chloride, and water that is obtained from steel finishing operations. The liquor is concentrated by heating to remove some of the water, followed by thermal decomposition in a “roaster” at temperatures (925 to 1050°C) sufficient for complete evaporation of water and decomposition of ferrous chloride into iron oxide (ferric oxide, Fe_2O_3) and hydrogen chloride (HCl) gas.[19] The iron oxide is separated for offsite recovery or

disposal. The hydrogen chloride gas is reabsorbed in water (sometimes rinsewater or scrubber water) to produce hydrochloric acid solution, which is reused in the pickling operation.

3. *Sulfuric acid recovery.* Recovery of sulfuric acid takes place by pumping the spent pickle liquor high in iron content into a crystallizer, where the iron is precipitated (under refrigeration or vacuum) as ferrous sulfate heptahydrate crystals. The water is removed as the crystals are formed and the free acid content of the solution increases to a level usable in the pickling operation. The byproduct ferrous sulfate heptahydrate, referred to as "copperas," is commercially marketable as a coagulant used for water and wastewater treatment. The Blow–Knox–Ruthner process may also be used for sulfuric acid recovery. In this process, the waste liquor is concentrated by evaporation and discharged to reactors where anhydrous hydrogen chloride gas is bubbled to react with the ferrous sulfate, producing sulfuric acid and ferrous chloride. Ferrous chloride is then separated from the sulfuric acid (which is returned to the pickling line) and converted to iron oxide in direct fired roaster. This is followed by the liberation of HCl, which may be recovered by scrubbing, stripping, and recycling to the reactor.[8]
4. *Acid purification and recycle.* This technology is used to process various acid pickling solutions such as the sulfuric acid and nitric/hydrofluoric acids used in stainless steel finishing mills. Acid is purified by adsorption on a bed of alkaline anion exchange resin that separates the acid from the metal ions. Acid is desorbed from the resin using water. The metal-rich, mildly acidic solution passes through the resin and is collected at the top of the bed. Water is then pumped downward through the bed and desorbs the acid from the resin. The purified acid solution is collected at the bottom of the bed and recycled back to the process. Acid purification and recycle reduces nitrate discharges and the overall volume of acid pickling wastewater discharged.

2.8.4 Extension of Process Solution Life

Prolonging the life of solutions reduces the additional investment of fresh process solutions and time spent replacing spent process solutions. The technologies to extend process solution life are as follows:

1. *In-tank filtration.* Steel finishing electroplating and alkaline cleaning operations use in-tank filters to extend process bath life by removing contaminants in the form of suspended solids. Solids are usually disposed of offsite. Devices such as granular activated carbon filters remove dissolved contaminants, such as organic constituents.
2. *Magnetic separation of fines in cold-rolling solution.* Magnetic separators are used to extend the life of cold-rolling solutions. The most effective systems use vertical or horizontal configurations of magnetic rods to remove metal fines.
3. *Evaporation with condensate recovery.* With this technology, steel finishing mills can recover electroplating chemicals such as chrome, nickel, and copper that are lost to electroplating rinsewater. There are two basic types of evaporators: atmospheric and vacuum. In a vacuum evaporator, evaporated water can be recovered as a condensate and reused on site. Generally deionized water is preferred as rinsewater to prevent unwanted contaminants from returning and accumulating in the electroplating process bath in addition to the dragout.

2.9 PROCESS MODIFICATIONS

2.9.1 Effluent-Free Pickling Process with Fluid Bed Hydrochloric Acid Regeneration

This pickling process is operated such that no wastewater is discharged from a hydrochloric acid pickling line. Spent pickle liquor is fed via a settling tank and venturi loop into the fluidized bed reactor. The fluidized bed consists of granulated iron oxide. Residual acid and water are evaporated at 850°C and the iron chloride is converted to hydrochloric acid gas. Growth and the new formation of iron oxide grains in the fluidized bed are controlled so that a dust-free granulated product is obtained. Because the fluidized bed process operates at approximately 850°C, rinse and scrubber water from the pickle line is used at the regeneration plant to cool fluidized bed off-gases, which contain hydrochloric acid vapor and a small amount of iron oxide dust. The off-gases are cooled to approximately 100°C in a venturi scrubber. The thermal energy of the off-gases helps to concentrate the pickling liquor by evaporation before it is fed to the reactor.[19]

From the venturi scrubber, the cooled gas stream goes to the absorber, where hydrogen chloride is absorbed with rinsewater from the pickling line and fresh water to produce hydrochloric acid. The acid is recycled directly to the pickling process or placed in a storage tank for later use. Having passed through the scrubbing stages and mist collector, the fluidized bed off-gases are virtually free of hydrochloric acid and are released to the atmosphere.

2.9.2 NITRIC-ACID-FREE PICKLING

Nitric-acid-free pickling requires the same equipment as conventional acid pickling processes and is also compatible with acid regeneration. This technology uses a nitric-acid-free solution that contains an inorganic mineral acid base, hydrogen peroxide, stabilizing agents, wetting agents, brighteners, and inhibitors.[19]

2.9.3 EFFLUENT-FREE EXHAUST CLEANING

Wet air pollution control (WAPC) devices are used to treat exhaust gases from stainless steel pickling operations, thereby generating wastewater, which are treated using the selective catalytic reduction (SCR) technology in which anhydrous ammonia is injected into the gas stream prior to a catalyst to reduce NO_x to nitrogen and water. The most common types of catalysts are a metal oxide, a noble metal, or zeolite.

2.9.4 ELIMINATION OF COKE WITH COKELESS TECHNOLOGIES

Some cokeless technologies in use or under development include the Japanese direct iron ore smelting (DIOS) process, in which molten iron is produced directly with coal and sinter feed ore, the HIsmelt process, where ore fines and coal are used to achieve a production rate of 8 t/h using ore directly in the smelter, and the Corex process, which has an integral coal desulfurizing step, making it amenable to a variety of coal types.[14]

2.9.5 REDUCING COKE OVEN EMISSIONS

These technologies in use or under development reduce the quantity of coke needed by changing the method by which coke is added to the blast furnace or by substituting a portion of the coke with other fuels, thereby reducing coking emissions. Pulverized coal injection substitutes pulverized coal for about 25 to 40% of coke in the blast furnace. Nonrecovery coke battery allows the combustion of the gases from the coking process, thus consuming the byproducts that are usually recovered. The Davy Still Autoprocess is a precombustion cleaning process in which coke oven battery process water is utilized to strip ammonia and hydrogen sulfide from coke oven emissions. Another option involves the use of alternative fuels such as natural gas, oil, and tar/pitch instead of coke into the blast furnace.[14]

Various treatment technologies are used at the iron and steel plant for recycle system water treatment prior to recycle and reuse, or end-of-pipe wastewater treatment prior to discharge to surface water or a POTW. The physical/chemical treatment technologies extensively used include equalization, tar removal, free and fixed ammonia stripping, cooling technologies, cyanide treatment technologies, oily wastewater treatment technologies, carbon dioxide injection, metals treatment technologies, solids separation technologies, and polishing technologies.

Ammonia stripping also removes cyanide, phenols, and other VOCs typically found in coke-making wastewater. Phenols may also be removed by conversion into nonodorous compounds or into crude phenol or sodium phenolate by either biological means (phenol concentration <25 mg/L) or by physical processes.[21] However, the Koppers dephenolization process is considered to be quite effective as it lowers the phenol content by 80 to 90% in ammonia still wastes. In this process a stream stripping process followed by mixing in a solution of caustic soda results in renewal of pure phenol with the flue gas.[8]

Blast furnace, vacuum degassing, continuous casting, and hot forming operations use cooling methods in recirculation systems. Byproduct recovery coke-making plants commonly use cooling prior to biological treatment systems, because high temperatures are detrimental to the biomass. Cyanide treatment technologies include alkaline and breakpoint chlorination using sodium hypochlorite or chlorine gas in a carefully controlled pH environment to remove cyanide and ammonia. In cyanide precipitation, cyanide combines with iron to form an insoluble iron–cyanide complex that can be precipitated and removed by gravity settling. Ozone oxidation results in the conversion of cyanide to cyanate. Oily wastewaters from hot forming and cold rolling operation are treated by gravity flotation, oil/water separation, emulsion breaking, followed by dissolved air flotation and ultrafiltration.[21–23] Carbon dioxide injection is one method of removing scale-forming metal ions that accumulate in water recirculation systems from BOF recycle water.

Strong reducing agents such as sulfur dioxide, sodium bisulfite, sodium metabisulfite, and ferrous sulfate are used in the iron and steel finishing sites to reduce hexavalent chromium to the trivalent form, which allows the metal to be removed from solution by chemical precipitation.[21–23] Metal-containing wastewaters may also be treated by chemical precipitation or ion-exchange.

Solid wastes, including scale, biosolids, precipitate from cyanide and chemical precipitation systems, and solids from filtration backwash may be treated using scale pits, classifiers, clarifiers, and the microfiltration technique.[19,24,25] Polishing technologies include multimedia filters following clarification to remove small concentrations (<20 mg/L) of entrained suspended solids, or carbon adsorption to remove trace concentrations of organic pollutants remaining in coke-making wastewater following biological treatment. Biological denitrification (anaerobic) can be used to treat coke-making wastewater following biological nitrification. Steel mill sludge thickening and dewatering may be accomplished using gravity thickeners, rotary vacuum filters, centrifugation, sludge drying, belt and pressure filters. However, it has been identified that rolling mill sludges are not amenable to vacuum filters and centrifuges.[9,24,25]

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3 Treatment of Nonferrous Metal Manufacturing Wastes

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CONTENTS

3.1 INDUSTRY DESCRIPTION

The nonferrous metals industry encompasses establishments that engage in the following: primary and secondary smelting and refining of nonferrous metal from ore or scrap; rolling, drawing, and alloying; and the manufacturing and casting of basic metal products such as nails, spikes, wire, and cable. Primary smelting and refining produces metals directly from ores, and secondary refining and smelting produces metals from scrap and process waste. Scrap is bits and pieces of metal parts, bars, turnings, sheets, and wire that are off-specification or worn out but capable of being recycled.[1] The industry does not include the mining and beneficiation of metal ores; rolling, drawing, or extruding metals; or scrap metal collection and preliminary grading.[2]

Two metal recovery technologies are generally used to produce refined metals. Pyrometallurgical technologies are processes that use heat to separate desired metals from other less or undesirable materials. These processes capitalize on the differences between constituent oxidation potential, melting point, vapor pressure, density, or miscibility when melted. Examples of pyrometallurgical processes include drying, calcining, roasting, sintering, retorting, and smelting. Hydrometallurgical technologies differ from pyrometallurgical processes in that the desired metals are separated from undesirables using techniques that capitalize on differences between constituent solubilities or electrochemical properties while in aqueous solutions. Examples of hydrometallurgical processes include leaching, chemical precipitation, electrolytic recovery, membrane separation, ion exchange, and solvent extraction.

During pyrometallic processing, an ore, after being concentrated by beneficiation (crushing, washing, and drying) is sintered, or combined by heat, with other materials such as baghouse dust and flux. The concentrate is then smelted, or melted, in a blast furnace in order to fuse the desired metals into impure molten bullion. This bullion then undergoes a third pyrometallic process to refine the metal to the desired level of purity. Each time the ore or bullion is heated, waste materials are created. Air emissions such as dust may be captured in a baghouse and are either disposed of or returned to the process depending upon the residual metal content. Sulfur is also captured, and when concentrations are above 4% it can be turned into sulfuric acid, a component of fertilizers. Depending upon the origin of the ore and its residual metals content, various metals such as gold and silver may also be produced as byproducts.

There are an estimated 800 plants in the U.S. involved in the primary or secondary recovery of nonferrous metals. These plants represent 61 subcategories. However, many of these subcategories are small, represented by only one or two plants, or do not discharge any wastewater. This chapter focuses on 296 facilities that produce the major nonferrous metals [aluminum, columbium (niobium), tantalum, copper, lead, silver, tungsten, and zinc]. The volume of wastewater discharged in this industry varies from 0 to 540 m^3/T (0 to 160,000 gal/t) of metal produced.[1,3] The global size of the industry is reflected in Table 3.1 (reported in 1000 USD) for the top 20 export countries for nonferrous base metal waste and scrap.[4] Here T = metric ton = 1000 kg = 2204.6 lb, t = 2000 lb.

Nonferrous metal facilities are distributed throughout the U.S. Most sites are located near ore production facilities, near adequate transportation facilities, or near adequate power supplies.

Table 3.2 presents an industry summary for the nonferrous metals industry indicating the number of subcategories and the number and type of dischargers. Table 3.3 presents best practicable technology (BPT) limitations that have been promulgated and reported in the Federal Register.[3,5]

Production operations are subject to a number of regulations, including those imposed by the Resource Conservation and Recovery Act (RCRA),[6,7] the Clean Water Act (CWA),[8] and the Clean Air Act (CAA).[9] A number of RCRA-listed hazardous wastes are produced during primary refining operations that require the heating of ores to remove impurities. Specific pretreatment standards under the CWA apply to the processes associated with copper and aluminum. Lastly, large amounts

TABLE 3.1
Global Size of the Nonferrous Metal Industry (1000 USD)

	2001	2002	2003	2004	2005
U.S.	1,168,979	1,205,751	1,525,103	1,959,119	2,732,399
Germany	1,026,226	987,855	1,188,257	1,586,034	1,782,619
U.K.	539,568	578,023	693,718	967,331	1,256,697
France	514,214	539,964	562,873	899,418	1,124,048
Mozambique	586	297	—	—	1,022,005
Canada	547,290	500,397	502,896	689,104	851,403
Netherlands	278,752	312,556	426,390	616,114	799,880
Belgium	275,577	268,371	295,804	554,500	535,881
Japan	124,748	150,086	215,931	314,197	533,532
Mexico	240,521	202,321	258,524	383,034	501,177
Spain	371,858	407,224	438,838	337,198	499,065
Australia	167,667	210,146	260,276	309,567	378,943
Italy	111,081	109,916	127,044	293,584	367,374
Switzerland	157,352	153,179	175,809	256,276	317,029
Chile	93,607	103,244	121,045	186,278	245,939
Thailand	43,885	49,214	76,483	134,662	224,893
Poland	98,152	105,213	142,727	177,777	223,185
Singapore	138,611	147,928	145,768	194,402	219,283
Sweden	98,071	107,138	140,437	176,010	217,977
Korea, Republic	28,725	30,580	61,183	176,905	200,589

of sulfur are released during copper, lead, and zinc smelting operations, which are regulated under the CAA.

3.2 NONFERROUS METAL PROCESSING INDUSTRY

The nonferrous metals industry is divided into 61 subcategories by the type and source of the metal to be smelted and/or refined and by similar wastewater sources. Twenty-six of these subcategories

TABLE 3.2
Nonferrous Metal Industry Summary

Item	Number
Total subcategories	61
Phase I	26
Phase II	35
Subcategories studied	12
Discharges in industry	
Direct	129
Indirect	79
Zero discharge	215

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.3
BPT Limitations for the Nonferrous Metals Industry[a]

		Secondary Aluminum Smelting						
Parameter	Primary Aluminum Smelting (kg/T of Product)	Chlorine Demagging (kg/T of Magnesium Removed)	Wet Processing (kg/T of Product)	Primary Copper Smelting[b]	Primary Copper Refining (kg/T)	Secondary Copper[b,c] (mg/L)	Primary Lead[b,c] (mg/L)	Primary Zinc (kg/T of Product)
COD	—	6.5	1.0	—	0.05	25	25	0.21
TSS	1.5	175	1.5	—	—	10	—	—
Oil and grease	—	—	—	—	—	—	—	—
Ammonia (as nitrogen)	—	—	0.01	—	—	—	—	—
pH, pH units	6.0–9.0	7.5–9.0	7.5–9.0	—	6.0–9.0	6.0–9.0	6.0–9.0	6.0–9.0
Fluoride	1.0	—	0.4	—	—	—	—	—
Aluminum	—	—	1.0	—	—	—	—	—
Arsenic	—	—	—	—	—	—	—	—
Cadmium	—	—	—	—	0.00003	—	0.5	0.0004
Copper	—	—	0.003	—	0.0008	0.25	—	—
Lead	—	—	—	—	0.00026	—	0.5	—
Selenium	—	—	—	—	—	—	—	0.04
Zinc	—	—	—	—	0.0003	5	5	0.04

Source: From 2-36, U.S. EPA, Effluent guidelines and standards for nonferrous metals, 4OCFR421; 39FR12822, April 8, 1974; Amended by 40FR8514, February 27, 1975; 40FR48348, October 15, 1975; 41FR 54850, December 15, 1976, U.S. EPA, Washington, DC, 1974–1976.

Dashes indicate parameters not regulated for BPT in this subcategory.

[a] Average daily value over 30 consecutive days; maximum daily value permitted is twice the average amount, except for the secondary aluminum subcategory for which maximum values are not available. T = metric ton = 1000 kg = 2204.6 lb.

[b] There shall be no discharge or process wastewater pollutants to navigable waters except for a volume equivalent to the precipitation in excess of the 10-yr 24-h rainfall event.

[c] BPT limitations established for the volume of wastewater equal to the difference between the mean precipitation for that month that falls within the impoundment and the mean evaporation from the pond water surface.

are grouped as Phase I. The remaining subcategories have been identified as Phase II of the nonferrous metals subcategories (Table 3.2).

3.2.1 ALUMINUM

The information on aluminum is collected from the U.S. EPA,[1,2] the Aluminum Association,[10] the U.S. Trade Commission[11] and the U.S. Department of Commerce.[12]

3.2.1.1 Industry Size and Geographic Distribution

The U.S. aluminum smelting industry consists of 23 smelting facilities operated by 13 firms, which employ approximately 20,000 people. The secondary smelting industry operates an estimated 68 plants, with 3600 employees. The majority of primary aluminum producers are located either in the Northwest (39.1% of U.S. capacity) or the Ohio River Valley (31.1% of U.S. capacity), while most secondary aluminum smelters are located in Southern California and the Great Lakes Region. The reason for the difference in plant locations is due to the energy-intensive nature of the primary aluminum smelting process and the cost of fuels. Primary smelters are located in the Northwest and Ohio River Valley to take advantage of the abundant supplies of hydroelectric and coal-based energy, and secondary smelters locate themselves near major industrial and consumer centers to take advantage of the large amounts of scrap generated. Secondary smelting uses 95% less energy to produce the same product as primary reduction. On average, a third of primary production costs are attributable to the cost of energy.

3.2.1.2 Product Characterization

The primary and secondary aluminum industry produces ingots of pure (greater than 99%) aluminum that serve as feedstock for other materials and processes. Within the U.S., the leading end-users of aluminum come from three industries: containers and packaging, transportation, and building and construction. Examples of materials produced with aluminum are sheet metal; aluminum plate and foil; rod, bar, and wire; beverage cans; automobiles; aircraft components; and window/door frames.

At present, the automotive sector is the largest end-user. The next largest end-user is the beverage can stock. Automotive use of aluminum is expected to sky-rocket as the sector increases its use of aluminum to increase fuel efficiency.

3.2.1.3 Industrial Process Description

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred offsite. This discussion, coupled with schematic drawings of the identified processes, provides a concise description of where wastes may be produced in the process.

Primary aluminum processing

Primary aluminum producers generally use a three step process to produce aluminum alloy ingots. First, alumina is extracted from bauxite ore using the Bayer process (Figure 3.1). In the Bayer process, finely crushed bauxite is mixed with an aqueous sodium hydroxide (caustic soda) solution to form slurry. The slurry is then reacted at a high temperature under steam pressure in a vessel known as a digester, and creates a mixture of dissolved aluminum oxides and bauxite residues. During the reaction a majority of the impurities such as silicon, iron, titanium, and calcium oxides drop to the bottom of the digester and form sludge. The remaining sodium aluminate slurry is then flash cooled by evaporation and sent for clarification. During clarification, agents such as starch are added to help any fine impurities that remain in the slurry, such as sand, to drop out, further purifying the sodium aluminate solution. The solution is then fed into a precipitation tank to be crystallized. In the precipitator the solution is allowed to cool with the addition of a small amount of aluminum

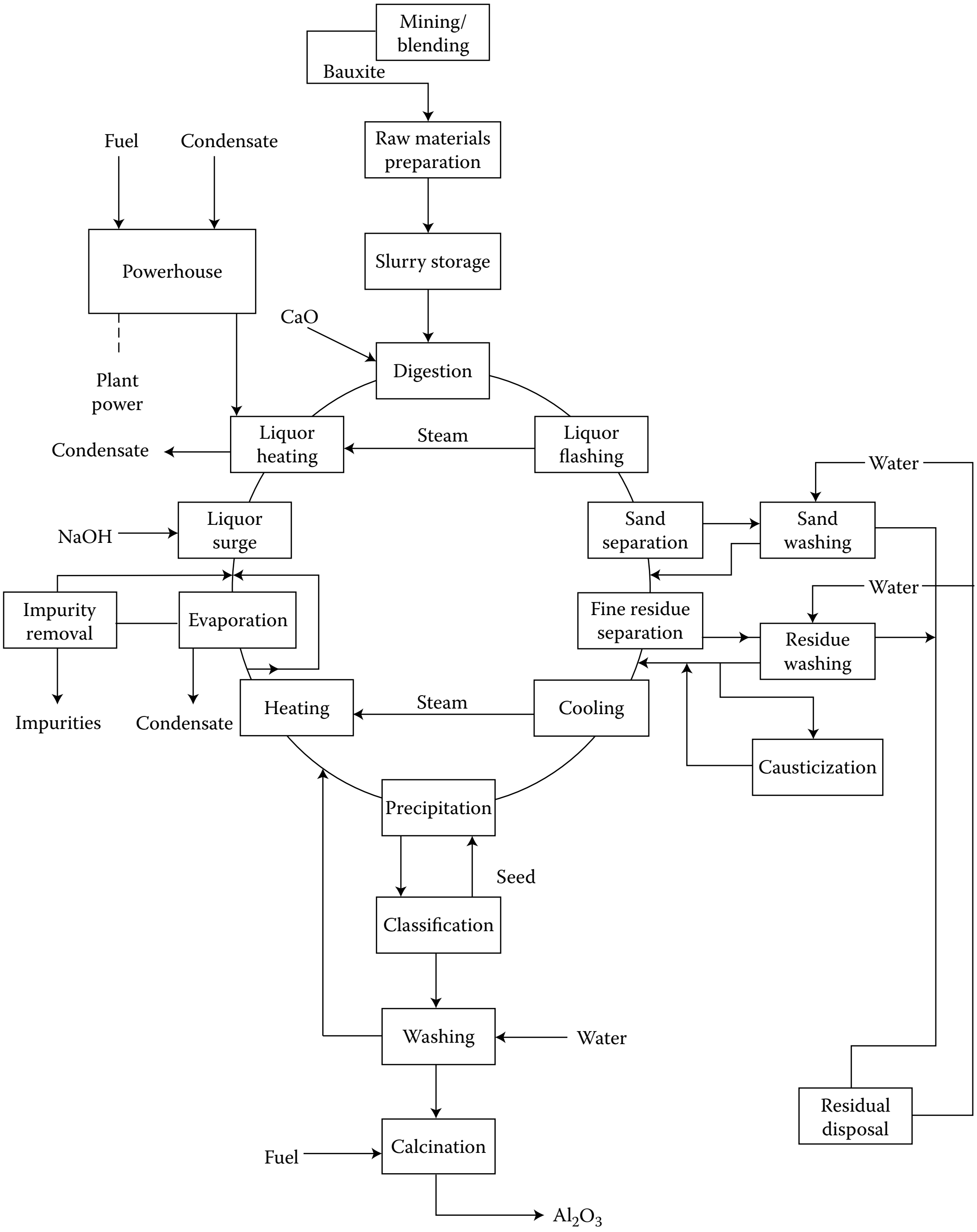


FIGURE 3.1 Bayer process for alumina refining. (From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.)

hydroxide "seed." The seed stimulates the precipitation of solid crystals of aluminum hydroxide and sodium hydroxide.

The aluminum hydroxide crystals settle to the tank bottom, and are removed. The crystals are then washed to remove any caustic soda residues, vacuum dewatered, and sent on for calcination. In the calciners (a type of rotating kiln) the aluminum hydroxide is roasted for further dewatering.

In the second step, the aluminum oxide (alumina) produced during the Bayer process is reduced to make pure molten aluminum. Alumina is a fine white powder, and consists of about equal weights of aluminum and oxygen. The strong chemical bond that exists between the aluminum and oxygen makes separating them difficult—pyrometallurgical separation requires a temperature of about 1980°C (3600°F). However, alumina will dissolve when placed in the molten metal cryolite at around only 950°C (1742°F). Once dissolved, the aluminum oxide is readily separated into aluminum and oxygen by an electric current. The Hall–Heroult process, as this type of electrolytic reduction is known begins with the placement of the alumina into electrolytic cells, or "pots," filled with molten cryolite (Figure 3.2). Although the process requires large amounts of electricity (13 or 15 kW of electricity per kg of aluminum produced), only a low voltage is needed. This allows the pots to be laid out in a series along one long electrical circuit to form what is known as a "potline." Within each pot a positive electric current is passed through the cryolite by means of a carbon anode submerged in the liquid cryolite. The oxygen atoms, separated from aluminum oxide, carry a negative electrical charge and are attracted to the carbon anodes. The carbon and the oxygen combine immediately to form carbon dioxide and carbon monoxide. These gases bubble free of the melt. The aluminum (which is more than 99% pure) collects at the bottom of the pot, is siphoned off, placed into crucibles, and then transferred to melting/holding furnaces.

The third step consists of either mixing the molten aluminum with other metals to form alloys of specific characteristics, or casting the aluminum into ingots for transport to fabricating shops.[1,13] Casting involves pouring molten aluminum into molds and cooling it with water. At some plants, the molten aluminum may be batch treated in furnaces to remove oxide, gaseous impurities, and active metals such as sodium and magnesium before casting. Some plants add a flux of chloride and fluoride salts and then bubble chlorine gas, usually mixed with an inert gas, through the molten mixture. Chloride reacts with the impurities to form HCl, Al_2O_3, and metal chloride emissions. Dross forms to float on the molten aluminum and is removed before casting.

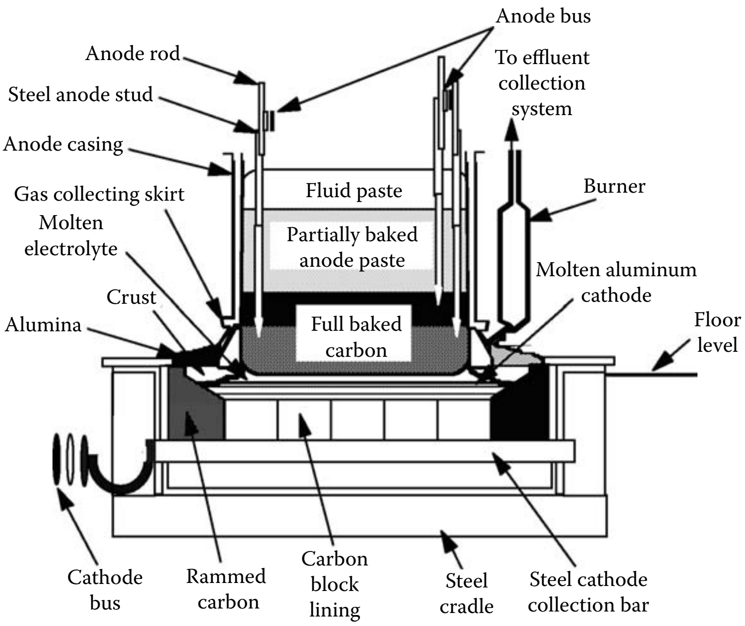
Two types of anodes may be used during the reduction process: either an anode paste or a prebaked anode. Because the carbon is consumed during the refining process (about 0.5 kg of carbon is consumed for every kg of aluminum produced), if anode paste (Soderberg anode) is used, it needs to be continuously fed through an opening in the steel shell of the pot. The drawback to prebaked anodes is that they require that a prebaked anode fabricating plant be located nearby or onsite. Most aluminum reduction plants include their own facilities to manufacture anode paste or prebaked anode blocks. These prebaked blocks, each of which may weigh about 300 kg, must be replaced after 14 to 20 d of service.

The waste materials produced during the primary production of aluminum are fluoride compounds. Fluoride compounds are principally produced during the reduction process. One reason that prebaked anodes are favored is that the closure of the pots during smelting facilitates the capture of fluoride emissions, although many modern smelters use other methods to capture and recycle fluorides and other emissions.

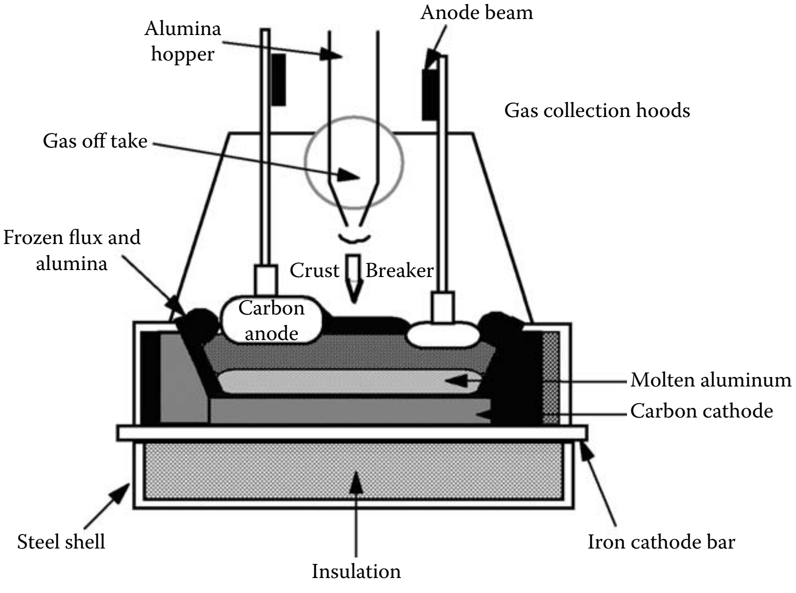
The pots used to hold the aluminum during smelting range in size from 9 to 15 m (30 to 50 ft) long, 2.7 to 3.6 m (9 to 12 ft) wide, and 0.9 to 1.2 m (3 to 4 ft) high, and are lined with refractory brick and carbon. Eventually, the carbon linings crack and must be removed and replaced. However, during the aluminum reduction process iron cyanide complexes form in the carbon portion of the liners. When the linings are removed they are "spent," and are considered to be RCRA-listed hazardous waste.

Secondary aluminum processing

In the secondary production of aluminum, scrap is usually melted in gas- or oil-fired reverberatory furnaces of 14,000 to over 45,000 kg capacities. The furnaces have one or two charging wells separated from the main bath by a refractory wall that permits only molten metal into the main bath. The principal processing of aluminum-base scrap involves the removal of magnesium by treating the molten bath with chlorine or with various fluxes such as aluminum chloride, aluminum fluoride,



Vertical stud soderberg cell



Center-worked prebake cell

FIGURE 3.2 Aluminum anodes. (From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.)

or mixtures of sodium and potassium chlorides and fluorides. To facilitate handling, a significant proportion of the old aluminum scrap, and in some cases new scrap, is simply melted to form sweated pig that must be processed further to make specification-grade ingot.

Another method of secondary aluminum recovery uses aluminum drosses as the charge instead of scrap. Traditionally, the term dross was defined as a thick liquid or solid phase that forms at the surface of molten aluminum, and is a byproduct of melting operations. It is formed with or without fluxing and the free aluminum content of this byproduct can vary considerably. Most people in the industry have generally referred to dross as being lower in aluminum content, while the material with higher aluminum content is referred to as "skim," or "rich" or "white dross." If a salt flux is used in the melting process, the byproduct is usually called a "black dross" or "salt cake." Drosses with about 30% metallic content are usually crushed and screened to bring the content up to about 60 to 70%. They are then melted in a rotary furnace, where the molten aluminum metal collects on the bottom of the furnace and is tapped off. Salt slags containing less than 30% metallic may be leached with water to separate the metallic. In addition to this classic dross-recycling process, a new dross treatment process using a water-cooled plasma gas arc heater (plasma torch) installed in a specially designed rotary furnace has been patented recently. The new process eliminates the use of salt flux in the conventional dross treatment process, and reports recovery efficiencies of 85 to 95%.

3.2.1.4 Material Inputs and Pollution Outputs

The material inputs and pollution outputs resulting from primary and secondary aluminum processing are presented in Table 3.4.

TABLE 3.4
Process Materials Inputs/Pollution Outputs for Aluminum

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Bauxite refining	Bauxite, sodium hydroxide	Particulates		Residue containing silicon, iron, titanium, calcium oxides, and caustic
Alumina clarification and precipitation	Alumina slurry, starch, water		Wastewater containing starch, sand, and caustic	
Alumina calcination	Aluminum hydrate	Particulates and water vapor		
Primary electrolytic aluminum smelting	Alumina, carbon anodes, electrolytic cells, cryolite	Fluoride, both gaseous and particulates, carbon dioxide, sulfur dioxide, carbon monoxide, C_2F_6, CF_4, and perfluorinated carbons (PFC)		Spent potliners
Secondary scrap aluminum smelting	Aluminum scrap, oil or gas, chlorine or other fluxes (aluminum chloride, aluminum fluoride, sodium and potassium chlorides, and fluorides)	Particulates and HCl/Cl_2		Slag containing magnesium and chlorides
Secondary aluminum dross recycling	Aluminum dross, water	Particulates	Wastewater, salts	

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

Primary aluminum processing

Primary aluminum processing activities result in air emissions, process wastes, and other solid-phase wastes. Large amounts of particulates are generated during the calcining of hydrated aluminum oxide, but the economic value of this dust for reuse in the process is such that extensive controls are used to reduce emissions to relatively small quantities. Small amounts of particulates are emitted from the bauxite grinding and materials handling processes. Emissions from aluminum reduction processes are primarily gaseous hydrogen fluoride and particulate fluorides, alumina, carbon monoxide, volatile organics, and sulfur dioxide from the reduction cells, and fluorides, vaporized organics and sulfur dioxide from the anode baking furnaces. A variety of control devices such as wet scrubbers are used to abate emissions from reduction cells and anode baking furnaces.

Wastewaters generated from primary aluminum processing are produced during clarification and precipitation, although much of this water is fed back into the process to be reused.

Solid-phase wastes are generated at two stages in the primary aluminum process; red mud is produced during bauxite refining, and spent potliners result from the reduction process. Red mud normally contains significant amounts of iron, aluminum, silicon, calcium, and sodium. The types and concentrations of minerals present in the mud depend on the composition of the ore and the operating conditions in the digesters. Red mud is managed onsite in surface impoundments, and has not been found to exhibit any of the characteristics of hazardous waste. The process does however, generate hazardous waste. The carbon potliners used to hold the alumina/cryolite solution during the electrolytic aluminum reduction process eventually crack and need to be removed and replaced. When the liners are removed they are "spent," and are considered to be RCRA-listed hazardous waste.

Secondary aluminum processing

Secondary aluminum processing also results in air emissions, wastewaters, and solid wastes. Atmospheric emissions from reverberatory (chlorine) smelting/refining represent a significant fraction of the total particulate and gaseous effluents generated in the secondary aluminum industry. Typical furnace effluent gases contain combustion products, chlorine, hydrogen chloride, and metal chlorides of zinc, magnesium, and aluminum, aluminum oxide and various metals and metal compounds, depending on the quality of the scrap charges. Emissions from reverberatory (fluorine) smelting/refining are similar to those from reverberatory (chlorine) smelting/refining. The use of AlF_3 rather than chlorine in the demagging step reduces demagging emissions. Fluorides are emitted as gaseous fluorides or as dusts. Baghouse scrubbers are usually used for fluoride emission control.

Solid-phase wastes are also generated during secondary scrap aluminum smelting. The slag generated during smelting contains chlorides resulting from the use of fluxes and magnesium. Wastewaters are also generated during secondary aluminum processing when water is added to the smelting slags to aid in the separation of metallics. The wastewaters are also likely to be contaminated with salt from the various fluxes used.

3.2.2 COPPER

The information on copper is collected from U.S EPA,[1,2] the U.S. Department of Commerce,[12] the U.S. Department of the Interior, the Bureau of Mines,[14] and the International Copper Association.[15]

3.2.2.1 Industry Size and Geographic Distribution

Copper ore is mined in both the Northern and Southern Hemispheres but is primarily processed and consumed by countries in the Northern Hemisphere. The U.S. is both a major producer (second only to Chile) and consumer of copper.[1]

The domestic primary unwrought, or unworked, integrated copper industry consists of mines, concentrators, smelters, refineries, and electrowinning plants (the nonferrous metals industry encompasses facilities engaging in primary smelting and refining, but not mining). Of the 65 mines actively producing copper in the U.S., 33 list copper as the primary product. The remaining 32 mines produce copper either as a byproduct or coproduct of gold, lead, zinc, or silver. Nineteen of the 33 active mines that primarily produce copper are located in Arizona, which accounts for 65% of domestically mined copper ore. The remaining mines are located throughout New Mexico and Utah, which together account for 28% of domestic production, and Michigan, Montana, and Missouri accounting for the remainder.[14] Five integrated producers produce over 90% of domestic primary copper.

According to the U.S. Bureau of Mines, 441,000 t of copper are recovered yearly by leaching/electrowinning methods.[14] Although solution operations are conducted throughout the Southwestern U.S., almost 75% of the facilities[14] are located in Arizona. There are two facilities in New Mexico, one in Utah, and one in Nevada.

Of recycled, or secondary copper, 56% is derived from new scrap, while 44% comes from old scrap. Domestically, the secondary copper smelting industry is led by four producers. Like the secondary aluminum industry, these producers buy the scrap they recycle on the open market, in addition to using scrap generated in their own downstream productions. The secondary copper industry is concentrated in Georgia, South Carolina, Illinois, and Missouri.

3.2.2.2 Product Characterization

Because of the superior electrical conductivity of copper, the leading domestic consumer of refined copper is wire mills, accounting for 75% of refined copper consumption. Brass mills producing copper and copper alloy semifabricated shapes are the other major domestic consumers at 23%. The dominant end-users of copper and copper alloy are the construction and electronic products industries, accounting for 65% of copper end-usage. Transportation equipment such as radiators also account for a fair amount of copper end-usage at 11.6%.[1] Copper and copper alloy powders are used for brake linings and bands, bushings, instruments, and filters in the automotive and aerospace industries, for electrical and electronic applications, for antifouling paints and coatings, and for various chemical and medical purposes. Copper chemicals, principally copper sulfate and the cupric and cuprous oxides, are widely used as algaecides, fungicides, wood preservatives, copper plating, pigments, electronic applications, and numerous special applications.

3.2.2.3 Industrial Process Description

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred offsite. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process.[16,17]

Primary copper processing

Copper is mined in both open pits and underground mines, depending upon the ore grade and the nature of the ore deposit. Copper ore typically contains less than 1% copper and is in the form of sulfide minerals. Once the ore is delivered above the ground, it is crushed and ground to a powdery fineness, after which it is concentrated for further processing. In the concentration process, ground ore is slurried with water, chemical reagents are added, and air is blown through the slurry. The air bubbles attach themselves to the copper minerals and are then skimmed off the top of the flotation cells. The concentrate contains between 20 and 30% copper. The “tailings,” or gangue minerals, from the ore fall to the bottom of the cells and are removed, dewatered by “thickeners,” and transported as slurry to a tailings pond for disposal. All water used in this operation, from dewatering thickeners and the tailings pond, is recovered and recycled back into the process.

Copper can be produced either pyrometallurgically or hydrometallurgically depending upon the ore type used as a charge. The ore concentrates, which contain copper sulfide and iron sulfide minerals, are treated by pyrometallurgical processes to yield high-purity copper products. Oxide ores, which contain copper oxide minerals that may occur in other parts of the mine, together with other oxidized waste materials, are treated by hydrometallurgical processes to yield high-purity copper products. Both processes are illustrated in Figure 3.3.

Copper conversion is accomplished by a pyrometallurgical process known as "smelting." During smelting the concentrates are dried and fed into one of several different types of furnaces. There the sulfide minerals are partially oxidized and melted to yield a layer of "matte," a mixed copper–iron sulfide, and "slag," an upper layer of waste.

The matte is further processed by a process known as "converting." The slag is tapped from the furnace and stored or discarded in slag piles onsite. A small amount of slag is sold for railroad ballast and for sand blasting grit. A third product of the smelting process is sulfur dioxide, a gas that is collected, purified, and made into sulfuric acid for sale or for use in hydrometallurgical leaching operations.

Following smelting, the copper matte is fed into a converter. During this process the copper matte is poured into a horizontal cylindrical vessel (approximately 10 × 4 m) fitted with a row of

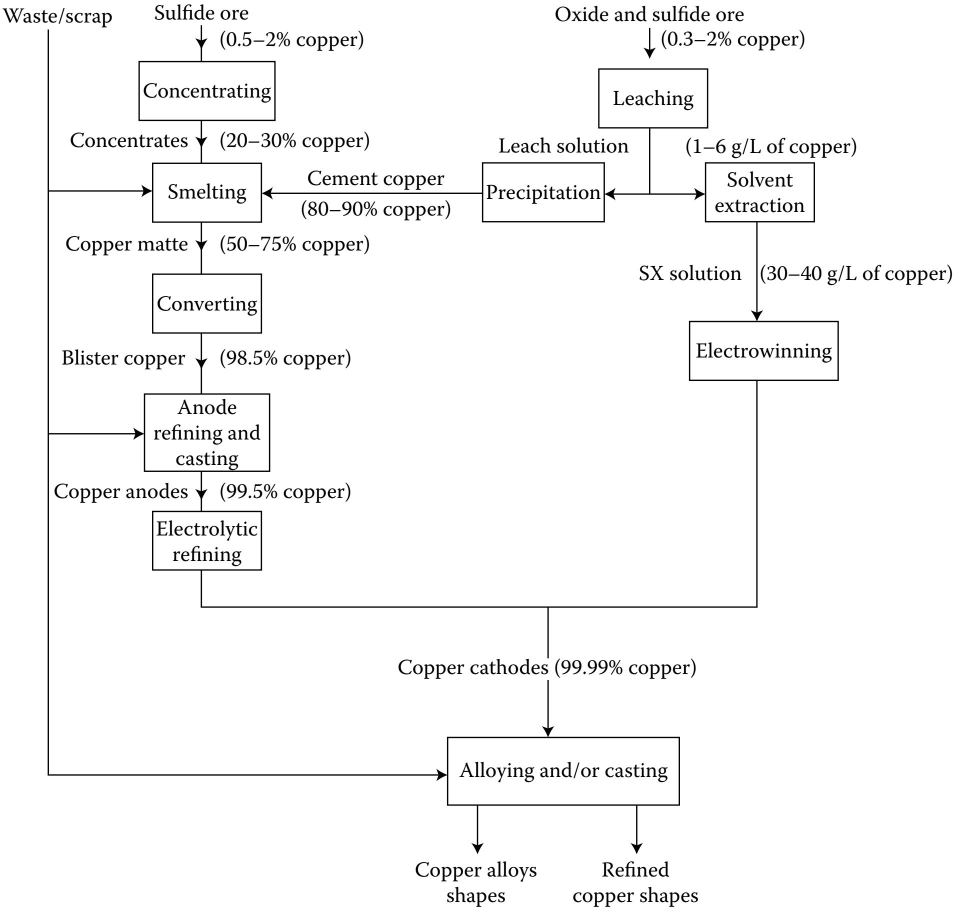


FIGURE 3.3 Copper production process. (From U.S. Congress, Copper Technology and Competitiveness, Congress of the United States, Office of Technology Assessment, Washington, DC, 1994.)

pipes. The pipes, known as "tuyeres," project into the cylinder and are used to introduce air into the converter. Lime and silica are added to the copper matte to react with the iron oxide produced in the process to form slag. Scrap copper may also be added to the converter. The furnace is rotated so that the tuyeres are submerged, and air is blown into the molten matte, causing the remainder of the iron sulfide to react with oxygen to form iron oxide and sulfur dioxide.

Following the "blow," the converter is rotated to pour off the iron silicate slag. Once all of the iron is removed, the converter is rotated back and given a second blow, during which the remainder of the sulfur is oxidized and removed from the copper sulfide. The converter is then rotated to pour off the molten copper, which at this point is called "blister" copper (so named because if allowed to solidify at this point, it will have a bumpy surface due to the presence of gaseous oxygen and sulfur). Sulfur dioxide from the converters is collected and fed into the gas purification system together with that from the smelting furnace, and made into sulfuric acid. Owing to its residual copper content, slag is recycled back to the smelting furnace.

Blister copper, containing a minimum of 98.5% copper, is refined to high-purity copper in two steps. The first step is "fire refining," in which the molten blister copper is poured into a cylindrical furnace, similar in appearance to a converter, where first air and then natural gas or propane are blown through the melt to remove the last of the sulfur and any residual oxygen from the copper. The molten copper is then poured into a casting wheel to form anodes pure enough for "electrorefining."

In electrorefining, the copper anodes are loaded into electrolytic cells and interspaced with copper "starting sheets," or cathodes, in a bath of copper sulfate solution. When a DC current is passed through the cell the copper is dissolved from the anode, transported through the electrolyte, and redeposited on the cathode starting sheets. When the cathodes have built up to a sufficient thickness they are removed from the electrolytic cell and a new set of starting sheets is put in their place. Solid impurities in the anodesus metals such fall to the bottom of the cell as a sludge, where they are ultimately collected and processed for the recovery of precio as gold and silver. This material is known as "anode slime."

The cathodes removed from the electrolytic cell are the primary product of the copper producer and contain >99.99% copper. These may be sold to wire-rod mills as cathodes or processed further to a product called "rod." In manufacturing rod, cathodes are melted in a shaft furnace and the molten copper is poured onto a casting wheel to form a bar suitable for rolling into a 3/8-in.-diameter continuous rod. This rod product is shipped to wire mills, where it is extruded into various sizes of copper wire.

In the hydrometallurgical process, the oxidized ores and waste materials are leached with sulfuric acid from the smelting process. Leaching is performed *in situ* or in specially prepared piles by distributing acid across the top and allowing it to percolate down through the material, where it is collected. The ground under the leach pads is lined with an acid-proof, impermeable plastic material to prevent leach liquor from contaminating groundwater. Once the copper-rich solutions are collected they can be processed by either of two processes—the "cementation" process or the "solvent extraction/electrowinning" process (SXEW).

In the SXEW process, the pregnant leach solution (PLS) is concentrated by solvent extraction. In solvent extraction, an organic chemical that extracts copper but not impurity metals (iron and other impurities) is mixed with the PLS. The copper-laden organic solution is then separated from the leachate in a settling tank. Sulfuric acid is added to the pregnant organic mixture, which strips the copper into an electrolytic solution. The stripped leachate, containing the iron and other impurities, is returned to the leaching operation where its acid is used for further leaching. The copper-rich strip solution is passed into an electrolytic cell known as an "electrowinning" cell. An electrowinning cell differs from an electrorefining cell in that it uses a permanent, insoluble anode. The copper in solution is then plated onto a starting sheet cathode in much the same manner as it is on the cathode in an electrorefining cell. The copper-depleted electrolyte is returned to the solvent extraction process where it is used to strip more copper from the organic. The cathodes produced from the electrowinning process are then sold or made into rod in the same manner as those produced from the electrorefining process.

Electrowinning cells are used also for the preparation of starting sheets for both the electrorefining and electrowinning processes. Here copper is plated onto either stainless steel or titanium cathodes. When sufficient thickness has built up, the cathodes are removed and the copper plating on both sides of the stainless steel or titanium is stripped off. After straightening and flattening, these copper sheets are fabricated into starting sheet cathodes by mechanically attaching copper strips to be used as hangers when they are in the electrolytic cell. Both the starting sheet and the strips become part of the final product. The same care in achieving and maintaining purity must be maintained with these materials as is practiced for the electrodeposited copper.

An activity that is carried out concurrently with primary copper production is sulfur fixation. As mentioned above, in the pyrometallurgical process most of the sulfur in the ore is transformed into sulfur dioxide (although a portion is discarded in the slag). The copper smelting and converting processes typically generate over 0.5 t of sulfur dioxide per ton of copper concentrate. In order to meet CAA emission standards, sulfur dioxide releases must be controlled. This is accomplished by elaborate gas collection and filtration systems, after which the sulfur dioxide contained in the off-gases is made into sulfuric acid. In general, if the sulfur dioxide concentration exceeds 4% it will be converted into sulfuric acid, an ingredient in fertilizer. Fugitive gases containing less than 4% sulfuric acid are either released to the atmosphere or scrubbed to remove the sulfur dioxide. The sulfur recovery process requires the emissions to flow through a filtering material in the air emissions scrubber to capture the sulfur. Blowdown slurry is formed from the mixture of the filtering material and sulfur emissions. This slurry contains not only sulfur, but cadmium and lead, metals that are present in copper ore. The acid plant blowdown slurry/sludge that results from thickening of blowdown slurry at primary copper facilities is regulated by the RCRA as hazardous waste.

Secondary copper processing

The primary processes involved in secondary copper recovery are scrap metal pretreatment and smelting. Pretreatment includes cleaning and concentration to prepare the material for the smelting furnace. Pretreatment of the feed material can be accomplished using several different procedures, either separately or in combination. Feed scrap is concentrated by manual and mechanical methods such as sorting, stripping, shredding, and magnetic separation. Feed scrap is sometimes briquetted in a hydraulic press. Pyrometallurgical pretreatment may include sweating, burning of insulation (especially from scrap wire), and drying (burning off oil and volatiles) in rotary kilns. Hydrometallurgical methods include flotation and leaching with chemical recovery.

After pretreatment, the scrap is ready for smelting. Although the type and quality of the feed material determines the processes the smelter will use, the general fire-refining process is essentially the same as for the primary copper smelting industry.

3.2.2.4 Material Inputs and Pollution Outputs

The material inputs and pollution outputs resulting from primary and secondary copper processing are presented in Table 3.5.

Primary copper processing

Primary copper processing results in air emissions, process wastes, and other solid-phase wastes. Particulate matter and sulfur dioxide are the principal air contaminants emitted by primary copper smelters. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, mercury, and zinc, may also be present, with metallic sulfates and sulfuric acid mist. Single-stage electrostatic precipitators are widely used in the primary copper industry to control these particulate emissions. Sulfur oxides contained in the off-gases are collected, filtered, and made into sulfuric acid.

TABLE 3.5
Process Materials Inputs/Pollution Outputs for Copper

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Copper concentration	Copper ore, water, chemical reagents, thickeners		Flotation wastewaters	Tailings containing waste minerals such as limestone, and quartz
Copper leaching	Copper concentrate, sulfuric acid		Uncontrolled leachate	Heap leach waste
Copper smelting	Copper concentrate, siliceous flux	Sulfur dioxide, particulate matter containing arsenic, antimony, cadmium, lead, mercury, and zinc		Acid plant blowdown slurry/sludge, slag containing iron sulfides, silica
Copper conversion	Copper matte, scrap copper, siliceous flux	Sulfur dioxide, particulate matter containing arsenic, antimony, cadmium, lead, mercury, and zinc		Acid plant blowdown slurry/sludge, slag containing iron sulfides, silica
Electrolytic copper refining	Blister copper		Process wastewater	Slimes containing impurities such as gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, and zinc
Secondary copper processing		Particulates	Slag granulation waste	Slag

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

Large amounts of water are used in the copper concentration process, although disposal of liquid wastes is rarely a problem because the vast majority of the water is recycled back into the process. Once the wastewater exits the flotation process it is sent to a sediment control pond where it is held long enough for most of the sediment to settle.

The seepage and leaking of sulfuric acid solutions used in leaching can also produce liquid wastes; however, this potential is offset by the copper producer's interest in collecting as much of the copper-bearing leachate as possible. Older operations generally do not have protective liners under the piles and experience some loss of leachate. New leaching operations use impermeable membranes to confine leach solutions and channel them to collection ponds.

Electrolytic refining does produce wastewaters that must be treated and discharged, reused, or disposed in some manner. Many facilities use a wastewater treatment operation to treat these wastes.

Primary copper processing primarily generates two solid-phase wastes: slag and blowdown slurry/sludge. Slag is generated during the smelting, converting, fire-refining, and electrolytic refining stages. Slag from smelting furnaces is higher in copper content than the original ores taken from the mines. These slags may therefore, be sent to a concentrator and the concentrate is returned to the smelter. This slag processing operation results in slag tailings. Slag resulting from converting and fire refining is also normally returned to the process to capture any remaining mineral values. Blowdown slurry/sludge that results from the sulfur recovery process is regulated by the RCRA as hazardous waste.

Secondary copper processing
Secondary copper processing produces the same types of wastes as primary pyrometallurgical copper processing. One type of secondary processing pollutant that differs from primary processing is the air emissions. Air pollutants are generated during the drying of chips and borings to remove excess oils and cuttings fluids and causes discharges of large amounts of dense smoke containing soot and unburned hydrocarbons. These emissions can be controlled by baghouses or direct-flame afterburners.

3.2.3 LEAD

The information on lead is collected from U.S. EPA,[1,2,17,18] the U.S. Department of Commerce,[12] and the U.S. Department of the Interior, Bureau of Mines.[14]

3.2.3.1 Industry Size and Geographic Distribution

The U.S. is the world's third largest primary lead producer, with one-seventh of all production reserves. Over 80% of the lead ore mined domestically comes from Missouri. The majority of lead ore mined in the U.S. is smelted in conventional blast furnaces and refined using pyrometallurgical methods.

The U.S. is the world's largest recycler of lead scrap and is able to meet about 72% of its total refined lead production needs from scrap recycling. The secondary lead industry consists of 16 companies that operate 23 battery breakers–smelters with capacities of between 10,000 and 120,000 t/yr; five smaller operations with capacities between 6000 and 10,000 t/yr; and 15 smaller plants that produce mainly specialty alloys for solders, brass and bronze ingots, and miscellaneous uses.

3.2.3.2 Product Characterization

Within the U.S., the power storage battery industry is the largest end-user of lead, accounting for 83% of domestically consumed lead. Industrial demand for batteries is rising due both to the growth in demand for stationary batteries used in telecommunications and back-up power systems for computers, lighting, and security systems, as well as an increased need for mobile batteries used in fork lifts and other battery-powered vehicles. Additional lead end-uses and users of consequence are ammunition, consumers of lead oxides used in television glass and computers, construction (including radiation shielding) and protective coatings, and miscellaneous uses such as ballasts, ceramics, and crystal glass.

3.2.3.3 Industrial Process Description

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred offsite. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process.

Primary lead processing
Primary lead production consists of four steps: sintering, smelting, drossing, and pyrometallurgical refining (Figure 3.4). To begin, a feedstock comprised mainly of lead concentrate is fed into a sintering machine. Other raw materials may be added, including iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and particulates gathered from pollution control devices. In the sintering machine the lead feedstock is subjected to blasts of hot air, which burn off the sulfur, creating sulfur dioxide. The lead material existing after this process contains about 9% of its weight in carbon.[1] The sinter is then fed along with coke, various recycled and cleanup materials, limestone, and other

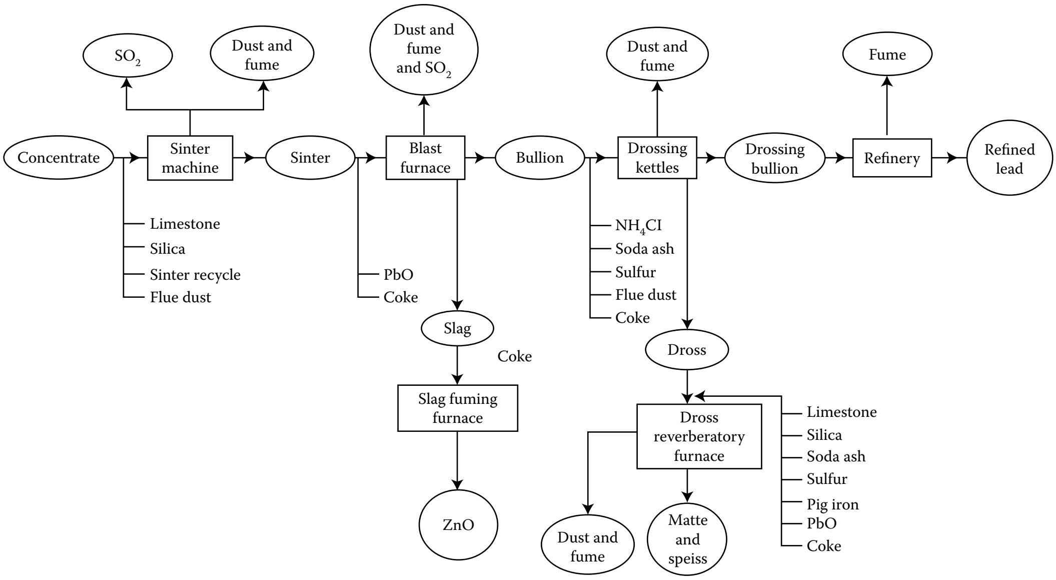


FIGURE 3.4 Primary lead production process. (From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.)

fluxing agents into a blast furnace for reducing, where the carbon acts as a fuel and smelts or melts the lead material. The molten lead flows to the bottom of the furnace where four layers form: "speiss" (the lightest material, basically arsenic and antimony); "matte" (copper sulfide and other metal sulfides); blast furnace slag (primarily silicates); and lead bullion (98% weight lead). All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag, which contains zinc, iron, silica, and lime, is stored in piles and is partially recycled. Sulfur oxide emissions are generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed.

Rough lead bullion from the blast furnace usually requires preliminary treatment in kettles before undergoing refining operations. During drossing the bullion is agitated in a drossing kettle and cooled to just above its freezing point (370 to 430°C). Dross, which is composed of lead oxide, along with copper, antimony, and other elements, floats to the top and solidifies above the molten lead.

The dross is removed and fed into a dross furnace for recovery of the nonlead mineral values. To enhance copper recovery, drossed lead bullion is treated by adding sulfur-bearing materials, zinc, and/or aluminum, lowering the copper content to approximately 0.01%.

During the fourth step the lead bullion is refined using pyrometallurgical methods to remove any remaining nonlead saleable materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as antimony, arsenic, tin, and copper oxide). The lead is refined in a cast iron kettle over five stages. Antimony, tin, and arsenic are removed first. Then gold and silver are removed by adding zinc. Next, the lead is refined by vacuum removal of zinc. Refining continues with the addition of calcium and magnesium. These two materials combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step caustic soda and/or nitrates may be added to the lead to remove any remaining traces of metal impurities. The refined lead will have a purity of 99.90 to 99.99%, and may be mixed with other metals to form alloys, or may be directly cast into shapes.

The processes used in the primary production of lead produce several wastestreams of concern under different regulatory scenarios. The listed RCRA hazardous wastes include smelting plant wastes that are sent to surface impoundments to settle. The impoundments are used to collect solids from miscellaneous slurries, such as acid plant blowdown, slag granulation water, and plant washings. Acid plant blowdown is generated during the production of lead in the same way it is produced at a copper plant—during the recovery of sulfur dioxide emissions. Slag granulation water is produced when hot slag from the process is sprayed with water to be cooled and granulated before transport to a slag pile. Plant washing is a housekeeping process and the washdown normally contains a substantial amount of lead and other process materials. When these materials accumulate in a surface impoundment or are dredged from the surface impoundment they are regulated as hazardous waste.

Secondary lead processing

The secondary production of lead begins with the recovery of old scrap from worn-out, damaged, or obsolete products and new scrap that is made of product wastes and smelter-refinery drosses, residues, and slags. The chief source of old scrap in the U.S. is lead-acid batteries, although cable coverings, pipe, sheet, and terne-bearing metals also serve as a source of scrap. Solder, a tin-based alloy, may also be recovered from the processing of circuit boards for use as lead charge.

Although some secondary lead is recovered directly for specialty products like babbitt metal, solder, re-melt, and copper-base alloys, about 97% of secondary lead is recovered at secondary lead smelters and refineries as either soft (unalloyed) or antimonial lead, most of which is recycled directly back into the manufacture of new batteries.[1] Unlike copper and zinc, where scrap processing varies tremendously by scrap type and ultimate use, the dominance of lead battery scrap allows for a more standard secondary recovery process. Before smelting, batteries must be broken by one of several techniques and then classified into their constituent products. The modern battery-breaking process classifies the lead into metallics, oxides, and sulfate fragments, and organics into separate casing and plate separator fractions. Cleaned polypropylene case fragments are recycled back into battery cases or other products. The dilute sulfuric acid is either neutralized for disposal or is recycled into the local acid market. One of three main smelting processes is then used to reduce the lead fractions to produce lead bullion.

The majority of domestic battery scrap is processed in blast furnaces or rotary reverberatory furnaces. Used to produce a semisoft lead, a reverberatory furnace is more suitable for processing fine particles and may be operated in conjunction with a blast furnace. The reverberatory furnace is a rectangular shell lined with refractory brick, and is fired directly with oil or gas to a temperature of 1260°C. The material is heated by direct contact with combustion gases. The average furnace can process about 45 t/d. About 47% of the charge is recovered as lead product and is periodically tapped into mold or holding pots. A total of 46% of the charge is removed as slag and later processed in blast furnaces. The remaining 7% of the furnace charge escapes as dust or fume. Short (batch) or long (continuous) rotary furnaces may be used. Slags from reverberatory furnaces are processed through the blast furnace for recovery of alloying elements.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (~4.5% of the charge), scrap iron (~4.5%), limestone (~3%), and coke (~5.5%). The remaining 82.5% of the charge comprises oxides, pot furnace refining drosses, and reverberatory slag. The proportions of rerun slags, limestone, and coke, respectively, vary to as high as 8%, 10%, and 8% of the charge.[1] The processing capacity of the blast furnace ranges from 20 to 70 t/d. Similar to iron cupolas, the blast furnace is a vertical steel cylinder lined with refractory brick. Combustion air at 350 to 530 kg m^{-2} (0.5 to 0.75 psi) is introduced through tuyeres (pipes) at the bottom of the furnace. Some of the coke combusts to melt the charge, and the remainder reduces lead oxides to elemental lead.

As the lead charge melts, limestone and iron float to the top of the molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate. The product lead constitutes roughly 70% of the charge. From the holding pot, the lead is usually cast into large ingots, called pigs or sows. About 18% of the charge is recovered as slag, with ~60% of this being matte. Roughly 5% of the charge is retained for reuse, and the remaining 7% of the charge escapes as dust or fume.

Refining/casting is the use of kettle-type furnaces for remelting, alloying, refining, and oxidizing processes. Materials charged for remelting are usually lead alloy ingots that require no further processing before casting. Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials. Refining furnaces, as in primary lead production, are used either to remove copper and antimony to produce soft lead, or to remove arsenic, copper, and nickel for hard lead production.

Newer secondary recovery plants use lead paste desulfurization to reduce sulfur dioxide emissions and waste sludge generation during smelting. Battery paste containing lead sulfate and lead oxide is desulfurized with soda ash to produce market-grade sodium sulfate solution. The desulfurized paste is processed in a reverberatory furnace. The lead carbonate product may then be treated in a short rotary furnace. The battery grids and posts are processed separately in a rotary smelter.

3.2.3.4 Raw Material Inputs and Pollution Outputs

The material inputs and pollution outputs resulting from primary and secondary lead processing are presented in Table 3.6.

Primary lead processing

Primary lead processing activities usually result in air emissions, process wastes, and other solid-phase wastes. The primary air emissions from lead processing are substantial quantities of SO_2 and/

TABLE 3.6

Process Materials Inputs/Pollution Outputs for Lead

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Lead sintering	Lead ore, iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and baghouse dust	Sulfur dioxide, particulate matter containing cadmium and lead		
Lead smelting	Lead sinter, coke	Sulfur dioxide, particulate matter containing cadmium and lead	Plant washdown wastewater, slag granulation water	Slag containing impurities such as zinc, iron, silica, and lime, surface impoundment solids
Lead drossing	Lead bullion, soda ash, sulfur, baghouse dust, coke			Slag containing such impurities as copper, surface impoundment solids
Lead refining	Lead drossing bullion			
Lead-acid battery breaking	Lead-acid batteries			Polypropylene case fragments, dilute sulfuric acid
Secondary lead smelting	Battery scrap, rerun slag, drosses, oxides, iron, limestone, and coke	Sulfur dioxide, particulate matter containing cadmium and lead		Slag, emission control dust

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

or particulates. Nearly 85% of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. The off-gas containing a strong stream of SO_2 (5 to 7% SO_2) is sent to a sulfuric acid plant, and the weak stream (less than 0.5% SO_2) is vented to the atmosphere after removal of particulates. Particulate emissions from sinter machines range from 5 to 20% of the concentrated ore feed. Approximately 15% of the sulfur in the ore concentrate fed to the sinter machine is eliminated in the blast furnace. However, only half of this amount, about 7% of the total sulfur in the ore, is emitted as SO_2. Particulate emissions from blast furnaces contain many different kinds of material, including a range of lead oxides, quartz, limestone, iron pyrites, iron-limestone-silicate slag, arsenic, and other metallic compounds associated with lead ores. The emission controls most commonly used are fabric filters and electrostatic precipitators.

As mentioned above, approximately 7% of the total sulfur present in lead ore is emitted as SO_2. The remainder is captured by the blast furnace slag. The blast furnace slag is composed primarily of iron and silicon oxides, as well as aluminum and calcium oxides. Other metals may also be present in smaller amounts, including antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, silver, and zinc. This blast furnace slag is either recycled back into the process or disposed of in piles on site. About 50 to 60% of the recovery furnace output is slag and residual lead, which are both returned to the blast furnace. The remainder of this dross furnace output is sold to copper smelters for recovery of the copper and other precious metals.

The smelting of primary lead produces a number of wastewaters and slurries, including acid plant blowdown, slag granulation water, and plant washdown water. Slag granulation water is generated when slag is disposed. It can either be sent directly to a slag pile or granulated in a water jet before being transported to the slag pile. The granulation process cools newly generated hot slag with a water spray. Slag granulation water is often transported to surface impoundments for settling. Plant washdown water results from plant housekeeping and normally contains a substantial amount of lead and other process materials. Acid plant blowdown results from the conversion of SO_2 to sulfuric acid. All of these materials are included in the definition of hazardous waste.

Secondary lead processing

Secondary lead processing results in the generation of air emissions and solid-phase wastes. As with primary lead processing, reverberatory and blast furnaces used in smelting account for the vast majority of the total lead emissions. Other emissions from secondary smelting include oxides of sulfur and nitrogen, antimony, arsenic, copper, and tin. Smelting emissions are generally controlled with a settling and cooling chamber, followed by a baghouse. Other air emissions are generated during battery breaking. Emissions from battery breaking are mainly sulfuric acid and dusts containing dirt, battery case material, and lead compounds. Emissions from crushing are also mainly dusts.

The solid-phase wastes generated by secondary processing are emission control dust and slag. Slag is generated from smelting, and the emission control dust, when captured and disposed of, is considered to be hazardous waste.

3.2.4 ZINC

The information on zinc is collected from U.S. EPA,[1,2] the U.S. Department of Commerce,[12] and the U.S. Department of the Interior, Bureau of Mines.[14]

3.2.4.1 Industry Size and Geographic Distribution

Zinc is the fourth most widely used metal after iron, aluminum, and copper (lead is fifth). In abundant supply world-wide, zinc is mined and produced mainly in Canada, the former Soviet Union, Australia, Peru, Mexico, and the U.S. Historically, in the U.S. recoverable zinc has been mined in

19 states: Alaska, Arizona, Colorado, Idaho, Illinois, Kansas, Missouri, Montana, Nevada, New Jersey, New Mexico, New York, Oklahoma, Pennsylvania, Tennessee, Utah, Virginia, Washington, and Wisconsin. Nearly 50% of all domestic zinc is produced in Alaska. Other top producing states in order of output are Tennessee, New York, and Missouri.

The zinc industry employs 2200 workers at mines and mills and 1400 at primary smelters.[14] The four primary zinc smelters in the U.S. are located in Illinois, Oklahoma, Tennessee, and Pennsylvania. There are ten secondary zinc recovery plants in the U.S.[17]

3.2.4.2 Product Characterization

The U.S. accounts for almost one-quarter of worldwide slab zinc consumption and is the world's single largest market. About 80% of zinc is used in metal form, and the rest is used in compound form. In total, 90% of zinc metal is used for galvanizing steel (a form of corrosion protection) and for alloys, and is used in a wide variety of materials in the automotive, construction, electrical, and machinery sectors of the economy. Zinc compound use also varies widely, but is mainly found in the agricultural, chemical, paint, pharmaceutical, and rubber sectors of the economy.

3.2.4.3 Industrial Process Description

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred offsite. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process.[1,2,14,18]

Primary zinc processing

The primary production of zinc begins with the reduction of zinc concentrates to metal. The zinc concentration process consists of separating the ore (which may be as little as 2% zinc) from waste rock by crushing and flotation, a process normally performed at the mining site and is discussed in the chapter on metal mining. Zinc reduction is accomplished in one of two ways: either pyrometallurgically by distillation (retorting in a furnace) or hydrometallurgically by electrowinning. Because hydrometallurgical refining accounts for more than 80% of total zinc refining, pyrometallurgical zinc refining will not be discussed in detail.

Four processing stages are generally used in hydrometallurgical zinc refining: calcining, leaching, purification, and electrowinning. Calcining, or roasting, is common to both pyrometallic and electrolytic (a form of hydrometallurgy) zinc refining, and is performed to eliminate sulfur and form leachable zinc oxide. Roasting is a high-temperature process that converts zinc sulfide concentrate to an impure zinc oxide called calcine. Roaster types include multiple-hearth, suspension, or fluidized-bed. In general, calcining begins with the mixing of zinc-containing materials with coal. This mixture is then heated, or roasted, to vaporize the zinc oxide, which is then moved out of the reaction chamber with the resulting gas stream. The gas stream is directed to the baghouse (filter) area, where the zinc oxide is captured in baghouse dust.

In a multiple-hearth roaster, the concentrate drops through a series of nine or more hearths stacked inside a brick-lined cylindrical column. As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine. Multiple hearth roasters are unpressurized and operate at ~700°C (1300°F).

In a suspension roaster, the concentrates are blown into a combustion chamber. The roaster consists of a refractory-lined cylindrical shell, with a large combustion space at the top and two to four hearths in the lower portion. Additional grinding, beyond that required for a multiple-hearth furnace, is normally required to ensure that heat transfer to the material is sufficiently rapid for the desulfurization and oxidation reaction to occur in the furnace chamber. Suspension roasters are also unpressurized and operate at about 980°C (1800°F).

Fluidized-bed roasters require that the sulfide concentrates be finely ground. The concentrates are then suspended and oxidized on a feedstock bed supported on an air column. As in the suspension bed roaster, the reduction rates for desulfurization are more rapid than in the older multiple-hearth processes. Fluidized-bed roasters operate under a pressure slightly lower than atmospheric and at temperatures averaging 980°C (1800°F). In the fluidized-bed process, no additional fuel is required after ignition has been achieved. The major advantages of this roaster are greater throughput capacities and greater sulfur removal capabilities. All of the above calcining processes generate sulfur dioxide, which is controlled and converted to sulfuric acid as a marketable process byproduct.

Electrolytic processing of desulfurized calcine consists of three basic steps: leaching, purification, and electrolysis. Leaching refers to the dissolving of the captured calcine in a solution of sulfuric acid to form a zinc sulfate solution. The calcine may be leached once or twice. In the double-leach method, the calcine is dissolved in a slightly acidic solution to remove the sulfates. The calcine is then leached a second time in a stronger solution that dissolves the zinc. This second leaching step is in fact the beginning of the third step of purification, because many of the iron impurities (such as goethite and hematite) drop out of the solution as well as the zinc.

After leaching, the solution is purified in two or more stages by adding zinc dust. The solution is purified as the dust forces deleterious elements to precipitate so that they can be filtered out. Purification is usually conducted in large agitation tanks. The process takes place at temperatures ranging from 40 to 85°C (104 to 185°F), and pressures ranging from atmospheric to 2.4 atm. The elements recovered during purification include copper as a cake and cadmium as a metal. After purification the solution is ready for the final step—electrowinning.

Zinc electrowinning takes place in an electrolytic cell and involves running an electric current from a lead–silver alloy anode through the aqueous zinc solution. This process charges the suspended zinc and forces it to deposit onto an aluminum cathode (a plate with an opposite charge) that is immersed in the solution. Every 24 to 48 h, each cell is shut down, the zinc-coated cathodes removed and rinsed, and the zinc mechanically stripped from the aluminum plates. The zinc concentrate is then melted and cast into ingots, and is often as high as 99.995% pure.

Electrolytic zinc smelters contain up to several hundred cells. A portion of the electrical energy is converted into heat, which increases the temperature of the electrolyte. Electrolytic cells operate at temperature ranges from 30 to 35°C (86 to 95°F) at atmospheric pressure. During electrowinning a portion of the electrolyte passes through cooling towers to decrease its temperature and to evaporate the water it collects during the process.

Sulfur dioxide is generated in large quantities during the primary zinc refining process and sulfur fixation is carried out concurrently with the primary production process in order to meet CAA emission standards. Concentrations of sulfur dioxide in the off-gas vary with the type of roaster operation. Typical concentrations for multiple-hearth, suspension, and fluidized-bed roasters are 4.5 to 6.5%, 10 to 13%, and 7 to 12%, respectively. This sulfur dioxide is then converted into sulfuric acid.

The sulfur recovery process requires that the emissions from the zinc calcining or roasting process, where over 90% of potential sulfur dioxide is generated during primary zinc refining, flow through a filtering material in the air emissions scrubber to capture the sulfur. Blowdown slurry is formed from the mixture of the filtering material and sulfur emissions. This slurry contains not only sulfur, but cadmium and lead, materials that are always present in zinc ore. The acid plant blowdown slurry/sludge that results from thickening of blowdown slurry at primary zinc facilities is regulated by RCRA as hazardous waste.

During the electrolytic refining of zinc, solid materials in the electrolytic solution that have not been captured previously during purification may precipitate out in the electrolytic cell. When the cells undergo their periodic shutdown to recover zinc, this precipitated waste (known as anode slimes/sludges) is collected during cell cleaning. Once collected it is sent to a wastewater treatment plant. The resulting sludges are also regulated by RCRA as hazardous waste.

Secondary zinc processing

The secondary zinc industry processes scrap metals for the recovery of zinc in the form of zinc slabs, zinc oxide, or zinc dust. Zinc recovery involves three general operations: pretreatment, melting, and refining. Secondary recovery begins with the separation of zinc-containing metals from other materials, usually by magnetics, sink-float, or hand sorting. In situations where nonferrous metals have been mixed, molten zinc collects at the bottom of the sweat furnace and is subsequently recovered. The remaining scrap is cooled and removed to be sold to other secondary processors. In the case of zinc-galvanized steel, the zinc will be recovered largely in furnace dust after the scrap is charged into a steel-making furnace and melted. Almost all of the zinc in electric arc furnace (EAF) dust is first recovered in an upgraded, impure zinc oxide product and is then shipped to a primary pyrometallurgical zinc smelter for refinement to metal.

Clean new scrap, mainly brass and rolled zinc clippings and reject diecastings, generally requires only remelting before reuse. During melting, the zinc-containing material is heated in kettle, crucible, and reverberatory and electric induction furnaces. Flux is used to trap impurities from the molten zinc. Facilitated by agitation, flux and impurities float to the surface of the melt as dross, which is skimmed from the surface. The remaining molten zinc may be poured into molds or transferred to the refining operation in a molten state. Drosses, fragmentized diecastings, and mixed high-grade scrap are typically remelted, followed by zinc distillation with recovery as metal, dust, or oxide. Sometimes, high-purity drosses are simply melted and reacted with various fluxes to release the metallic content; often the recovered metal can be used directly as a galvanizing brightener or master alloy. Zinc alloys are produced from pretreated scrap during sweating and melting processes. The alloys may contain small amounts of copper, aluminum, magnesium, iron, lead, cadmium, and tin. Alloys containing 0.65 to 1.25% copper are significantly stronger than unalloyed zinc.

Medium- and low-grade skims, oxidic dust, ash, and residues generally undergo an intermediate reduction-distillation pyrometallurgical step to upgrade the zinc product before further treatment, or they are leached with acid, alkaline, or ammoniacal solutions to extract zinc. For leaching, the zinc-containing material is crushed and washed with water, separating contaminants from the zinc-containing material. The contaminated aqueous stream is treated with sodium carbonate to convert zinc chloride into sodium chloride and insoluble zinc hydroxide. The sodium chloride is separated from the insoluble residues by filtration and settling. The precipitate zinc hydroxide is dried and calcined (dehydrated into a powder at high temperature) to convert it into crude zinc oxide. The zinc oxide product is usually refined to zinc at primary zinc smelters. The washed zinc-containing metal portion becomes the raw material for the melting process.

Distillation retorts and furnaces are used either to reclaim zinc from alloys or to refine crude zinc. Bottle retort furnaces consist of a pear-shaped ceramic retort (a long-necked vessel used for distillation). Bottle retorts are filled with zinc alloys and heated until most of the zinc is vaporized, sometimes for as long as 24 h. Distillation involves vaporization of zinc at temperatures from 980 to 1250°C (1800 to 2280°F), and condensation as zinc dust or liquid zinc. Zinc dust is produced by vaporization and rapid cooling, and liquid zinc results when the vaporous product is condensed slowly at moderate temperatures.

Air pollution control can be an area of concern when pyrometallurgical processes are used in the secondary recovery of zinc. When the recovery process used is simply an iron pot remelt operation to produce zinc metal, fumes will not normally be generated. If slab zinc is needed and a rotary furnace is used, any air emissions are captured directly from the venting system (a rotating furnace sweats, or melts, the zinc separating it from drosses with different melting points, which allows it to be poured off separately). Air emissions become more of a concern when more complicated processes are used to produce zinc powder. Retort and muffle furnaces used to produce zinc powder heat the zinc and other charges to such a high temperature that the zinc vaporizes and is captured in the pollution control equipment. It is this zinc oxide dust that is the process' marketable product. Hoods are utilized around the furnace openings that are used to add additional charge.

The fumes collected from the hoods are not normally of high quality and are used for products such as fertilizer and animal feed.

For the most part, the zinc materials recovered from secondary materials such as slab zinc, alloys, dusts, and compounds are comparable in quality to primary products. Zinc in brass is the principal form of secondary recovery, although secondary slab zinc has risen substantially over the last few years because it has been the principal zinc product of electric arc furnace (EAF) dust recycling. Impure zinc oxide products and zinc-bearing slags are sometimes used as trace element additives in fertilizers and animal feeds. About 10% of the domestic requirement for zinc is satisfied by old scrap.

As a result of environmental concerns, both domestic and worldwide secondary recovery of zinc (versus disposal) is expected to increase. However, the prospect for gains higher than 35 to 40% of zinc consumption is relatively poor because of the dissipative nature of zinc vapor.

3.2.4.4 Material Inputs and Pollution Outputs

The material inputs and pollution outputs resulting from primary and secondary zinc processing are presented in Table 3.7.

Primary zinc processing

Primary zinc processing activities generate air emissions, process wastes, and other solid-phase wastes. Air emissions are generated during roasting, which is responsible for more than 90% of

TABLE 3.7
Process Materials Inputs/Pollution Outputs for Zinc

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Zinc calcining	Zinc ore, coke	Sulfur dioxide, particulate matter containing zinc and lead		Acid plant blowdown slurry
Zinc leaching	Zinc calcine, sulfuric acid, limestone, spent electrolyte		Wastewaters containing sulfuric acid	
Zinc purification	Zinc-acid solution, zinc dust		Wastewaters containing sulfuric acid, iron	Copper cake, cadmium
Zinc electrowinning	Zinc in a sulfuric acid/aqueous solution, lead-silver alloy anodes, aluminum cathodes, barium carbonate, or strontium, colloidal additives		Dilute sulfuric acid	Electrolytic cell slimes/sludges
Secondary zinc smelting	Zinc scrap, electric arc furnace dust, drosses, diecastings, fluxes	Particulates		Slags containing copper, aluminum, iron, lead, and other impurities
Secondary zinc reduction distillation	Medium-grade zinc drosses, oxidic dust, acids, alkalines, or ammoniacal solutions	Zinc oxide fumes		Slags containing copper, aluminum, iron, lead, and other impurities

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

the potential SO_2 emissions. Approximately 93 to 97% of the sulfur in the feed is emitted as sulfur oxides. Sulfur dioxide emissions from the roasting process at all four primary zinc processing facilities are recovered at onsite sulfuric acid plants. Much of the particulate matter emitted from primary zinc facilities is also attributable to roasters. Although the amount and composition of particulates varies with operating parameters, the particulates are likely to contain zinc and lead.

Wastewaters may be generated during the leaching, purification, and electrowinning stages of primary zinc processing when electrolyte and acid solutions become too contaminated to be reused again. This wastewater needs to be treated before discharge.

Solid wastes, some of which are hazardous, are generated at various stages in primary zinc processing. Slurry generated during the operation of sulfuric acid plants is regulated as hazardous waste, as is the sludge removed from the bottom of electrolytic cells. The solid copper cake generated during purification is generally sent offsite to recover the copper.

Secondary zinc processing

Secondary zinc processing generates air emissions and solid-phase wastes. Air emissions result from sweating and melting and consist of particulates, zinc fumes, other volatile metals, flux fumes, and smoke generated by the incomplete combustion of grease, rubber, and plastics in the zinc scrap. Zinc fumes are negligible at low furnace temperatures. Substantial emissions may arise from incomplete combustion of carbonaceous material in the zinc scrap. These contaminants are usually controlled by afterburners, and particulate emissions are most commonly recovered by fabric filters. Emissions from refining operations are mainly metallic fumes. Distillation/oxidations operations emit their entire zinc oxide product in the exhaust dust. Zinc oxide is usually recovered in fabric filters with collection efficiencies of 9 to 99%.

The secondary zinc recovery process generates slags that contain metals such as copper, aluminum, iron, and lead. Although slag generated during primary pyrometallurgical processes is exempt from regulation as a hazardous waste under RCRA, slag resulting from secondary processing is not automatically exempt. Therefore if secondary processing slag exhibits a characteristic (e.g., toxicity for lead) it would need to be managed as a hazardous waste.

3.2.5 COLUMBIUM AND TANTALUM

Columbium (also known as niobium) and tantalum metals are produced from purified salts, which are prepared from ore concentrates and slags resulting from foreign tin production. The concentrates and slags are leached with hydrofluoric acid to dissolve the metal salts. Solvent extraction or ion exchange is used to purify the columbium and tantalum. The salts of these metals are then reduced by means of one of several techniques, including aluminothermic reduction, sodium reduction, carbon reduction, and electrolysis.[19–21] Owing to the reactivity of these metals, special techniques are used to purify and work the metal produced.

3.2.6 SILVER

There are four primary silver production facilities in the U.S. Of these, two discharge wastewaters. Wastes containing silver include materials from photography, the arts, electrical components, industry, and miscellaneous sources. These wastes are processed by a wide variety of techniques to recover the silver.[2] Because the process is highly specific for the type of waste, no attempt to discuss the various processes will be made in this chapter.

3.2.7 TUNGSTEN

There are several variations in the processes of this industry depending on the ore. In each process, one of the intermediate products is tungstic acid. The tungstic acid is converted to ammonium tungstate, which is dried and heated to form ammonium paratungstate. This intermediate is converted to oxides in a nitrogen–hydrogen atmosphere. Finally, the oxides are reduced to tungsten metal powder at high temperature in a hydrogen atmosphere.[2]

3.2.8 Beryllium

Primary beryllium production occurs at two plants within the U.S. One of these plants discharges its wastewater to the environment. Because of the limited number of facilities, beryllium production will not be discussed in this chapter.

3.2.9 Selenium

Primary selenium recovery occurs at a single site that does not discharge to the environment. Consequently, this subcategory is not discussed further in this chapter.

3.3 WASTEWATER CHARACTERIZATION

Each metal subcategory uses different processes and emits different pollutant concentrations and types in the process wastewater. The following paragraphs and tables present information on the wastewater streams for each of the subcategories.[2, 3]

Raw waste characteristics for the industry generally reflect the products and the methods used to manufacture them. Because there is such diversity in products, processing, raw materials, and process control, there is a wide range of characteristics. The variations exist among different streams within each subcategory, as well as among similar streams (such as casting wastewater) in different subcategories. Discharge of nonprocess wastes (sanitary, boiler blowdown, noncontact cooling water, and so on) with process wastestreams and other nonprocess-related variables such as raw water quality can contribute to this lack of uniformity.

3.3.1 Primary Aluminum

Process wastewater sources for this subcategory are primarily related to air pollution control. Wet air pollution controls on anode bake furnaces generate wastewater in plants utilizing prebaked anodes. Suspended solids, oil and grease, sulfur compounds, and fuel combustion products characterize this stream. Some organics may also be present as a result of the release of coal tar products during anode baking. Degassing with chlorine requires wet air pollution control methods and results in a wastewater stream. Cryolite recovery also produces a wastewater stream that has significant amounts of fluoride, suspended solids, and TOC. Other wastestreams may also be produced by cooling water, in cathode making, and from storm water runoff. Tables 3.8 and 3.9 present classical and toxic data for the primary aluminum subcategory.

3.3.2 Secondary Aluminum

Sources of process wastewater in the secondary aluminum industry include demagging air pollution control, wet nulling of residues, and contact cooling water. Removal of magnesium (demagging) involves the passage of chlorine or aluminum fluoride through the melt, leading to the release of magnesium in heavy fuming. The wastestreams from the air pollution control devices contain significant levels of suspended solids and chlorides or fluorides, as well as moderate amounts of heavy metals. Milling streams also contain suspended solids, and contact cooling water contains oil and grease, chlorides, and suspended solids. Tables 3.10 and 3.11 present classical and toxic pollutant concentrations found in the wastewater streams of this subcategory.

TABLE 3.8
Classical Pollutants in the Raw Wastewater of the Primary Aluminum Subcategory

			Concentration (mg/L)		
Pollutant	**Number of Samples**	**Number of Detections**	**Range**	**Median**	**Mean**
COD	2	2	3.1–5700		2900
TOC	2	2	140–440		290
TSS	2	2	2100–11,000		6600
Total phenol	3	3	0.11–0.27	0.13	0.17
Oil and grease	2	2	4.2–5.5		4.9
Ammonia	1	1	25		
Fluoride	3	3	0.46–2700	170	960

Source: From Wang, L.K., Hung, Y.T., and Shammas, N.K., Eds., *Advanced Physicochemical Treatment Processes*, Humana Press, Totowa, NJ, 2006.

TABLE 3.9
Concentrations of Toxic Pollutants Found in Primary Aluminum Wastewater

			Concentration (μg/L)		
Toxic Pollutant	**Number of Samples**	**Number of Detections >10 μg/L**	**Range**	**Median**	**Mean**
Metals and Inorganics					
Antimony	3	2	ND–770	100	290
Arsenic	3	2	ND–260	130	130
Asbestos (fibers/L)	1	1	2.3×10^{10}	—	—
Beryllium	3	2	ND–75	33	36
Cadmium	3	2	2.3– <200	<24	<75
Chromium	3	2	ND–2200	84	760
Copper	3	3	13–140	77	77
Cyanide	3	2	<4–28,000	22	9300
Lead	3	2	0.56–770	650	470
Mercury	3	0	<0.1–1.3	<0.38	<0.59
Nickel	3	3	500–730	640	620
Selenium	3	1	ND–450	<0.19	150
Silver	3	1	ND–<250	<0.38	<83
Thallium	3	1	ND–<50	ND	<17
Zinc	3	2	ND–540	25	190
Phthalates					
Bis(2-ethylhexyl) phthalate	7	5	ND–450	—[a]	82
Butyl benzyl phthalate	7	2	ND–86	—[a]	22
Di-n-butyl phthalate	7	1	ND–120	—[a]	19
Diethyl phthalate	7	0	ND–2.5	—[a]	0.4
Phenols					
Phenol	6	1	ND–70	—[a]	12

Continued

TABLE 3.9 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Aromatics					
Benzene	8	1	ND–6.0	—[a]	0.8
Toluene	8	0	ND–1.0	—[a]	0.2
2,4-Dinitrotoluene	7	0	ND	—	—
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	7	1	ND–50	—[a]	8.4
Acenaphthylene	7	1	ND–30	—[a]	5.6
Anthracene	7	4	ND–150	8.6	40
Benz (a) anthracene	7	3	ND–180	—[a]	38
Benzo (a) pyrene	7	3	ND–570	—[a]	95
Benzo (b) fluoranthene	7	1	ND–260	—[a]	37
1,12-Benzoperylene	7	1	ND–150	—[a]	24
Benzo (k) fluoranthene	7	2	ND–210	—[a]	39
Chrysene	7	2	ND–230	—[a]	40
Dibenz (a,h) anthracene	7	1	ND–110	—[a]	16
Fluoranthene	7	4	ND–320	49	95
Fluorene	7	1	ND–50	—[a]	7.4
Indeno(1,2,3-cd)pyrene	7	2	ND–350	—[a]	53
Naphthalene	7	1	ND–20	—[a]	3.0
Pyrene	7	4	ND–220	39	70
Phenanthrene	7	3	ND–230	—[a]	50
Halogenated Aliphatics					
Chloroform	8	0	ND–6.0	—[a]	0.8
Methylene chloride	8	1	ND–15	—[a]	3.0
Pesticides and Metabolites					
Gamma-BHC	7	0	ND–0.01	—[a]	—[b]

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

3.3.3 PRIMARY COLUMBIUM AND TANTALUM

The production of columbium and tantalum involves the processing of ore concentrates and slags to obtain columbium and tantalum salts, and the subsequent reduction of those salts to the respective metals. The ore concentrates are dissolved by hydrofluoric acid, and the insoluble gangue is removed by filtration. Waste gangue is generally settled in holding ponds. Overflow from this pond is extremely acidic and contains metals, fluorides, and suspended solids. After filtration, the digested solution is extracted with an organic solvent, and the raffinate is discharged as a wastestream with high concentrations of organics, fluorides, metals, and suspended solids. The organic stream is then stripped with water to yield aqueous solutions of columbium and tantalum. Precipitation of the salts is accomplished by the addition of ammonia and is followed by filtration. The filtrate typically

TABLE 3.10
Classical Pollutants in the Raw Wastewater of the Secondary Aluminum Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L) Range	Median	Mean
COD	4	4	9–580	35	160
TOC	4	3	ND–140	3.8	37
TSS	4	4	63–13,000	150	3300
Total phenol	4	4	0.003–0.025	0.01	0.012
Oil and grease	4	4	3.2–98	13	32
Ammonia	2	2	<0.10–140	—	70
Chloride	3	3	400–6000	1400	2600

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

TABLE 3.11
Concentrations of Toxic Pollutants Found in Secondary Aluminum Wastewater

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
Metals and Inorganics					
Antimony	4	2	ND–950	150	310
Arsenic	4	3	ND–4000	32	1000
Asbestos (fibers/L)	1	1	7.5×10^8	—	—
Beryllium	4	4	<7.0–310	69	<110
Cadmium	4	4	<35–2000	260	<640
Chromium	4	4	<5–1200	68	<340
Copper	4	4	<70–6100	440	<1800
Cyanide	4	4	<1–7.8	4.6	<4.5
Lead	4	4	<65–5600	1500	<2200
Mercury	4	3	ND–6.4	0.38	1.8
Nickel	4	3	ND–620	<28	<170
Selenium	4	1	ND–200	ND	50
Silver	4	2	ND–30	<13	<14
Thallium	3	1	ND–540	ND	180
Zinc	4	4	<2000–5900	2200	<3100
Phthalates					
Bis(2-ethylhexyl) phthalate	6	4	ND–2000	46	380
Butyl benzyl phthalate	6	2	ND–98	—[a]	19
Di-n-butyl phthalate	6	3	ND–44	—[a]	16
Dimethyl phthalate	6	1	ND–56	—[a]	9.5
Di-n-octyl phthalate	6	1	ND–25	—[a]	4.2
Nitrogen Compounds					
3,3′-Dichlorobenzidine	6	0	ND–2.0	—[a]	0.3

Continued

TABLE 3.11 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Aromatics					
Benzene	10	1	ND–94	—[a]	9.4
1,4-Dichlorobenzene	6	1	ND–26	—[a]	4.3
Polycyclic Aromatic Hydrocarbons					
Acenaphthylene	6	1	ND–17	—[a]	2.8
Anthracene	6	0	ND–4.0	—[a]	0.7
Benzo (a) pyrene	6	1	ND–12	—[a]	2.0
Chrysene	6	1	ND–190	—[a]	32
Fluoranthene	6	2	ND–12	—[a]	3.8
Naphthalene	6	0	ND–1.0	—[a]	0.2
Phenanthrene	6	0	ND–10	—[a]	1.7
Pyrene	6	1	ND–24	—[a]	4.0
Polychlorinated Biphenyls					
Aroclor 1248	6	0	ND–0.3	—[a]	0.1
Aroclor 1254	6	0	ND–0.9	—[a]	0.4
Halogenated Aliphatics					
Carbon tetrachloride	10	0	ND–10	—[a]	1.0
Chloroform	10	6	ND–31	—[a]	3.4
Dichlorobromomethane	10	1	ND–19	—[a]	1.9
1,2-Dicloroethane	10	0	ND–1.0	—[a]	0.1
1,2-*trans*-Dichloroethylene	10	5	ND–57	9.5	19
Methylene chloride	10	1	ND–93	—[a]	9.3
Tetrachloroethylene	10	1	ND–310	—[a]	31
Trichloroethylene	10	5	ND–530	—[a]	61
Pesticides and Metabolites					
Alpha-BHC	6	0	ND–0.1	—[a]	—[b]
Beta-BHC	6	0	ND–0.4	—[a]	—[b]
Gamma-BHC	6	0	ND–0.1	—[a]	—[b]
Chlordane	6	0	ND–0.3	—[a]	0.1
4,4′-DDE	6	0	ND–0.01	—[a]	—[b]
4,4′-DDT	6	0	ND–0.02	—[a]	—[b]
Dieldrin	6	0	ND–0.2	—[a]	—[b]
Endrin	6	0	ND–0.01	—[a]	—[bt]
Endrin aldehyde	6	0	ND–0.04	—[a]	0.01
Heptachlor	6	0	ND–0.04	—[a]	0.01
Heptachlor epoxide	6	0	ND–0.2	—[a]	—[b]
Isophorone	6	0	ND–3.0	—[a]	0.5

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

contains high concentrations of ammonia as well as significant levels of fluoride, various metals, and suspended solids. Conversion of the salts to metals produces wastewater from air pollution control scrubbers and reduction leachates. These streams contain high levels of dissolved solids and significant concentrations of fluoride.[2] Tables 3.12 and 3.13 present classical and toxic pollutant concentration data for this subcategory.

TABLE 3.12
Classical Pollutants in the Raw Wastewater of the Primary Columbium and Tantalum Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L)		
			Range	Median	Mean
COD	3	3	140–6600	400	2400
TOC	3	3	45–1000	120	390
TSS	3	3	570–8600	3900	4400
Total phenol	3	3	0.016–0.10	0.02	0.04
Oil and grease	3	3	5.3–16	7.3	9.5
Ammonia	3	3	31–2400	380	940
Fluoride	3	3	2200–6400	3500	4000
Chloride	1	1	120	—	—

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.13
Concentrations of Toxic Pollutants Found in Primary Columbium and Tantalum Wastewater

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Metals and Inorganics					
Antimony	3	2	ND–11,000	10	3700
Arsenic	3	3	180–14,000	380	4900
Asbestos (fibers/L)	1	1	8.9×10^7	—	—
Beryllium	3	3	20–190	89	100
Cadmium	3	2	8.0–20,000	48	6700
Chromium	3	3	3000–510,000	3000	170,000
Copper	3	3	400–270,000	500	90,000
Cyanide	3	4	2–12	4	6
Lead	3	3	$3000–2.8 \times 10^7$	3000	8.7×10^6
Mercury	3	1	<0.1–36	6.0	<14

Continued

TABLE 3.13 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Concentration (µg/L)		
			Range	Median	Mean
Nickel	3	3	600–2700	2000	1800
Selenium	3	1	ND–24,000	<10	8000
Silver	3	3	<20–620	60	230
Thallium	3	2	ND–<100	25	<42
Zinc	3	3	<540–710,000	6000	240,000
Phthalates					
Bis(2-ethylhexyl)phthalate	15	12	ND–1100	22	150
Butyl benzyl phthalate	15	2	ND–47	—[a]	6.3
Di-n-butyl phthalate	15	5	ND–60	—[a]	12
Diethyl phthalate	15	1	ND–17	—[a]	1.7
Dimethyl phthalate	15	2	ND–39	—[a]	4.1
Di-n-octyl phthalate	15	1	ND–95	—[a]	6.6
Phenols					
Pentachlorophenol	8	1	ND–17	—[a]	2.1
Aromatics					
Benzene	22	2	ND–44	—[a]	4.4
2,4-Dinitrotoluene	15	1	ND–16	—[a]	1.7
2,6-Dinitrotoluene	15	1	ND–16	—[a]	—[b]
Nitrobenzene	15	2	ND–160	—[a]	18
1,2,4-Trichlorobenzene	15	2	ND–260	—[a]	22
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	15	1	ND–17	—[a]	1.1
Acenaphthylene	15	0	ND–2.0	—[a]	0.2
Anthracene	15	0	ND–2.0	—[a]	0.3
Benz (a) anthracene	15	0	ND–1.0	—[a]	0.1
Benzo (a) pyrene	15	0	ND–1.0	—[a]	0.1
Benzo (ghi) perylene	15	0	ND–2.0	—[a]	0.2
2-Chloronaphthalene	15	0	ND–3.0	—[a]	0.3
Chrysene	15	1	ND–45	—[a]	3.1
Dibenz (ah) anthracene	15	0	ND–4.0	—[a]	0.3
Fluoranthene	15	0	ND–7.2	—[a]	1.1
Fluorene	15	2	ND–20	—[a]	1.3
Indeno (1,2,3-cd) pyrene	15	0	ND–4.0	—[a]	0.3
Naphthalene	15	1	ND–84	—[a]	6.1
Phenanthrene	15	0	ND–2.0	—[a]	0.3
Pyrene	15	0	ND–3.0	—[a]	0.5
Polychlorinated Biphenyls					
Aroclor 1248	15	1	ND–32	—[a]	2.6
Aroclor 1254	15	1	ND–52	—[a]	4.1

Continued

TABLE 3.13 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Concentration (µg/L) Range	Median	Mean
Halogenated Aliphatics					
Bromoform	22	1	ND–21	—[a]	1.2
Carbon tetrachloride	22	2	ND–74	—[a]	5.1
Chlorodibromomethane	22	3	ND–81	—[a]	5.2
Chloroform	22	7	ND–140	—[a]	7.8
Dichlorobromomethane	22	1	ND–13	—[a]	0.6
1,2-Dicloroethane	22	6	ND–150	—[a]	13
1,1-Dichloroethylene	22	1	ND–22	—[a]	1.4
1,2-*trans*-Dichloroethylene	22	6	ND–480	—[a]	49
Hexachloroethane	15	1	ND–23	—[a]	1.5
Methylene chloride	22	1	ND–88,000	—[a]	4000
1,1,2,2-Tetrachloroethane	22	0	ND–6.0	—[a]	0.5
Tetrachloroethylene	22	1	ND–65	—[a]	3.6
1,1,1-Trichloroethane	22	2	ND–40	—[a]	2.5
1,1,2-Trichloroethane	22	2	ND–29	—[a]	2.1
Trichloroethylene	22	3	ND–230	—[a]	21
Pesticides and Metabolites					
Aldrin	15	0	ND–4.0	—[a]	0.3
Alpha-BHC	15	0	ND–0.04	—[a]	—[b]
Beta-BHC	15	0	ND–4.5	—[a]	0.4
Delta-BHC	15	0	ND–4.0	—[a]	0.3
Gamma-BHC	15	0	ND–0.03	—[a]	—[b]
Chlordane	15	0	ND–0.8	—[a]	0.1
4,4′-DDE	15	0	ND–0.4	—[a]	—[b]
4,4′-DDT	15	0	ND–1.0	—[a]	0.1
Dieldrin	15	0	ND–0.1	—[a]	—[b]
Alpha-endosulfan	15	0	ND–0.01	—[a]	—[b]
Endosulfan sulfate	15	0	ND–0.03	—[a]	—[b]
Endrin	15	0	ND–5.4	—[a]	0.4
Endrin aldehyde	15	0	ND–0.2	—[a]	—[b]
Heptachlor	15	0	ND–0.5	—[a]	—[b]
Heptachlor epoxide	15	0	ND–0.1	—[a]	—[b]
Isophorone	15	1	ND–29	—[a]	2.1
Toxaphene	15	0	ND–0.1	—[a]	—[b]

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

3.3.4 PRIMARY COPPER

Both smelting and refining are practiced by the primary copper industry. Some plants engage in smelting only, others practice only refining, and some facilities practice both operations. Significant differences in the wastewater characteristics associated with smelting and refining are found.

Smelting process wastewater sources include acid plant blowdown, contact cooling, and slag granulation. Acid plant blowdown results from the recovery of sulfur from the smelting operation. Contact casting cooling water used by primary copper smelters is normally recycled after cooling in towers or ponds. Furnace slag is disposed of by either dumping or granulation. Molten slag is granulated by using high-pressure water jets. The wastewater from this granulation is typically high in both suspended and dissolved solids and contains some toxic metals.

Refining operations have two principal wastestreams, waste electrolyte and cathode and anode washwater. Spent electrolyte is normally recycled. A bleed stream is treated to reduce copper and impurity concentration. Varying degrees of treatment are necessary because of the differences in the anode copper. Anode impurities, including nickel, arsenic, and traces of antimony and bismuth, may be present in the effluent if the spent electrolyte bleed stream is discharged. Tables 3.14 and 3.15 present classical and toxic pollutant data for raw wastewater in this subcategory.

3.3.5 SECONDARY COPPER

Wastewater is generated by several processes in this subcategory. Slag milling and classification generates wastewater that is high in suspended solids, copper, lead, and zinc. Air pollution control at the site generates acidic wastewater that contains significant levels of copper. Other wastewater sources may include contact cooling, electrolyte disposal, and slag granulation. Tables 3.16 and 3.17 present classical and toxic pollutant data for the secondary copper recovery subcategory.

3.3.6 PRIMARY LEAD

Primary lead facilities have two major processes associated with wastewater generation. The smelting process generates a major wastestream from the sintering operation. These wastewaters are typically high in dissolved solids and metals such as cadmium, lead, and zinc. Acid plant blowdown, slag granulation, and air pollution control methods are also associated with smelting operations. Refining operations also generate wastewater from air pollution equipment and from

TABLE 3.14
Classical Pollutants in Raw Wastewater from the Primary Copper Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L)		
			Range	Median	Mean
COD	3	3	<2.0–810	25	280
TOC	3	3	3.5–7.0	4.9	5.1
TSS	3	3	5.4–4500	18	1500
Total phenol	2	2	0.0055–0.033	—	0.019
Oil and grease	1	1	6.1	—	—

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.15
Concentrations of Toxic Pollutants Found in Primary Copper Wastewater

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Metals and Inorganics					
Antimony	3	3	<50–3500	100	1200
Arsenic	3	3	<2.0–340,000	9300	120,000
Beryllium	3	0	<2–<7.7	6.0	<5.2
Cadmium	3	1	<5–9500	7.0	3200
Chromium	3	2	<10–73	51	45
Copper	3	3	1600–450,000	2300	150,000
Cyanide	2	1	1–20	—[a]	11
Lead	3	3	<20–170,000	470	57,000
Mercury	3	1	<0.5–49	4.6	18
Nickel	3	3	<20–1000	340	450
Selenium	3	2	7.5–310	15	110
Silver	3	3	20–510	54	190
Thallium	3	3	27–<100	<100	<76
Zinc	3	3	30–140,000	400	47,000
Phthalates					
Bis(2-ethylhexyl)phthalate	11	5	ND–78	—[a]	17
Butyl benzyl phthalate	11	0	ND–1.0	—[a]	0.1
Di-n-butyl phthalate	11	1	ND–75	0.7	7.6
Di-n-octyl phthalate	11	0	ND–3.0	—[a]	0.3
Phenols					
2,4-Dimethylphenol	2	1	ND–14	—[a]	7.0
Aromatics					
Benzene	11	0	ND–3.0	—[a]	0.7
Toluene	11	0	ND–1.0	—[a]	0.2
Polycyclic Aromatic Hydrocarbons					
Acenaphthylene	11	0	ND–3.0	—[a]	0.3
Anthracene	11	4	ND–21	—[a]	6.1
Benz (a) anthracene	11	0	ND–1.0	—[a]	0.1
Fluoranthene	11	0	ND–1.0	—[a]	0.3
Fluorene	11	0	ND–1.0	—[a]	0.1
Phenanthrene	11	4	ND–21	7.0	7.1
Pyrene	11	0	ND–1.0	—[a]	0.4
Polychlorinated Biphenyls					
Aroclor 1248	9	0	ND–0.6	—[a]	0.1
Aroclor 1254	11	0	ND–0.7	—[a]	0.1
Halogenated Aliphatics					
Carbon tetrachloride	11	3	ND–40	—[a]	8.4
Chlorodibromomethane	11	1	ND–13	—[a]	1.2

Continued

TABLE 3.15 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
Chloroform	11	3	ND–93	5.0	16
Dichlorobromomethane	11	1	ND–14	—[a]	1.3
1,2-Dichloroethane	11	0	ND–7.0	—[a]	0.6
Methylene chloride	11	0	ND–6.8	—[a]	0.6
1,1,2,2-Tetrachloroethane	11	3	ND–12	—[a]	1.9
Tetrachloroethylene	11	4	ND–15	4.0	5.4
1,1,2-Trichloroethane	11	0	ND–2.0	—[a]	0.2
Trichloroethylene	11	0	ND–9.0	—[a]	1.5
Pesticides and Metabolites					
Beta-BHC	11	0	ND–0.01	—[a]	—[b]
Gamma-BHC	11	0	ND–0.04	—[a]	—[b]
Chlordane	11	0	ND–0.2	—[a]	—[b]
4,4′-DDD	11	0	ND–0.01	—[a]	—[b]
4,4′-DDT	11	0	ND–0.02	—[a]	—[b]
Dieldrin	11	0	ND–0.02	—[a]	—[b]
Beta-endosulfan	11	0	ND–0.01	—[a]	—[b]
Endrin	11	0	ND–0.1	—[a]	—[b]
Endrin aldehyde	11	0	ND–0.4	—[a]	—[b]
Heptachlor	11	0	ND–0.01	—[a]	—[b]
Heptachlor epoxide	11	0	ND–0.01	—[a]	—[b]
Isophorone	11	0	ND–3.0	—[a]	—[b]

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.16
Concentrations of Classical Pollutants in the Raw Wastewater of the Secondary Copper Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L) Range	Median	Mean
COD	5	5	9.7–900	75	230
TOC	5	5	6.0–99	30	40
TSS	5	5	4.0–11,000	65	2700
Total phenol	4	4	0.0063–0.22	0.045	0.079
Oil and grease	4	4	1.7–30	4.2	10
Fluoride	1	1	0.29	—	—

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.17
Concentrations of Toxic Pollutants in the Raw Wastewater of the Secondary Copper Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Metals and Inorganics					
Antimony	5	2	ND–11,000	ND	2200
Arsenic	5	3	ND–4200	100	940
Asbestos (fibers/L)	2	2	3.3×10^7–1.0×10^{11}	—[a]	5.5×10^{10}
Beryllium	5	4	ND–160	30	58
Cadmium	5	4	5.0–1200	50	390
Chromium	5	4	5.0–2100	<240	<640
Copper	5	5	620–2.1×10^6	40,000	450,000
Cyanide	4	1	<1–26	6	<9.8
Lead	5	5	450–53,000	10,000	17,000
Mercury	5	0	ND–0.6	0.53	0.35
Nickel	5	4	7.0–3.1×10^6	3000	620,000
Selenium	5	2	ND–270	ND	98
Silver	5	3	ND–1600	<10	370
Thallium	5	2	ND–53	ND	21
Zinc	5	5	1400–1.5×10^6	40,000	330,000
Phthalates					
Bis(2-ethylhexyl) phthalate	12	9	ND–7000	53	1100
Butyl benzyl phthalate	12	1	ND–56	—[a]	5.3
Di-n-butyl phthalate	12	5	ND–390	9.5	56
Diethyl phthalate	12	2	ND–83	—[a]	11
Di-n-octyl phthalate	12	1	ND–67	5.8	—[b]
Aromatics					
Benzene	10	1	ND–13	—[a]	1.3
Ethylbenzene	10	0	ND–4.0	—[a]	0.4
Hexachlorobenzene	12	1	ND–5000	—[a]	420
Toluene	10	0	ND–10	—[a]	1.7
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	12	2	ND–36	—[a]	4.6
Acenaphthylene	12	3	ND–120	—[a]	23
Anthracene	12	2	ND–3000	—[a]	260
Benzo (a) pyrene	12	0	ND–1.0	—[a]	0.1
Chrysene	12	2	ND–10,000	—[a]	840
Fluoranthene	12	3	ND–3000	1.0	280
Fluorene	12	3	ND–94	—[a]	14
Naphthalene	12	3	ND–5000	—[a]	550
Phenanthrene	12	3	ND–3000	—[a]	260
Pyrene	12	3	ND–7000	—[a]	610

Continued

TABLE 3.17 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Polychlorinated Biphenyls					
Aroclor 1248	14	0	ND–2.0	—[a]	0.5
Aroclor 1254	14	0	ND–3.0	—[a]	0.5
Halogenated Aliphatics					
Carbon tetrachloride	10	1	ND–120	—[a]	12
Chloroform	10	5	ND–1000	7.0	130
1,2-Dichloroethane	10	1	ND–32	—[a]	3.2
1,1-Dichloroethylene	10	2	ND–530	—[a]	57
1,2-*trans*-Dichloroethylene	10	0	ND–5.0	—[a]	0.5
Methylene chloride	10	2	ND–510	—[a]	80
1,1,2,2-Tetrachloroethane	10	0	ND–4.0	—[a]	0.4
Tetrachloroethylene	10	2	ND–72	—[a]	8.8
Trichloroethylene	10	1	ND–70	—[a]	7.1
Pesticides and Metabolites					
Aldrin	14	0	ND–0.2	—[a]	—[b]
Alpha-BHC	14	0	ND–0.2	—[a]	—[b]
Beta-BHC	14	0	ND–0.02	—[a]	—[b]
Delta-BHC	14	0	ND–0.2	—[a]	—[b]
Gamma-BHC	14	0	ND–0.04	—[a]	—[b]
Chlordane	14	0	ND–0.7	—[a]	0.1
4,4′-DDE	14	0	ND–0.02	—[a]	—[b]
4,4′-DDD	14	0	ND–0.1	—[a]	—[b]
4,4′-DDT	14	0	ND–0.03	—[a]	—[b]
Dieldrin	14	0	ND–0.03	—[a]	—[b]
Alpha-endosulfan	14	0	ND–0.3	—[a]	—[b]
Beta-endosulfan	14	0	ND–0.3	—[a]	—[b]
Endrin	14	0	ND–0.4	—[a]	—[b]
Endrin aldehyde	14	0	ND–0.3	—[a]	—[b]
Heptachlor	14	0	ND–0.02	—[a]	—[b]
Toxaphene	14	0	ND–0.4	—[a]	—[b]

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

noncontact cooling water. Tables 3.18 and 3.19 present classical and toxic pollutant data of the raw wastewater generated in this subcategory.

3.3.7 SECONDARY LEAD

The principal raw material for the secondary lead industry is scrap batteries. Wastewater is generated from battery acid streams, washdown streams, and saw cooling for cracking the batteries. These

TABLE 3.18
Concentrations of Classical Pollutants in the Raw Wastewater of the Primary Lead Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L) Range	Median	Mean
COD	2	2	3.7–170		87
TOC	2	1	ND–3.3		1.6
TSS	2	1	ND–26		13
Total phenol	2	1	ND–0.050		0.025
Ammonia	2	2	ND–3.8		1.9
Oil and grease	2	0	ND		—

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

TABLE 3.19
Concentrations of Toxic Pollutants in the Raw Wastewater of the Primary Lead Subcategory

Toxic Pollutant	Number of Samples	Number of Detections 10 μg/L	Concentration (μg/L) Range	Median	Mean
Metals and Inorganics					
Antimony	2	1	ND–<330	—	<170
Arsenic	2	2	58–96	—	76
Beryllium	2	0	ND–6.7	—	3.4
Cadmium	2	2	700–1300	—	1000
Chromium	2	2	14–30	—	22
Copper	2	2	100–620	—	360
Cyanide	2	0	<0.02–0.12	—	0.07
Lead	2	2	7900–24,000	—	16,000
Mercury	2	0	0.67–7.5	—	4.1
Nickel	2	2	50–130	—	90
Selenium	2	1	5.4–<13	—	<9.2
Silver	2	1	ND–<20	—	<10
Thallium	2	1	ND–<100	—	<50
Zinc	2	2	5300–20,000	—	13,000
Polycyclic Aromatic Hydrocarbons					
Pyrene	3	0	ND–7.0	—	2.3
Halogenated Aliphatics					
Methylene chloride	4	1	ND–25	3.0	7.8

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

streams contain significant levels of suspended solids, antimony, arsenic, cadmium, lead, and zinc. Smelting operations for this subcategory generate wastewater from air pollution control devices and contact cooling streams. Tables 3.20 and 3.21 present classical and toxic pollutant data for the raw wastewater in this subcategory.

3.3.8 SECONDARY SILVER

Secondary silver is recovered from photographic and nonphotographic sources. Wastewater sources from photographic wastes include leaching and stripping, precipitation and filtration of silver, electrolysis, and pollution control. Nonphotographic scrap wastewater is generated by similar processes. These wastewater streams contain significant concentrations of chromium, copper, lead, and zinc as well as some organic priority pollutants. Tables 3.22 and 3.23 present pollutant data for this subcategory.

TABLE 3.20
Concentrations of Classical Pollutants in the Raw Wastewater of the Secondary Lead Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L) Range	Median	Mean
COD	3	3	65–230	160	150
TOC	3	3	4–140	70	71
TSS	4	4	0.056–4000	770	1400
Total phenol	4	4	<0.004–0.012	0.0091	0.0086
Oil and grease	3	3	6.5–40	36	28
Ammonia	1	1	12	—	—
Chloride	1	1	53	—	—

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.21
Concentrations of Toxic Pollutants in the Raw Wastewater of the Secondary Lead Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
Metals and Inorganics					
Antimony	4	4	1600–80,000	39,000	40,000
Arsenic	3	3	3000–13,000	7100	7700
Asbestos (fibers/L)	1	1	1.3×10^{11}	—	—
Beryllium	3	1	1.0–30	4.5	12
Cadmium	4	4	240–2000	800	960
Chromium	4	4	110–1000	490	520
Copper	4	4	230–8000	3200	3600

Continued

TABLE 3.21 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Concentration (µg/L) Range	Median	Mean
Lead	4	4	7000–2.0 × 10^6	24,000	510,000
Mercury	4	1	0.6–12	0.84	3.6
Nickel	4	4	210–2000	<970	1000
Selenium	3	0	ND–<10	<2.0	<4.0
Silver	3	3	110–250	120	160
Thallium	3	3	50–750	370	390
Zinc	4	4	870–15,000	3600	5700
Phthalates					
Bis(2-ethylhexyl) phthalate	5	4	ND–580	30	180
Butyl benzyl phthalate	5	1	ND–85	—[a]	17
Di-n-butyl phthalate	5	3	ND–27	13	12
Dimethyl phthalate	5	2	ND–13	—[a]	2.6
Di-n-octyl phthalate	5	2	ND–27	2.0	9.0
Nitrogen Compounds					
Benzidine	5	0	ND–6.0	—[a]	1.2
Aromatics					
Benzene	10	0	ND–2.0	—[a]	0.2
Chlorobenzene	10	0	ND–5.0	—[a]	0.5
Ethylbenzene	10	0	ND–1.2	—[a]	0.3
Nitrobonzene	5	1	ND–16	—[a]	3.2
Polycyclic Aromatic Hydrocarbons					
Acenaphthylene	5	1	ND–35	3.0	8.6
Anthracene	5	1	ND–20	—[a]	4.0
Benzo (a) pyrene	5	1	ND–10	—[a]	2.0
Benzo (b) fluoranthene	5	0	ND–5.3	—[a]	1.6
Benzo (k) fluoranthene	5	0	ND–5.3	—[a]	1.6
Chrysene	5	1	ND–546	40	110
Fluoranthene	5	2	ND–27	—[a]	7.6
Fluorene	5	0	ND–2.0	1.0	0.4
Indeno(1,2,3-cd)pyrene	5	0	ND–1.0	—[a]	0.2
Naphthalene	5	0	ND–4.0	—[a]	0.8
Phenanthrene	5	1	ND–20	—[a]	4.6
Pyrene	5	2	ND–38	1.0	10
Polychlorinated Biphenyls					
Aroclor 1248	5	0	ND–3.1	1.3	1.4
Aroclor 1254	5	0	ND–2.6	1.8	1.3
Halogenated Aliphatics					
Bromoform	10	1	ND–49	—[a]	5.7
Chloroform	10	3	ND–31	3.0	6.9
1,2-Dicloroethane	10	1	ND–10	4.0	4.0
1,1-Dichloroethylene	10	1	ND–10	2.0	3.7

Continued

TABLE 3.21 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
1,1,2,2-Tetrachloroethane	10	0	ND–4.0	—[a]	1.0
Tetrachloroethylene	10	0	ND–5.0	—[a]	1.1
Trichloroethylene	10	0	ND–6.0	—[a]	0.8
Pesticides and Metabolites					
Aldrin	5	0	ND–0.1	—[a]	—[b]
Alpha-BHC	5	0	ND–0.2	—[a]	—[b]
Beta-BHC	5	0	ND–0.3	0.1	0.1
Gamma-BHC	5	0	ND–0.1	—[a]	—[b]
Chlordane	5	0	ND–0.2	0.2	0.2
4,4′-DDE	5	0	ND–0.2	—[a]	—[b]
4,4′-DDT	5	0	ND–0.1	—[a]	—[b]
Dieldrin	5	0	ND–0.2	—[a]	—[b]
Alpha-endosulfan	5	0	ND–0.2	—[a]	—[b]
Endrin	5	0	ND–4.0	—[a]	1.0
Endrin aldehyde	5	0	ND–0.6	—[a]	0.1
Heptachlor	5	0	ND–0.3	0.1	0.1
Heptachlor epoxide	5	0	ND–0.2	0.1	0.1
Isophorone	5	0	ND–2.7	—[a]	1.8

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.22
Concentrations of Classical Pollutants in the Raw Wastewater of the Secondary Silver Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L) Range	Median	Mean
COD	3	3	230–12,000	3000	5100
TOC	3	3	19–9100	430	3200
TSS	3	3	110–1100	110	440
Total phenol	3	3	0.02–28	0.04	9.4
Oil and grease	3	3	8.0–100	17	42
Ammonia	2	2	12–1500	—	760
Fluoride	1	1	1.2	—	—
Chloride	1	1	32,000	—	—

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.23
Concentrations of Toxic Pollutants in the Raw Wastewater of the Secondary Silver Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Concentration (µg/L)		
			Range	Median	Mean
Metals and Inorganics					
Antimony	3	1	ND–25,000	ND	8300
Arsenic	3	3	40–920	40	330
Asbestos (fibers/L)	1	1	2×10^9	—	—
Beryllium	3	2	ND–20	19	13
Cadmium	3	3	1000–80,000	3200	28,000
Chromium	3	3	2000–27,000	20,000	16,000
Copper	3	3	7300–70,000	60,000	46,000
Cyanide	3	2	1–2100	50	720
Lead	3	3	4000–50,000	4200	19,000
Mercury	3	0	ND–5.5	ND	1.8
Nickel	3	3	1100–800,000	30,000	280,000
Selenium	3	1	ND–590	ND	200
Silver	3	3	250–4700	410	1800
Thallium	3	1	ND–510	ND	170
Zinc	3	3	$8400–2.0 \times 10^6$	20,000	680,000
Phthalates					
Bis(2-ethylhexyl) phthalate	5	4	7.0–34	11	18
Butyl benzyl phthalate	5	1	ND–53	—[a]	11
Di-n-butyl phthalate	5	4	ND–300	15	75
Diethyl phthalate	5	1	ND–38	—[a]	7.6
Di-n-octyl phthalate	5	3	ND–58	33	30
Aromatics					
Benzene	6	4	3.0–160	66	75
Chlorobenzene	6	0	ND–9.0	0.5	2.8
Ethylbenzene	6	3	ND–21	—[a]	9.2
Toluene	6	4	3.0–55	18	21
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	5	1	ND–10	—[a]	2.0
Anthracene	5	0	ND–4.0	—[a]	0.8
Naphthalene	5	0	ND–1.0	—[a]	0.2
Phenanthrene	5	0	ND–4.0	—[a]	0.8
Pyrene	5	1	ND–2100	—[a]	430
Polychlorinated Biphenyls					
Aroclor 1248	3	0	ND–0.5	—[a]	0.2
Aroclor 1254	3	0	ND–0.7	—[a]	0.2
Halogenated Aliphatics					
Bromoform	6	1	ND–65	—[a]	11
Carbon tetrachloride	6	1	ND–2300	—[a]	380

Continued

TABLE 3.23 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
Chlorodibromomethane	6	1	ND–64	—[a]	11
Chloroform	6	3	ND–890	8.5	160
1,2-Dichloroethane	6	3	ND–560	21	120
1,1-Dichloroethylene	6	2	ND–6100	—[a]	1100
Methylene chloride	6	3	ND–3100	170	1000
1,1,2,2-Tetrachloroethane	4	1	ND–32	—[a]	8.0
Tetrachloroethylene	6	5	ND–110	36	43
1,1,1-Trichloroethane	6	2	ND–22	—[a]	7.3
Trichloroethylene	6	5	ND–900	230	360
Pesticides and Metabolites					
Aldrin	3	0	ND–1.1	—[a]	0.4
Beta-BHC	3	0	ND–0.02	—[a]	—[b]
Delta-BHC	3	0	ND–1.1	—[a]	0.4
Chlordane	3	0	ND–0.1	—[a]	—[b]
4,4′-DDE	3	0	ND–0.01	—[a]	—[b]
4,4′-DDD	3	0	ND–0.1	—[a]	—[b]
4,4′-DDT	3	0	ND–0.01	—[a]	—[b]
Dieldrin	3	0	ND–0.01	—[a]	—[b]
Endrin	3	0	ND–2.0	—[a]	0.7
Heptachlor	3	0	ND–0.02	—[a]	—[b]

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

3.3.9 PRIMARY TUNGSTEN

Tungsten production involves processing ore concentrates to obtain the salt ammonium paratungstate (APT), and subsequent reduction of APT to metallic tungsten. Wastewater is generated during all three processes and results from the precipitation and filtration of the salt, leaching to convert it to tungstic acid, and air pollution control methods associated with the processes. Wastewaters may be acidic and contain significant concentrations of chlorides, arsenic, lead, zinc, and ammonia. Tables 3.24 and 3.25 present classical and toxic pollutant data for the primary tungsten subcategory.

3.3.10 PRIMARY ZINC AND CADMIUM

Wastewater is generated in the primary zinc and primary cadmium recovery subcategories by acid plant blowdown, which results from sulfuric acid recovery, air pollution control, leaching, anode/cathode washing, and contact cooling. The streams may contain significant concentrations of lead, arsenic, cadmium, and zinc. Tables 3.26 and 3.27 present classical and toxic pollutant data for the primary zinc and primary cadmium subcategories.

TABLE 3.24
Concentrations of Classical Pollutants in the Raw Wastewater of the Primary Tungsten Subcategory

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L) Range	Median	Mean
COD	3	3	120–880	320	440
TOC	3	3	6.0–270	27	100
TSS	3	3	42–6700	210	2300
Total phenol	3	3	0.038–0.089	0.039	0.055
Oil and grease	3	3	6.3–17	6.8	10
Ammonia	3	3	3.9–1600	900	830
Chloride	2	2	850–26,000	—	13,000

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.25
Concentrations of Toxic Pollutants in the Raw Wastewater of the Primary Tungsten Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
Metals and Inorganics					
Antimony	3	1	ND–800	ND	270
Arsenic	3	3	20–7200	210	2500
Asbestos (fibers/L)	1	1	6.0×10^9	—	—
Beryllium	3	1	2.0–29	9	13
Cadmium	3	3	19–190	20	76
Chromium	3	3	44–2000	48	700
Copper	3	3	95–3000	120	1700
Cyanide	3	2	2–140	13	52
Lead	3	3	180–20,000	240	6800
Mercury	3	0	0.21–3	1.0	1.4
Nickel	3	3	45–1000	92	380
Selenium	3	2	ND–1000	20	340
Silver	3	3	76–270	86	140
Thallium	3	2	ND–600	200	270
Zinc	3	3	250–1900	520	890
Phthalates					
Bis(2-ethylhexyl) phthalate	5	4	ND–880	10	180
Di-n-butyl phthalate	5	2	ND–23	—[a]	—[b]
Di-n-octyl phthalate	5	1	ND–1.0	—[a]	0.2
Aromatics					
Benzene	9	0	ND–3.0	—[a]	0.7
Ethylbenzene	9	1	ND–11	—[a]	2.2
Toluene	9	2	ND–45	3.0	11

Continued

TABLE 3.25 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	5	1	ND–100	—[a]	21
Acenaphthylene	5	1	ND–110	—[a]	23
Anthracene	5	1	ND–150	—[a]	30
Benzo (a) pyrene	5	0	ND–1.0	—[a]	0.2
Chrysene	5	1	ND–240	—[a]	48
Fluoranthene	5	0	ND–1.0	—[a]	0.2
Fluorene	5	1	ND–55	—[a]	11
Naphthalene	5	1	ND–1100	—[a]	220
Polychlorinated Biphenyls					
Aroclor 1248	5	0	ND–1.0	0.2	0.3
Aroclor 1254	5	0	ND–5.4	0.4	1.4
Halogenated Aliphatics					
Bromoform	9	2	ND–48	—[a]	9.3
Chlorodibromomethane	9	1	ND–38	—[a]	4.2
Chloroform	9	2	ND–1800	—[a]	210
1,2-Dichloroethane	9	0	ND–8.0	—[a]	2.1
1,1-Dichloroethylene	9	2	ND–19	—[a]	4.3
1,2-*trans*-Dichloroethylene	9	0	ND–2.0	—[a]	0.2
1,1,2,2-Tetrachloroethane	9	1	ND–35	—[a]	5.2
Tetrachloroethylene	9	5	ND–69	—[a]	20
1,1,1-Trichloroethene	9	1	ND–10	—[a]	1.1
Trichloroethylene	9	2	ND–19	—[a]	2.9
Pesticides and Metabolites					
Aldrin	5	0	ND–7.0	—[a]	1.4
Alpha-BHC	5	0	ND–0.6	—[a]	0.1
Beta-BHC	5	0	ND–0.2	—[a]	0.1
Gamma-BHC	5	0	ND–0.2	—[a]	0.1
Chlordane	5	0	ND–1.2	—[a]	0.2
4,4′-DDT	5	0	ND–0.1	—[a]	—
Dieldrin	5	0	ND–0.1	—[a]	0.1
Alpha-Endosulfan	5	1	ND–15	0.1	3.2
Beta-Endosulfan	5	1	ND–15	—[a]	3.1
Endrin	5	0	ND–0.8	—[a]	0.2
Endrin aldehyde	5	0	ND–0.9	0.2	0.3
Heptachlor	5	0	ND–0.2	—[a]	0.1
Heptachlor epoxide	5	0	ND–0.2	—[a]	0.1

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.26
Concentrations of Classical Pollutants in the Raw Wastewater of the Primary Zinc and Cadmium Subcategories

Pollutant	Number of Samples	Number of Detections	Concentration (mg/L)		
			Range	Median	Mean
COD	2	2	20–59	—	40
TOC	2	2	7.3–9.3	—	8.3
TSS	2	2	13–15	—	14
Total phenol	4	4	0.002–0.025	0.007	0.010
Oil and grease	2	2	10–14	—	12

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

TABLE 3.27
Concentrations of Toxic Pollutants in the Raw Wastewater of the Primary Zinc and Cadmium Subcategories

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L)		
			Range	Median	Mean
Metals and Inorganics					
Antimony	4	4	2.0–2100	59	550
Arsenic	4	4	3.0–3000	150	820
Asbestos (fibers/L)	2	2	3.2×10^7–4.3×10^7	—	3.8×10^7
Beryllium	4	1	2.0–20	7.5	9.3
Cadmium	4	4	350–44,000	3500	13,000
Chromium	4	4	24–610	65	190
Copper	4	4	37–26,000	1200	7100
Cyanide	4	2	2–380	6.7	99
Lead	4	4	280–18,000	4400	6700
Mercury	4	1	2.9–52	5.5	16
Nickel	4	4	50–4300	590	1400
Selenium	4	4	24–1200	360	490
Silver	4	4	25–740	58	220
Thallium	2	2	20–360	—	190
Zinc	4	4	8700–1.7×10^6	160,000	510,000
Phthalates					
Bis(2-ethylhexyl) phthalate	9	6	ND–98	15	28
Butyl benzyl phthalate	9	1	ND–30	—[a]	3.3
Di-n-butyl phthalate	9	1	ND–26	5.0	3.6
Diethyl phthalate	9	1	ND–18	—[a]	2.7
Dimethyl phthalate	9	1	ND–22	—[a]	2.4

Continued

TABLE 3.27 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Concentration (μg/L) Range	Median	Mean
Phenols					
Pentachlorophenol	9	0	ND–8.0	—[a]	0.9
Aromatics					
Benzene	9	1	ND–24	—[a]	2.7
Ethylbenzene	9	0	ND–2.0	—[a]	0.2
Hexachlorobenzene	9	1	ND–100	—[a]	11
Toluene	9	1	ND–54	7.0	7.5
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	9	1	ND–18	—[a]	2.0
Anthracene	9	0	ND–0.4	—[a]	—[b]
Chrysene	9	1	ND–11	—[a]	2.2
Fluoranthene	9	1	ND–15	—[a]	1.7
Fluorene	9	2	ND–14	—[a]	1.6
Pyrene	9	2	ND–15	—[a]	3.2
Halogenated Aliphatics					
Chloroform	9	3	ND–71	53	16
1,1-Dichloroethane	9	1	ND–180	—[a]	20
1,2-Dichloroethane	9	1	ND–22	—[a]	2.9
1,1-Dichloroethylene	9	1	ND–23	—[a]	2.6
Methylene chloride	9	4	ND–2,600	—[a]	350
Tetrachloroethylene	9	0	ND–8.0	—[a]	0.9
Trichloroethylene	9	1	ND–160	7.2	19
Trichlorofluoromethane	9	1	ND–100	—[a]	12
Pesticides and Metabolites					
Isophorone	9	1	ND–18	—[a]	2.0

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

3.4 POLLUTANT REMOVABILITY AND TREATMENT

There are several methods for pollutant removal currently used in this industry. Some are used industry-wide; others are used only in specific applications. Those used industry-wide include physical-chemical methods (precipitation,[22] coagulation and flocculation,[24] pH adjustment, and stripping and physical separation methods), filtration,[24] sedimentation,[25] and centrifugation.[26] Lime, caustic, soda ash, and calcium chloride are used as precipitants in the industry, especially for removal of soluble metals. In the coagulation-flocculation system, polymer, lime, and iron or aluminum salts are mixed into the wastestream to facilitate agglomeration of colloidal suspensions. Air/steam stripping are widely practiced techniques for the reduction of volatile compounds such as ammonia, hydrogen sulfide, and organics.

The physical separation methods find wide application in this industry because of the nature of the wastes. Centrifugation may be feasible in some applications, but it is not suitable for abrasive or very fine particles (less than 5 μm).

There are several potential treatment technologies that may be applicable, but are more expensive than the methods currently used. These potential treatments include: sulfide precipitation, ultrafiltration, reverse osmosis, deep-well disposal, activated carbon adsorption or activated alumina adsorption, solidification, or ion exchange.[19–21]

Pollutant removal data for toxic organic pollutants in the subcategories are presented in Tables 3.28 through 3.37. The average removal percentage was determined by comparing the average raw wastewater concentrations found in Section 3.3 with the average treated wastewater concentrations presented in these tables.

TABLE 3.28
Removability of Toxic Organic Pollutants from Wastewater in the Primary Aluminum Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
Phthalates						
Bis(2-ethylhexyl) phthalate	9	2	ND–120	—[a]	17	79
Butyl benzyl phthalate	9	1	ND–75	—[a]	9.6	56
Di-n-butyl phthalate	9	3	ND–30	—[a]	5	74
Diethyl phthalate	9	0	ND	—	—	NM
Dimethyl phthalate	9	0	ND–5.0	—[a]	1	NM
Di-n-octyl phthalate	9	1	ND–13	—[a]	1.8	NM
Phenols						
Phenol	4	0	ND	—	—	>99
Aromatics						
Benzene	14	2	ND–33	—[a]	4.0	NM
2,4-Dinitrotoluene	9	0	ND–7.0	—[a]	0.9	NM
2,6-Dinitrotoluene	9	0	ND–1.0	—[a]	0.1	NM
Ethylbenzene	14	1	ND–12	—[a]	0.8	NM
Toluene	14	0	ND–6.8	—[a]	0.5	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthene	9	4	ND–13	—[a]	5.0	40
Acenaphthylene	9	0	ND–7.0	—[a]	1.9	66
Anthracene	9	2	ND–11	2.6	4.7	88
Benz (a) anthracene	9	0	ND–6.0	—[a]	0.7	98
Benzo (a) pyrene	9	0	ND–8.0	—[a]	2.1	98
Benzo (b) fluoranthene	9	0	ND–6.0	—[a]	0.7	98
Benzo (ghi) perylene	9	1	ND–11	—[a]	0.1	>99
Benzo (k) fluoranthene	9	0	ND–6.0	—[a]	1.1	97
Chrysene	9	1	ND–140	—[a]	17	58
Dibenz (ah) anthracene	9	0	ND	—	—	>99

Continued

TABLE 3.28 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L) Range	Median	Mean	Average Percent Removal
Fluoranthene	9	5	ND–79	11	22	77
Fluorene	9	0	ND–1.0	—[a]	0.2	97
Indeno (1,2,3-cd) pyrene	9	0	ND–1.0	—[a]	0.1	>99
Naphthalene	9	0	ND–1.0	—[a]	0.1	97
Phenanthrene	9	2	ND–11	—[a]	44	NM
Pyrene	9	3	ND–80	9.0	20	71
Halogenated Aliphatics						
Chloroform	14	2	ND–320	—[a]	23	NM
1,2-Dichloroethane	14	0	ND–5.5	—[a]	0.4	NM
1,1-Dichloroethylene	14	1	ND–4100	—[a]	290	NM
Methylene chloride	14	6	ND–4200	—[a]	360	NM
1,1,2,2-Tetrachloroethane	14	0	ND–1.0	—[a]	0.1	NM
Tetrachloroethylene	14	1	ND–61	—[a]	44	NM
Trichloroethylene	14	1	ND–120	—[a]	8.5	NM
Pesticides and Metabolites						
Aldrin	8	0	ND–0.1	—[a]	—[b]	NM
Delta-BHC	8	0	ND–0.1	—[a]	—[b]	NM
Gamma-BHC	8	0	ND–0.01	—[a]	—[b]	NM
Chlordane	8	0	ND–0.1	—[a]	—[b]	NM
4,4′-DDT	8	0	ND–0.01	—[a]	—[b]	NM
Dieldrin	8	0	ND–0.1	—[a]	—[b]	NM
Endrin aldehyde	8	0	ND–0.2	—[a]	—[b]	NM
Heptachlor	8	0	ND–0.2	—[a]	—[b]	NM
Heptachlor epoxide	8	0	ND–0.2	—[a]	—[b]	NM
Isophorone	9	0	ND	—[a]	—[b]	>99
PCB 1248	8	0	ND–0.4	—[a]	—[b]	NM
PCB 1254	8	0	ND–0.2	—[a]	—[b]	NM

Source: From U.S. EPA, Treatability Manual, Volume II Industrial Descriptions, report EPA-600/2-82-001b, U.S. EPA, Washington, DC, September 1981.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

3.5 MANAGEMENT OF CHEMICALS IN THE WASTESTREAM

The Pollution Prevention Act of 1990[27] requires facilities to report information about the management of Toxic Relief Inventory (TRI) chemicals in waste and efforts made to eliminate or reduce those quantities. The data summarized in Table 3.38 cover a four-year period and is meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends in these methods.[1] TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

Although the quantities reported for the first two years are estimates of quantities already managed, the quantities reported for the third and fourth years are projections only. U.S. EPA requires these projections to encourage facilities to consider future waste generation and source reduction of those quantities as well as movement up the waste management hierarchy. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Table 3.38 shows that the primary and secondary metals industry managed 905,000 t of production-related waste (total quantity of TRI chemicals in the waste from routine production operations) in Year 2 (column B). Column C reveals that of this production-related waste, 35% was either transferred offsite or was released to the environment. Column C is calculated by dividing the total TRI transfers and releases by the total quantity of production-related waste. In other words, about 70% of the industry's TRI wastes were managed onsite through recycling, energy recovery, or treatment, as shown in columns D, E, and F, respectively. The majority of waste that is released or transferred offsite can be divided into portions that are recycled offsite, recovered for energy offsite, or treated offsite as shown in columns G, H, and I, respectively. The remaining portion of the production-related wastes (12.85%), shown in column J, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed offsite.

TABLE 3.29
Removability of Toxic Organic Pollutants from Wastewater in the Secondary Aluminum Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L) Range	Median	Mean	Average Percent Removal
Phthalates						
Bis(2-ethylhexyl) phthalate	7	6	ND–1200	5.3	290	24
Butyl benzyl phthalate	7	0	ND–2.0	—[a]	0.6	97
Di-n-butyl phthalate	7	3	ND–50	—[a]	13	19
Dimethyl phthalate	7	0	ND–3.0	—[a]	0.6	94
Di-n-octyl phthalate	7	1	ND–100	—[a]	15	NM
Nitrogen Compounds						
3,3′-Dichlorobenzidine	7	0	ND	—	—	>99
Aromatics						
Benzene	11	0	ND–5.0	—[a]	0.7	93
Chlorobenzene	11	0	ND–7.0	—[a]	1.5	NM
1,4-Dichlorobenzene	7	0	ND	—	—	>99
Ethylbenzene	11	0	ND–6.0	—[a]	0.5	NM
1,2,4-Trichlorobenzene	7	1	ND–2.0	—[a]	0.3	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthylene	7	0	ND	—	—	<99
Benzo (a) pyrene	7	0	ND–1.0	—[a]	0.1	95
Benzo (b) fluoranthene	7	0	ND–2.0	—[a]	0.3	NM
Benzo (k) fluoranthene	7	0	ND–2.0	—[a]	0.3	NM
Benzo (ghi) perylene	7	0	ND–2	—[a]	0.3	NM
Chrysene	7	0	ND–2.5	—[a]	0.4	99
Fluoranthene	7	0	ND	—	—	>99
Naphthalene	7	0	ND–1.0	—[a]	0.1	50

Continued

TABLE 3.29 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L)			Average Percent Removal
			Range	Median	Mean	
Pyrene	7	0	ND–1.0	—[a]	0.1	98
Anthranene/Phenanthrene	7	0	ND	—	—	>99
PCB 1254	7	0	ND–0.3	—[a]	—[b]	0
PCB 1248	7	0	ND–0.3	—[a]	—[b]	0
Halogenated Aliphatics						
Bromoform	11	0	ND–4.7	—[a]	1.0	NM
Carbon tetrachloride	11	0	ND–6.0	—[a]	0.5	50
Chlorodibromomethane	11	2	ND–29	—[a]	4.9	NM
Chloroform	11	6	ND–170	—[a]	32	NM
Dichlorobromomethane	11	3	ND–18	—[a]	3.0	NM
1,1-Dichloroethane	11	0	ND–7.0	—[a]	0.6	NM
1,2-Dichloroethane	11	2	ND–20	—[a]	2.3	NM
1,2-*trans*-Dichloroethylene	11	2	ND–75	1.0	9.2	52
Methylene chloride	11	1	ND–200	—[a]	16	NM
1,1,2,2-Tetrachloroethane	11	0	ND–1.0	—[a]	0.1	NM
1,1,1-Trichloroethane	11	0	ND–5.0	—[a]	0.5	NM
1,1,2-Trichloroethane	11	0	ND–8.5	—[a]	2.3	NM
Tetrachloroethylene	11	0	ND–4	—[a]	0.8	98
Trichloroethylene	11	0	ND–7	—[a]	1.0	98
Pesticides and Metabolites						
Isophorone	7	0	ND	—	—	>99
Chlordane	7	0	ND	—	—	>99
Aldrin	7	0	ND–0.1	—[a]	—[b]	NM
Dieldrin	7	0	ND	—	—	>99
4,4′-DDT	7	0	ND–0.1	—[a]	—[b]	NM
4,4′-DDE	7	0	ND–0.04	—[a]	—[b]	NM
Alpha-Endosulfan	7	0	ND–0.03	—[a]	—[b]	NM
Endrin	7	0	ND–0.4	—[a]	—[b]	NM
Endrin aldehyde	7	0	ND–0.6	—[a]	0.1	0
Heptachlor	7	0	ND	—[a]	—	>99
Heptachlor epoxide	7	0	ND–0.1	—[a]	—[b]	NM
Alpha-BHC	7	0	ND–0.2	—[a]	—[b]	NM
Beta-BHC	7	0	ND–0.1	—[a]	—[b]	65
Gamma-BHC	7	0	ND–0.02	—[a]	—[b]	80

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 622 pp, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.30
Removability of Toxic Organic Pollutants from Wastewater in the Primary Columbium and Tantalum Subcategories

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L)			Average Percent Removal
			Range	Median	Mean	
Phthalates						
Bis(2-ethylhexyl) phthalate	4	0	ND–9.5	2.8	3.8	97
Butyl benzyl phthalate	4	0	ND	—	—	>99
Di-n-butyl phthalate	4	0	ND–9.0	—[a]	2.2	82
Diethyl phthalate	4	0	ND–2.0	—[a]	0.5	71
Dimethyl phthalate	4	1	ND–20	—[a]	5.0	NM
Di-n-octyl phthalate	4	0	ND–2.0	—[a]	0.5	92
Phenols						
Pentachlorophenol	2	0	ND	—	—	>99
Aromatics						
Benzene	7	1	ND–40	—[a]	6.9	NM
Chlorobenzene	7	1	ND–65	—[a]	13	NM
2,4-Dinitrotoluene	4	0	ND	—[a]	—	>99
2,6-Dinitrotoluene	4	0	ND	—	—	>99
Ethylbenzene	7	1	ND–49	—[a]	7.0	NM
Nitrobenzene	4	0	ND	—	—	>99
Toluene	7	2	ND–92	—[a]	15	NM
1,2,4-Trichlorobenzene	4	2	ND–17	7.5	8.0	64
Polycyclic Aromatic Hydrocarbons						
Acenaphthene	4	2	ND–16	6.9	7.4	NM
Acenaphthylene	4	0	ND–2.8	0.9	1.2	NM
Anthracene	4	0	ND–12	1.5	3.8	NM
Benz (a) anthracene	4	0	ND	—	—	>99
Benzo (a) pyrene	4	0	ND	—	—	>99
Benzo (b) fluoranthene	4	0	ND–2.0	—[a]	0.5	NM
Benzo (ghi) perylene	4	0	ND–1.0	—[a]	0.2	0
Benzo (k) fluoranthene	4	0	ND–2.0	—[a]	0.5	NM
2-Chloronaphthalene	4	0	ND	—	—	>99
Chrysene	4	0	ND	—	—	>99
Dibenz (ah) anthracene	4	0	ND	—	—	>99
Fluoranthene	4	0	ND	—	—	>99
Fluorene	4	1	ND–69	—[a]	17	NM
Indeno (1,2,3-cd) pyrene	4	0	ND	—	—	>99
Naphthalene	4	0	ND	—	—	>99
Phenanthrene	4	1	ND–12	1.5	3.8	NM
Pyrene	4	0	ND–4.9	0.4	1.4	NM
Polychlorinated Biphenyls						
Aroclor 1248	3	0	ND	—	—	>99
Aroclor 1254	3	0	ND	—	—	>99

Continued

TABLE 3.30 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
Halogenated Aliphatics						
Bromoform	7	0	ND	—	—	>99
Carbon tetrachloride	7	2	ND–110	—[a]	21	NM
Chlorodibromomethane	7	0	ND–5.0	—[a]	0.7	87
Chloroform	7	3	ND–47	—[a]	9.0	NM
Dichlorobromomethane	7	1	ND–16	—[a]	2.3	NM
1,2-Dichloroethane	7	2	ND–18	3.0	5.9	55
1,1-Dichloroethylene	7	2	ND–140	—[a]	21	NM
1,2-*trans*-Dichloroethylene	7	0	ND	—	—	>99
Hexachloroethane	4	0	ND	—	—	>99
Methylene chloride	7	1	ND–600	—[a]	85	98
1,1,2,2-Tetrachloroethane	7	1	ND–49	—[a]	7.0	NM
Tetrachloroethylene	7	4	ND–190	10	54	NM
1,1,1-Trichloroethane	7	0	ND	—	—	>99
1,1,2-Trichloroethane	6	0	ND–5.0	—[a]	—[b]	83
Trichloroethylene	7	3	ND–190	—[a]	32	NM
Pesticides and Metabolites						
Aldrin	3	0	ND–0.5	—[a]	0.2	33
Alpha-BHC	3	0	ND–0.01	—[a]	—[b]	75
Beta-BHC	3	0	ND–0.3	0.1	0.1	75
Delta-BHC	3	0	ND–0.5	—[a]	0.2	33
Gamma-BHC	3	0	ND	—	—	>99
Chlordane	3	0	ND–1.0	—[a]	—[b]	NM
4,4′-DDE	3	0	ND	—	—	>99
4,4′-DDT	3	0	ND	—	—	>99
Dieldrin	3	0	ND–0.01	—[a]	—[b]	90
Alpha-endosulfan	3	0	ND	—	—	>99
Beta-endosulfan	3	0	ND	—	—	>99
Endosulfan sulfate	3	0	ND	—	—	>99
Endrin	3	0	ND–0.01	—[a]	—[b]	99
Endrin aldehyde	3	0	ND	—	—	>99
Heptachlor	3	0	ND–0.3	—[a]	0.1	40
Heptachlor epoxide	3	0	ND	—	—	>99
Isophorone	4	0	ND	—	—	>99
Toxaphene	3	0	ND	—	—	>99

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 622 pp, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.31
Removability of Toxic Organic Pollutants from Wastewater in the Primary Copper Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
Phthalates						
Bis(2-ethylhexyl) phthalate	5	4	ND–480	17	110	NM
Butyl benzyl phthalate	5	1	ND–48	—[a]	9.6	NM
Di-n-butyl phthalate	5	2	ND–73	—[a]	25	NM
Di-n-octyl phthalate	5	1	ND–190	—[a]	38	NM
Phenols						
2,4-Dimethylphenol	2	0	ND	—	—	>99
Aromatics						
Benzene	5	0	ND–1.0	—[a]	0.4	43
Chlorobenzene	5	0	ND–6.0	—[a]	1.2	NM
Toluene	5	0	ND	—	—	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthylene	5	0	ND	—	—	>99
Anthracene	5	3	ND–17	—[a]	6.2	NM
Benz (a) anthracene	5	0	ND	—	—	>99
Chrysene	5	0	ND–2.0	—[a]	0.4	NM
Fluoranthene	5	0	ND–2.0	—[a]	0.4	NM
Fluorene	5	1	ND–14	—[a]	2.8	NM
Phenanthrene	5	1	ND–17	—[a]	3.4	52
Pyrene	5	0	ND	—	—	>99
Polychlorinated Biphenyls						
Aroclor 1248	5	0	ND–1.0	1.0	0.8	NM
Aroclor 1254	5	0	ND–1.5	—[a]	0.5	NM
Halogenated Aliphatics						
Carbon tetrachloride	5	0	ND	—	—	>99
Chlorodibromomethane	5	0	ND	—	—	>99
Chloroform	5	0	ND	—	—	>99
Dichlorobromomethane	5	0	ND	—	—	>99
1,2-Dichloroethane	5	0	ND	—	—	>99
1,1-Dichloroethylene	5	0	ND–10	—	3.8	NM
Methylene chloride	5	0	ND	—	—	>99
1,1,2,2-Tetrachloroethane	5	0	ND–9.0	—	3.2	NM
Tetrachloroethylene	5	0	ND–3.0	—	1.0	81
1,1,1-Trichloroethane	5	0	ND–10	—	3.4	NM
1,1,2-Trichloroethane	5	0	ND	—	—	>99
Trichloroethylene	5	0	ND–3.0	—	0.6	60
Pesticides and Metabolites						
Beta-BHC	5	0	ND–0.2	—[a]	0.1	NM
Gamma-BHC	5	0	ND–0.01	—[a]	—[b]	75
Chlordane	5	0	ND–0.9	—[a]	0.2	0

Continued

TABLE 3.31 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
4,4′-DDE	5	0	ND–0.1	—[a]	—[b]	NM
4,4′-DDT	5	0	ND–0.1	—[a]	—[b]	NM
Dieldrin	5	0	ND	—[a]	—[b]	>99
Alpha-endosulfan	5	0	ND–0.04	—[a]	—[b]	NM
Beta-endosulfan	5	0	ND	—	—	>99
Endosulfan sulfate	5	0	ND–0.2	—[a]	0.1	NM
Endrin	5	0	ND–0.1	—[a]	—[b]	0
Endrin aldehyde	5	0	ND–0.4	—[a]	0.1	0
Heptachlor	5	0	ND–0.2	—[a]	—[b]	NM
Heptachlor epoxide	5	0	ND–0.1	—[a]	—[b]	NM
Isophorone	5	0	ND	—	—	>99
4,4′-DDD	5	0	ND	—	—	>99

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 622 pp, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.32
Removability of Toxic Organic Pollutants from Wastewater in the Secondary Copper Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
Phthalates						
Bis(2-ethylhexyl) phthalate	13	10	ND–590	34.0	84	92
Butyl benzyl phthalate	13	2	ND–23	—[a]	3.3	38
Di-n-butyl phthalate	13	7	ND–110	16.0	32	43
Diethyl phthalate	13	3	ND–82	—[a]	15	NM
Dimethyl phthalate	13	4	ND–1.3×10^3	1.0	210	NM
Di-n-octyl phthalate	13	2	ND–170	—[a]	15	NM
Aromatics						
Benzene	13	0	ND–3.0	—[a]	0.2	85
Ethylbenzene	13	0	ND–2.0	—[a]	0.2	50
Hexachlorobenzene	13	2	ND–220	—[a]	30	93
Nitrobenzene	13	0	ND–1.0	—[a]	—[b]	NM
Toluene	13	1	ND–69	—[a]	5.6	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthene	13	1	ND–36	—[a]	2.8	39
Acenaphthylene	13	0	ND	—	—	>99
Anthracene	13	5	ND–140	5.0	19	93
Benzo (a) pyrene	13	0	ND–9.0	—[a]	1.5	NM

Continued

TABLE 3.32 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L)			Average Percent Removal
			Range	Median	Mean	
Benzo (b) fluoranthene	13	1	ND–12	—[a]	—[b]	NM
Benzo (k) fluoranthene	13	1	ND–12	—[a]	—[b]	NM
Chrysene	13	0	ND–8.0	—[a]	0.8	>99
Dibenz (ah) anthracene	13	0	ND–8.0	—[a]	0.6	NM
Fluoranthene	13	1	ND–17	2.0	3.9	99
Fluorene	13	3	ND–100	—[a]	23	NM
Indeno (1,2,3-cd) pyrene	13	0	ND–8.0	—[a]	0.6	NM
Naphthalene	13	2	ND–930	—[a]	87	84
Phenanthrene	13	5	ND–140	5.0	19	93
Pyrene	13	3	ND–38	3.0	7.8	99
Polychlorinated Biphenyls						
Aroclor 1248	13	0	ND–2.2	—[a]	0.2	60
Aroclor 1254	13	0	ND–1.7	—[a]	0.2	60
Halogenated Aliphatics						
Carbon tetrachloride	13	1	ND–260	—[a]	20	NM
Chloroform	13	6	ND–320	—[a]	43	67
Dichlorobromomethane	13	0	ND–7.0	—[a]	0.5	NM
1,2-Dichloroethane	13	0	ND–1.0	—[a]	—[b]	97
1,1-Dichloroethylene	13	0	ND	—	—	>99
1,2-*trans*-Dichloroethylene	13	0	ND	—	—	>99
Methylene chloride	13	0	ND	—	—	>99
1,1,2,2-Tetrachloroethane	13	1	ND–14	—[a]	2.6	NM
Tetrachloroethylene	13	1	ND–12	—[a]	1.7	81
Trichloroethylene	13	0	ND–2.0	—[a]	0.2	97
Pesticides and Metabolites						
Aldrin	13	0	ND	—	—	>99
Alpha-BHC	13	0	ND–0.2	—[a]	—[b]	0
Beta-BHC	13	0	ND–0.2	—[a]	—[b]	95
Gamma-BHC	13	0	ND–0.1	—[a]	—[b]	NM
Chlordane	13	0	ND–0.5	—[a]	0.1	0
4,4′-DDE	13	0	ND–0.1	—[a]	0.1	NM
4.4′-DDD	13	0	ND–0.04	—[a]	—[b]	60
4,4′-DDT	13	0	ND–0.1	—[a]	0.1	NM
Dieldrin	13	0	ND–0.2	—[a]	—[b]	NM
Alpha-endosulfan	13	0	ND–0.6	—[a]	0.1	NM
Beta-endosulfan	13	0	ND–0.1	—[a]	—[b]	67
Endrin	13	0	ND–0.1	—[a]	—[b]	75
Endrin aldehyde	13	0	ND–0.4	—[a]	0.1	NM
Heptachlor	13	0	ND–0.2	—[a]	—[b]	NM
Heptachlor epoxide	13	0	ND–0.1	—[a]	—[b]	NM
Toxaphene	13	0	ND	—	—	>99

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 622 pp, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.33
Removability of Toxic Organic Pollutants from Wastewater in the Primary Lead Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L)			Average Percent Removal
			Range	Median	Mean	
Pyrene	1	0	ND	—	—	>99
Methylene chloride	1	1	54	—	—	NM

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/1-79/019-a, U.S. EPA, Washington, DC, 622 pp, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.34
Removability of Toxic Organic Pollutants from Wastewater in the Secondary Lead Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L)			Average Percent Removal
			Range	Median	Mean	
Phthalates						
Bis(2-ethylhexyl) phthalate	4	2	ND–22	9.5	12	97
Butyl benzyl phthalate	4	0	ND–4.0	—[a]	1.0	94
Di-n-butyl phthalate	4	1	ND–35	1.5	9.5	21
Dimethyl phthalate	4	0	ND	—	—	>99
Di-n-octyl phthalate	4	0	ND–2.0	—[a]	0.5	94
Nitrogen Compounds						
Benzidine	4	0	ND	—	—	>99
Aromatics						
Benzene	7	0	ND–7.0	—[a]	1.0	NM
Chlorobenzene	7	0	ND	—	—	>99
Ethylbenzene	7	0	ND–4.0	—[a]	0.6	NM
Nitrobenzene	4	0	ND	—	—	NM
Toluene	7	0	ND–1.0	—[a]	0.3	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthylene	4	0	ND	—	—	>99
Anthracene	4	0	ND–2.0	—[a]	0.5	88
Benzo (a) pyrene	4	0	ND	—	—	>99
Benzo (b) fluoranthene	4	0	ND	—	—	>99
Benzo (ghi) perylene	4	0	ND–1.0	—[a]	0.3	NM
Benzo (k) fluoranthene	4	0	ND	—	—	>99

Continued

TABLE 3.34 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L)			Average Percent Removal
			Range	Median	Mean	
Chrysene	4	0	ND–2.0	—[a]	0.5	>99
Fluoranthene	4	0	ND	—	—	>99
Fluorene	4	0	ND	—	—	>99
Indeno (1,2,3-cd) pyrene	4	0	ND	—	—	>99
Naphthalene	3	0	ND–3.0	—[a]	0.8	0
Phenanthrene	4	0	ND–2.0	—[a]	0.5	89
Pyrene	4	0	ND	—	—	<99
Polychlorinated Biphenyls						
Aroclor 1248	4	0	ND–1.6	1.0	0.9	36
Aroclor 1254	4	0	ND–1.9	1.3	1.1	15
Halogenated Aliphatics						
Bromoform	7	0	ND	—	—	>99
Chloroform	7	4	ND–32	—[a]	4.6	33
1,2-Dichloroethane	7	0	ND–2.0	—[a]	0.3	93
1,1-Dichloroethylene	7	1	ND–17	—[a]	2.4	35
1,2-*trans*-Dichloroethylene	7	1	ND–22	—[a]	3.1	NM
1,1,2,2-Tetrachloroethane	7	0	ND	—	—	>99
Tetrachloroethylene	7	0	ND–3.0	—[a]	0.6	45
1,1,2-Trichloroethane	7	0	ND–7.2	—[a]	1.0	NM
Trichloroethylene	7	1	ND–28	1.0	4.7	NM
Pesticides and Metabolites						
Aldrin	4	0	ND	—	—	>99
Alpha-BHC	4	0	ND–0.04	—[a]	—[b]	80
Beta-BHC	4	0	ND–0.3	—[a]	0.1	0
Gamma-BHC	4	0	ND–0.02	—[a]	—[b]	80
Chlordane	4	1	ND–31	9.0	15	NM
4,4′-DDE	4	0	ND–0.02	—[a]	—[b]	90
4,4′-DDT	4	0	ND–0.1	—[a]	—[b]	0
Dieldrin	4	0	ND–0.4	0.2	0.1	NM
Alpha-endosulfan	4	0	ND	—[a]	—[b]	>99
Beta-endosulfan	4	0	ND–0.1	—[a]	—[b]	NM
Endrin	4	0	ND	—	—	>99
Endrin aldehyde	4	0	ND	—	—	>99
Heptachlor	4	0	ND–0.3	—[a]	0.1	0
Heptachlor epoxide	4	0	ND–0.1	—[a]	—[b]	>99
Isophorone	4	0	ND	—	—	>99

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 1979.

ND, not detected; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.35
Removability of Toxic Organic Pollutants from Wastewater in the Secondary Silver Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L)			Average Percent Removal
			Range	Median	Mean	
Phthalates						
Bis(2-ethylhexyl) phthalate	5	3	3.4–120	17	37	NM
Butyl benzyl phthalate	5	2	ND–52	1.0	18	NM
Di-n-butyl phthalate	5	1	ND–79	7.0	19	75
Diethyl phthalate	5	0	ND	—	—	>99
Di-n-octyl phthalate	5	2	ND–69	—[a]	16	47
Aromatics						
Benzene	9	4	ND–59	—[a]	14	81
Chlorobenzene	9	0	ND–4.0	—[a]	0.4	86
Ethylbenzene	9	2	ND–14	—[a]	3.9	58
Toluene	9	1	ND–19	—[a]	2.7	87
Polycyclic Aromatic Hydrocarbons						
Acenaphthene	5	0	ND	—	—	>99
Anthracene	5	0	ND	—	—	>99
Fluoranthene	5	1	ND–200	—[a]	40	NM
Naphthalene	5	0	ND	—	—	>99
Phenanthrene	5	0	ND	—	—	>99
Pyrene	5	1	ND–180	—[a]	36	92
Polychlorinated Biphenyls						
Aroclor 1248	2	0	0.3–1.9	1.1	1.1	NM
Aroclor 1254	2	0	0.2–2.6	1.4	1.4	NM
Halogenated Aliphatics						
Bromoform	9	1	ND–13	—[a]	1.4	87
Carbon tetrachloride	9	5	ND–1700	19	310	18
Chlorodibromomethane	9	4	ND–2800	—[a]	750	NM
Chloroform	9	6	ND–2900	130	440	NM
1,2-Dichloroethane	9	3	ND–240	2.0	48	60
1,1-Dichloroethylene	9	3	ND–3400	—[a]	390	65
1,3-Dichloropropylene	9	0	ND	—	—	—
1,2-*trans*-Dichloroethylene	9	1	ND–44	—[a]	4.9	NM
Methylene chloride	9	2	ND–790	—[a]	160	84
1,1,2,2-Tetrachloroethane	8	2	ND–25	—[a]	5.9	26
Tetrachloroethylene	9	4	ND–35	—[a]	8.3	81
1,1,1-Trichloroethane	9	0	ND–5.0	—[a]	0.6	92
Trichloroethylene	9	3	ND–330	—[a]	51	86
Pesticides and Metabolites						
Aldrin	2	0	ND	—	—	>99
Alpha-BHC	2	0	ND–0.1		0.05	NM
Beta-BHC	2	0	0.01–0.04		0.025	NM
Delta-BHC	2	0	ND		—	>99

Continued

TABLE 3.35 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L) Range	Median	Mean	Average Percent Removal
Gamma-BHC	2	0	ND–0.03		0.015	NM
Chlordane	2	0	ND–0.1		0.05	0
4,4′-DDE	2	0	ND–0.01		0.005	NM
4,4′-DDD	2	0	ND–0.01		0.005	NM
4,4′-DDT	2	0	0.02–0.03		0.025	NM
Dieldrin	2	0	ND–0.1		0.05	NM
Endrin	2	0	ND–0.2		0.1	86
Endrin aldehyde	2	0	ND–0.5		0.25	NM
Heptachlor	2	0	0.01–0.04		0.025	NM

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.36
Removability of Toxic Organic Pollutants from Wastewater in the Primary Tungsten Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 µg/L	Treated Effluent Concentration (µg/L) Range	Median	Mean	Average Percent Removal
Phthalates						
Bis(2-ethylhexyl) phthalate	2	2	32–730	—	380	NM
Di-n-butyl phthalate	2	2	22–66	—	44	NM
Diethyl phthalate	2	1	ND–16	—	8.0	NM
Dimethyl phthalate	2	1	ND–230	—	120	NM
Di-n-octyl phthalate	2	1	ND–43	—	22	NM
Aromatics						
Benzene	4	1	ND–17	7.5	8.0	NM
Chlorobenzene	4	0	ND–1.0	—[a]	—[b]	NM
Ethylbenzene	4	0	ND–1.0	—[a]	0.3	86
Nitrobenzene	2	0	ND–5.5	—[a]	2.8	NM
Toluene	4	0	ND–1.0	—[a]	0.3	97
1,2,4-Trichlorobenzene	2	0	4.0–5.5	—[a]	4.8	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthene	2	0	ND	—	—	>99
Acenaphthylene	2	0	ND	—	—	>99
Anthracene	2	0	ND–8.0	—	4.0	87
Benzo (a) pyrene	2	0	ND–1.0	—	0.5	NM

Continued

TABLE 3.36 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
Chrysene	2	0	ND	—	—	>99
Fluoranthene	2	0	ND–1.0	—	0.5	NM
Fluorene	2	0	ND	—	—	>99
Naphthalene	2	1	ND–32	—	16	93
Phenanthrene	2	0	ND–8.0	—	4.0	NM
Pyrene	2	1	ND–15	—	7.5	NM
Polychlorinated Biphenyls						
Aroclor 1248	2	0	ND–2.4	—	1.2	NM
Aroclor 1254	2	0	ND–1.9	—	1.0	29
Halogenated Aliphatics						
Bromoform	4	0	ND	—	—	>99
Chlorodibromomethane	4	0	ND	—	—	>99
Chloroform	4	2	ND–870	29	230	NM
Dichlorobromomethane	4	1	ND–12	6.0	6.0	NM
1,2-Dichloroethane	4	2	ND–29	7.5	11	NM
1,1-Dichloroethylene	4	2	ND–29	10	12	NM
1,2-*trans*-Dichloroethylene	4	0	ND–2.0	—	0.5	NM
1,1,2,2-Tetrachloroethane	4	0	ND–9.0	5.3	5.0	4
Tetrachloroethylene	4	1	3.0–20	7.0	9.3	54
1,1,1-Trichloroethane	4	0	ND	—	—	>99
Trichloroethylene	4	3	ND–86	38	41	NM
Pesticides and Metabolites						
Aldrin	2	0	ND	—	—	>99
Alpha-BHC	2	0	ND	—	—	>99
Beta-BHC	2	0	ND	—	—	>99
Gamma-BHC	2	0	ND–0.1	—	—	50
Chlordane	2	0	ND–0.5	—	0.3	NM
4,4′-DDD	2	0	ND–0.2	—	0.1	NM
4,4′-DDT	2	0	ND	—	—	>99
Dieldrin	2	0	ND	—	—	>99
Alpha-endosulfan	2	0	ND–0.6	—	0.3	91
Beta-endosulfan	2	0	ND–0.2	—	0.1	97
Endrin	2	0	ND	—	—	>99
Endrin aldehyde	2	0	ND	—	—	>99
Heptachlor	2	0	ND	—	—	>99
Heptachlor epoxide	2	0	ND	—	—	>99
Isophorone	2	0	ND–6.0	—	3.0	NM

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.37
Removability of Toxic Organic Pollutants from Wastewater in the Primary Zinc Subcategory

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L)			Average Percent Removal
			Range	Median	Mean	
Phthalates						
Bis(2-ethylhexyl) phthalate	11	4	ND–170	14	22	21
Butyl benzyl phthalate	11	0	ND–0.1	—[a]	—[b]	99
Di-n-butyl phthalate	11	1	ND–12	4.0	1.6	56
Diethyl phthalate	11	0	ND–0.9	—[a]	0.1	96
Dimethyl phthalate	11	1	ND–22	—	2.4	96
Di-n-octyl phthalate	11	0	ND–1.0	—	0.1	NM
Nitrogen Compounds						
3,3′-Dichlorobenzidine	11	0	ND–2.0	—[a]	0.2	NM
Phenols						
Pentachlorophenol	11	0	ND	—	—	>99
Aromatics						
Benzene	11	0	ND–3.0	—[a]	0.4	85
Ethylbenzene	11	0	ND–6.0	—[a]	0.5	NM
Hexachlorobenzene	11	0	ND	—	—	>99
Toluene	11	0	ND–5.3	3.0	0.8	89
1,2,4-Trichlorobenzene	11	1	ND–47	—[a]	4.3	NM
Polycyclic Aromatic Hydrocarbons						
Acenaphthylene	11	0	ND–8.0	—[a]	0.7	65
Anthracene	11	0	ND–9.0	7.0	1.6	NM
Chrysene	11	0	ND–0.7	—[a]	—[b]	94
Fluoranthene	11	0	ND	—	—	>99
Fluorene	11	0	ND–3.0	—[a]	0.3	81
Naphthalene	11	0	ND–6.0	—[a]	0.5	NM
Phenanthrene	11	0	ND–9.0	—[a]	1.4	NM
Pyrene	11	0	ND–8.0	—[a]	0.9	72
Polychlorinated Biphenyls						
Aroclor 1248	11	0	ND–7.0	—[a]	0.6	NM
Aroclor 1254	11	0	ND–9.8	—[a]	0.9	NM
Halogenated Aliphatics						
Bromoform	11	1	ND–44	—[a]	4.0	NM
Chloroform	11	1	ND–54	—[a]	5.4	66
1,1-Dichloroethane	11	0	ND	—	—	>99
1,2-Dichloroethane	11	0	ND	—	—	>99
1,1-Dichloroethylene	11	0	ND	—	—	>99
Methylene chloride	11	0	ND–7.0	—[a]	0.8	>99
Tetrachloroethylene	11	1	ND–22	—[a]	2.6	NM
Trichloroethylene	11	1	ND–19	—[a]	2.0	89
Trichlorofluoromethane	11	0	ND	—	—	>99

Continued

TABLE 3.37 (continued)

Toxic Pollutant	Number of Samples	Number of Detections >10 μg/L	Treated Effluent Concentration (μg/L) Range	Median	Mean	Average Percent Removal
Pesticides and Metabolites						
Alpha-BHC	11	0	ND–0.7	—[a]	0.1	NM
Beta-BHC	11	0	ND–0.03	—[a]	—	NM
Chlordane	11	0	ND–1.6	—[a]	0.2	NM
4,4′-DDE	11	0	ND–0.2	—[a]	0.01	NM
4,4′-DDT	11	0	ND–0.4	—[a]	0.03	NM
Dieldrin	11	0	ND–0.03	—[a]	—	NM
Heptachlor	11	0	ND–0.7	—[a]	0.1	NM
Heptachlor epoxide	11	0	ND–0.7	—[a]	0.1	NM
Isophorone	11	0	ND	—	—	>99
Nitrogen Compounds						
3,3′-Dichlorobenzidene	11	0	ND–2.0	—[a]	0.2	NM

Source: From U.S. EPA, Development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category, report EPA-440/l-79/0l9-a, U.S. EPA, Washington, DC, 1979.

ND, not detectable; NM, not meaningful.

[a] No median concentration is available in the reference.

[b] No mean concentration is available in the reference.

TABLE 3.38
Source Reduction and Recycling Activity for Nonferrous Metals Manufacturing Wastes

Year	Production Related Waste (metric ton)	% Reported as Released and Transferred	% Recycled	Onsite % Energy Recovery	% Treated	% Recycled	Offsite % Energy Recovery	% Treated	% Remaining Releases and Disposal
1	852,000	28	42.98	1.05	23.93	17.38	0.15	0.89	12.68
2	905,000	35	44.77	0.99	23.75	17.17	0.16	0.33	12.85
3	915,000	—	46.79	0.88	23.12	16.60	0.14	0.35	12.11
4	920,000	—	48.42	1.01	21.16	16.39	0.18	0.39	12.45

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

From the presented yearly data it is apparent that the portion of TRI wastes reported as recycled onsite has increased and the portions treated or managed through energy recovery onsite have remained steady, but are projected to decrease between the first and fourth years.

3.5.1 CHEMICAL RELEASE AND TRANSFER PROFILE

This section is designed to provide background information on the pollutant releases that are reported by this industry. The best source of comparative pollutant release information is the TRI.

Pursuant to the Emergency Planning and Community Right-to-Know Act (EPCRA),[28] TRI includes self-reported facility release and transfer data for over 600 toxic chemicals. Facilities within manufacturing industries that have more than ten employees and that are above weight-based reporting thresholds are required to report TRI onsite releases and offsite transfers. The information presented in here focuses primarily on the onsite releases reported by each sector. Because TRI requires consistent reporting regardless of sector, it is an excellent tool for drawing comparisons across industries.

Although this section does not present historical information regarding TRI chemical releases over time, note that, in general, toxic chemical releases have been declining.[13] Although onsite releases have decreased, the total amount of reported toxic waste has not declined because the amount of toxic chemicals transferred offsite has increased. Better management practices have led to increases in offsite transfers of toxic chemicals for recycling. More detailed information can be obtained from U.S. EPA's annual Toxics Release Inventory Public Data Release book, or directly from the Toxic Release Inventory System database.

Tables 3.39 and 3.40 illustrate TRI releases and transfers for the primary nonferrous metals smelting and refining industry. For this industry as a whole, chlorine comprises the largest number of TRI releases. This is reflected in the fact that chlorine is a byproduct of the magnesium industry and the largest reporter is a magnesium facility. The other top releases are copper compounds, zinc compounds, lead compounds, and sulfuric acid.

Tables 3.41 and 3.42 illustrate the TRI releases and transfers for the secondary nonferrous metals smelting and refining industry. For the industry as a whole, the largest releases were the various metals: aluminum (fume or dust), zinc compounds, lead compounds, copper, and zinc (fume or dust).

3.5.2 SUMMARY OF THE TOXICITY OF TOP CHEMICALS

The following is a synopsis of current scientific toxicity and fate information for the top chemicals (by weight) that facilities within this sector self-reported as released to the environment based upon TRI data. The information contained below is based upon exposure assumptions that have been conducted using standard scientific procedures. The effects listed must be taken in context of these exposure assumptions that are more fully explained within the full chemical profiles in the Hazardous Substances Data Bank (HSDB) and the Integrated Risk Information System (IRIS), both accessed via the Internet.

3.5.2.1 Chlorine

Chlorine is a highly reactive gas. Most of the chlorine released to the environment will quickly evaporate. Breathing small amounts of chlorine for short periods of time can affect the respiratory tract in humans, causing symptoms such as coughing and chest pain. It is irritating to the skin, eyes, and respiratory tract. Repeated long-term exposure to chlorine can cause adverse effects on the blood and respiratory systems. There is currently no evidence to suggest that this chemical is carcinogenic. Ecologically, chlorine is highly toxic to aquatic organisms at low doses.

3.5.2.2 Copper

Metallic copper probably has little or no toxicity, although copper salts are more toxic. Inhalation of copper oxide fumes and dust has been shown to cause metal fume fever: irritation of the upper respiratory tract, nausea, sneezing, coughing, chills, aching muscles, gastric pain, and diarrhea. However, the respiratory symptoms may be due to a nonspecific reaction to the inhaled dust as a foreign body in the lung, and the gastrointestinal symptoms may be attributed to the conversion of copper to copper salts in the body.

It is unclear whether long-term copper poisoning exists in humans. Some have related certain central nervous system disorders, such as giddiness, loss of appetite, excessive perspiration, and

TABLE 3.39
Transfers for Primary Smelting and Refining in lb/yr (1 kg/yr = 0.454 lb/yr)

Chemical Name	No. of Facilities Reporting	Fugitive Air	Point Air	Water Discharges	Under-Ground Injection	Land Disposal	Total Releases	Average Releases per Facility
Copper	20	9412	248,340	508	0	500,254	758,514	37,926
Chlorine	19	153,751	67,037,082	2803	0	11	67,193,647	3,536,508
Sulfuric acid	15	24,527	1,013,009	0	5,700,000	100,920	6,838,456	455,897
Hydrogen fluoride	14	1,565,588	1,520,212	5	0	0	3,085,805	220,415
Manganese	11	15	5130	0	0	5	5150	468
Zinc compounds	10	47,545	102,940	8505	5	42,345,637	42,504,632	4,250,463
Chromium	8	10	398	5	0	0	413	52
Copper compounds	8	559,987	408,015	1502	65,000	27,574,267	28,608,771	3,576,096
Hydrochloric acid	8	3853	6,155,294	0	5	5	6,159,157	769,895
Lead compounds	8	68,834	274,504	7263	730	7,713,452	8,064,783	1,008,098
Arsenic compounds	7	7147	30,181	3005	52,000	2,190,652	2,282,985	326,141
Antimony compounds	6	6319	4398	3143	2100	661,740	677,700	112,950
Cadmium compounds	6	1286	18,912	311	0	39,734	60,243	10,041
Nickel compounds	6	1323	8956	225	4200	1,149,028	1,163,732	193,955
Nitric acid	6	15	23,670	0	5	15	23,705	3951
Aluminum (fume or dust)	5	5760	32,472	44	0	5	38,281	7656
Lead	5	138,589	96,836	18	0	2,352,628	2,588,071	517,614
Nickel	5	345	781	4	0	29,052	30,182	6036
Silver compounds	5	848	2210	270	100	19,633	23,061	4612
Barium compounds	4	5	1850	0	890	456,308	459,053	114,763
Arsenic	3	270	28,264	9	0	7114	35,657	11,886
Cadmium	3	981	6181	11	0	4824	11,997	3999

Chromium compounds	3	250	592	250	0	190,005	191,097	63,699
Manganese compounds	3	620	823	0	0	2,400,643	2,402,086	800,695
Selenium compounds	3	1350	38,000	250	2300	120,265	162,165	54,055
Zinc (fume or dust)	3	10,190	25,682	46	0	4,010,295	4,046,213	1,348,738
1,1,1-Trichloroethane	3	75,031	0	0	0	0	75,031	25,010
Anthracene	2	250	25,487	0	0	0	25,737	12,869
Antimony	2	500	10,915	5	0	0	11,420	5710
Cobalt	2	250	5	0	0	0	255	128
Cobalt compounds	2	669	262	255	0	5	1191	596
Cyanide compounds	2	0	0	500	0	0	500	250
Ethylene glycol	2	0	0	0	0	0	0	0
Phosphoric acid	2	0	0	0	0	0	0	0
Thiourea	2	60	0	0	5300	255	5615	2808
Ammonia	1	250	0	0	0	0	250	250
Beryllium compounds	1	0	0	0	0	0	0	0
Cresol (mixed isomers)	1	250	0	250	0	750	1250	1250
Decabromodiphenyl oxide	1	0	250	0	0	0	250	250
Dichlorodifluoromethane	1	18,000	0	0	0	0	18,000	18,000
M-Xylene	1	14,000	0	0	0	0	14,000	14,000
Naphthalene	1	0	467	0	0	0	467	467
Phenol	1	0	0	1	0	0	1	1
Styrene	1	1900	0	0	0	5	1905	1905
Thallium	1	5	250	0	0	755	1010	1010
Titanium tetrachloride	1	250	250	0	0	0	500	500
1,2,4-Trimethylbenzene	1	18,000	0	0	0	0	18,000	18,000
Total	—	2,738,235	77,122,618	29,188	5,832,635	91,868,262	177,590,938	—

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

TABLE 3.40
Transfers for Primary Smelting and Refining in lb/yr (1 kg/yr = 0.454 lb/yr)

Chemical Name	No. of Reporting Facilities	POTW Discharge	Disposal	Recycling	Treatment	Energy Recovery	Total Transfers	Average per Facility
Copper	20	5	17,596	124,723	0	0	142,324	7116
Chlorine	19	0		9991	0	0	9991	526
Sulfuric acid	15	1	600	6,454,346	0	0	6,454,947	430,330
Hydrogen fluoride	14	0	0	0	0	0	0	0
Manganese	11	0	14	46,752	0	0	46,766	4251
Zinc compounds	10	760	2,692,570	750,680	833,231	0	4,277,241	427,724
Chromium	8	0	0	2361	0	0	2361	295
Copper compounds	8	459	2,900,850	3,882,069	93,989	0	6,877,367	859,671
Hydrochloric acid	8	0	0	0	0	0	0	0
Lead compounds	8	2401	2,253,086	2,289,461	11,239	0	4,556,187	569,523
Arsenic compounds	7	386	1,649,205	174,013	634,487	0	2,458,091	351,156
Antimony compounds	6	1749	345,100	29,836	15,262	0	391,947	65,325
Cadmium compounds	6	346	26,097	420,187	62,987	0	509,617	84,936
Nickel compounds	6	260	5	237,910	3931	0	242,106	40,351
Nitric acid	6	0	5	0	11,000	0	11,005	1834
Aluminum	5	0	317,650	3,826,700	0	0	4,144,350	828,870
Lead	5	5	5	640,899	0	0	640,909	128,182
Nickel	5	5		633	0	0	638	128
Silver compounds	5	174	5765	8756	255	0	14,950	2990
Barium compounds	4	0	0	0	0	0	0	0
Arsenic	3	5	250	55,713	0	0	55,968	18,656
Cadmium	3	5		212,387	0	0	212,392	70,797

Chromium compounds	3	0	1200	15,000	0	0	16,200	5400
Manganese compounds	3	41	0	5639	0	0	5680	1893
Selenium compounds	3	0	19,005	0	0	0	19,005	6335
Zinc (fume or dust)	3	250	0	412,568	0	0	412,818	137,606
1,1,1-Trichloroethane	3	0	0	0	250	0	250	83
Anthracene	2	0	14,032	0	0	0	14,032	7016
Antimony	2	0	4110	1,911,550	0	0	1,915,660	957,830
Cobalt	2	0	0	0	0	0	0	0
Cobalt compounds	2	250	0	77,640	0	0	77,890	38,945
Cyanide compounds	2	0	53,213	0	1813	0	55,026	27,513
Ethylene glycol	2	0	0	0	8673	0	8673	4337
Phosphoric acid	2	0	0	0	160	0	160	80
Thiourea	2	0	0	0	0	0	0	0
Ammonia	1	0	0	0	0	0	0	0
Beryllium compounds	1	0	0	0	0	0	0	0
Cresol (mixed isomers)	1	0	0	0	0	0	0	0
Decabromodiphenyl oxide	1	0	4374	0	0	0	4374	4374
Dichlorodifluoromethane	1	0	0	0	0	0	0	0
M-Xylene	1	0	0	0	0	0	0	0
Naphthalene	1	0	0	0	0	0	0	0
Phenol	1	0	0	0	0	0	0	0
Styrene	1	0	0	0	0	0	0	0
Thallium	1	5	0	750	0	0	755	755
Titanium tetrachloride	1	0	0	0	0	0	0	0
4-Trimethylbenzene	1	0	0	0	0	0	0	0
Total	225	7107	10,304,732	21,590,56	1,677,277	0	33,579,680	108187.82

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

TABLE 3.41
Transfers for Secondary Smelting and Refining in lb/yr (1 kg/yr = 0.454 lb/yr)

Chemical Name	No. of Facilities Reporting Chemical	Fugitive Air	Point Air	Water Discharges	Underground Injection	Land Disposal	Total Releases	Average Releases per Facility
Copper	74	17,235	56,198	2720	0	221,287	297,440	4019
Nickel	38	5646	5873	262	0	12,934	24,715	650
Chlorine	32	5103	6304	0	0	0	11,407	356
Lead	30	13,964	29,230	571	0	750	44,515	1484
Copper compounds	29	11,921	35,205	358	0	1500	48,984	1689
Lead compounds	25	11,211	115,573	404	0	147,930	275,118	11,005
Manganese	25	7848	3547	10	0	74,536	85,941	3,438
Aluminum (fume or dust)	24	34,297	196,604	922	11	641,760	873,594	36,400
Zinc compounds	24	41,195	263,420	3049	0	0	307,664	12,819
Sulfuric acid	21	6917	1730	0	0	0	8647	412
Chromium	19	1465	1937	255	0	2005	5662	298
Zinc (fume or dust)	19	57,759	79,392	331	0	0	137,482	7236
Hydrochloric acid	14	17,116	604,670	0	0	0	621,786	44,413
Nickel compounds	13	1113	1492	297	0	0	2902	223
Chromium compounds	10	276	617	0	0	0	893	89
Ammonia	9	1,343,335	168,094	53,229	57,053	353,800	1,975,511	219,501
Antimony	9	364	373	586	0	5	1328	148
Antimony compounds	9	115	1294	44	0	67,760	69,213	7690
Silver	9	21	517	251	0	0	789	88
Silver compounds	9	1033	823	5	0	0	1861	207
Manganese compounds	8	1074	3426	570	0	0	5070	634

Nitric acid	8	1008	2628	0	0	0	3636	455
Arsenic	7	310	308	36	0	5	659	94
Arsenic compounds	7	10	573	16	0	27,104	27,703	3958
Barium compounds	6	298	2011	0	0	0	2309	385
Cadmium compounds	6	545	5409	20	0	0	5974	996
Cobalt	6	905	680	5	0	20	1610	268
Cadmium	3	250	874	281	0	0	1405	468
Hexachloroethane	3	0	11,536	0	0	0	11536	3845
Aluminum oxide (fibrous form)	2	0	53	0	0	0	53	27
Barium	2	20	45	0	0	0	65	33
Beryllium	2	0	5	0	0	0	5	3
Methanol	2	1000	0	0	0	0	1000	500
Molybdenum trioxide	2	500	4205	18,750	0	0	23,455	11,728
Ammonium sulfate (solution)	1	250	0	0	0	0	250	250
Cobalt compounds	1	0	0	0	0	0	0	0
Mercury compounds	1	250	5	5	0	5	265	265
Phosphoric acid	1	0	0	0	0	0	0	0
Phosphorus (yellow or white)	1	0	0	0	0	0	0	0
Polychlorinated Biphenyls	1	0	0	0	0	0	0	0
Selenium	1	0	1	0	0	0	1	1
Xylene (mixed isomers)	1	250	0	0	0	0	250	250
1,1,1-Trichloroethane	1	250	0	0	0	0	250	250
Totals	—	1,584,854	1,604,652	82,977	57,064	1,551,401	4,880,948	—

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

TABLE 3.42
Transfers for Secondary Smelting and Refining in lb/yr (1 kg/yr = 0.454 lb/yr)

Chemical Name	No. of Facilities Reporting Chemical	POTW Discharge	Disposal	Recycling	Treatment	Energy Recovery	Total Transfers	Average per Facility
Copper	74	7024	139,130	20,126,255	20,233	0	20,292,642	274,225
Nickel	38	282	9366	78,143	3984	0	91,775	2415
Chlorine	32	2545	0	0	0	0	2545	80
Lead	30	1106	675,459	1,749,221	16,055	0	2,441,841	81,395
Copper compounds	29	82	658,756	806,437	537,038	0	2,002,313	69,045
Lead compounds	25	810	5,543,943	11,216,399	1,020,276	0	17,781,428	711,257
Manganese	25	501	108,806	67,048	1236	0	177,591	7104
Aluminum (fume or dust)	24	500	966,226	15,417	0	0	982,143	40,923
Zinc compounds	24	1661	129,752	5,571,000	229,930	0	5,932,343	247,181
Sulfuric acid	21	5	0	7,332,842	0	0	7,332,847	349,183
Chromium	19	51	11,812	43,378	83	0	55,324	2912
Zinc (fume or dust)	19	5	164,242	1,048,567	8180	0	1,220,994	64,263
Hydrochloric acid	14	0	750	56,965	27,557	0	85,272	6091
Nickel compounds	13	23	34,996	1,531,600	4777	0	1,571,396	120,877
Chromium compounds	10	251	165,015	214,000	4664	0	383,930	38,393
Ammonia	9	0	621,718	0	0	0	621,718	69,080
Antimony	9	927	127,443	8180	880	0	137,430	15,270
Antimony compounds	9	614	935,418	641,800	10,710	0	1,588,542	176,505
Silver	9	755	0	8680	0	0	9435	1048
Silver compounds	9	20	835	485,550	186	0	486,591	54,066
Manganese compounds	8	75	29,005	128,500	0	0	157,580	19,698
Nitric acid	8	5	1500	11,299	750	0	13,554	1694
Arsenic	7	67	51,353	0	1784	0	53,204	7601

Arsenic compounds	7	110	196,876	55,734	0	0	252,720	36,103
Barium compounds	6	4448	115,647	82,700	31,094	0	233,889	38,982
Cadmium compounds	6	257	0	393,000	0	0	393,257	65,543
Cobalt	6	5	905	35,045	15	0	35,970	5995
Cadmium	3	0	12,930	23,795	900	0	37,625	12,542
Hexachloroethane	3	0	0	0	0	0	0	0
Aluminum oxide (fibrous form)	2	0	0	0	0	0	0	0
Barium	2	5	62,710	0	250	0	62,965	31,483
Beryllium	2	0	0	7,930	—	0	7930	3965
Methanol	2	0	0	0	0	0	0	0
Molybdenum trioxide	2	0	—	165,100	17,150	0	182,250	91,125
Ammonium sulfate (solution)	1	0	0	0	0	0	0	0
Cobalt compounds	1	0	0	0	0	0	0	0
Mercury compounds	1	0	33,200	0	10	0	33,210	33,210
Phosphoric acid	1	0	0	0	0	0	0	0
Phosphorus (yellow or white)	1	250	0	0	0	0	250	250
Polychlorinated Biphenyls	1	0	255	0	0	0	255	255
Selenium	1	0	2673	0	510	0	3183	3183
Xylene (mixed isomers)	1	0	0	0	0	0	0	0
1,1,1-Trichloroethane	1	0	0	0	0	0	0	0
Totals	—	22,384	10,800,721	51,904,585	1,938,252	0	64,665,942	—

Source: From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.

drowsiness to copper poisoning. Long-term exposure to copper may also cause hair, skin, and teeth discoloration, apparently without other adverse effects. There is currently no evidence to suggest that this chemical is carcinogenic.

People at special risk from exposure to copper include those with impaired pulmonary function, especially those with obstructive airway diseases, because the breathing of copper fumes might cause exacerbation of pre-existing symptoms due to its irritant properties.

Ecologically, copper is a trace element essential to many plants and animals. However, high levels of copper in soil can be directly toxic to certain soil microorganisms and can disrupt important microbial processes in soil, such as nitrogen and phosphorus cycling. Copper is typically found in the environment as a solid metal in soils and soil sediment in surface water. There is no evidence that biotransformation processes have a significant bearing on the fate and transport of copper in water.

3.5.2.3 Hydrochloric Acid

Concentrated hydrochloric acid is highly corrosive. Hydrochloric acid is primarily a concern in its aerosol form. Acid aerosols have been implicated in causing and exacerbating a variety of respiratory ailments. Dermal exposure and ingestion of highly concentrated hydrochloric acid can result in corrosivity. There is currently no evidence to suggest that this chemical is carcinogenic.

Ecologically, accidental releases of solution forms of hydrochloric acid may adversely affect aquatic life by including a transient lowering of the pH (i.e., increasing the acidity) of surface waters. Releases of hydrochloric acid to surface waters and soils will be neutralized to an extent due to the buffering capacities of both systems. The extent of these reactions will depend on the characteristics of the specific environment.

3.5.2.4 Lead

Short-term lead poisoning is relatively infrequent and occurs from ingestion of acid-soluble lead compounds or inhalation of lead vapors. Symptoms include nausea, severe abdominal pain, vomiting, diarrhea or constipation, shock, tingling, pain, muscle weakness, and kidney damage. Death may occur in one to two days. If the patient survives the acute episode, characteristic signs and symptoms of chronic lead poisoning are likely to appear. Chronic lead poisoning affects the gastrointestinal, neuromuscular, blood, kidney, and central nervous systems. Individuals with chronic lead poisoning appear ashen, with an appearance of "premature aging," with stooped posture, poor muscle tone, and emaciation. Neuromuscular syndrome (muscle weakness, easy fatigue, localized paralysis) and central nervous system syndrome (progressive mental deterioration, decreased intelligence, loss of motor skills and speech, hyperkinetic and aggressive behavior disorders, poorly controlled convulsive disorder, severe learning impairment) usually result from intense exposure, while the abdominal syndrome (anorexia, muscle discomfort, malaise, headache, constipation, severe abdominal pain, persistent metallic taste) is a more common manifestation of a very slowly and insidiously developing intoxication.

In the U.S., the central nervous system syndrome is usually more common among children, and the gastrointestinal syndrome is more prevalent in adults. Exposure to lead is also linked to decreased fertility in men. Lead is a probable human carcinogen, based on sufficient animal evidence. Populations at increased risk of toxicity from exposure to lead include developing fetuses and young children, individuals with decreased kidney function, and children with sickle-cell anemia.

If released or deposited on soil, lead will be retained in the upper 2 to 5 cm of soil. Leaching is not important under normal conditions, nor generally is the uptake of lead from soil into plants. Lead enters water from atmospheric fallout, runoff, or wastewater; it is effectively removed from the water column to the sediment predominantly by adsorption to organic matter and clay minerals. Some lead re-enters the water column through methylation by microorganisms. Volatilization is negligible. Lead does not appear to bioconcentrate significantly in fish but does in some shellfish such as mussels. When released to the atmosphere, lead will generally be in dust or adsorbed to particulate matter and subject to gravitational settling.

3.5.2.5 Zinc and Zinc Compounds

Zinc is a nutritional trace element; toxicity from ingestion is low. Severe exposure to zinc might give rise to gastritis with vomiting due to swallowing of zinc dust. Short-term exposure to very high levels of zinc is linked to lethargy, dizziness, nausea, fever, diarrhea, and reversible pancreatic and neurological damage. Long-term zinc poisoning causes irritability, muscular stiffness and pain, loss of appetite, and nausea. There is currently no evidence to suggest that this chemical is carcinogenic.

Zinc chloride fumes cause injury to mucous membranes and to the skin. Ingestion of soluble zinc salts may cause nausea, vomiting, and purging.

Significant zinc contamination of soil is only seen in the vicinity of industrial point sources. Zinc is a relatively stable soft metal, although it burns in air. Zinc bioconcentrates in aquatic organisms.

3.5.3 COMPARISON OF TOXIC RELEASE INVENTORY BETWEEN INDUSTRIES

Figure 3.5 is a graphical representation of a summary of the TRI data for the nonferrous metals industry and the other sectors. The bar graph presents the total TRI releases and total transfers on the left axis and the triangle points show the average releases per facility on the right axis. Industry sectors are presented in the order of increasing total TRI releases. The graph is meant to facilitate comparisons between the relative amounts of releases, transfers, and releases per facility both within and between these sectors.

3.5.4 POLLUTION PREVENTION OPPORTUNITIES

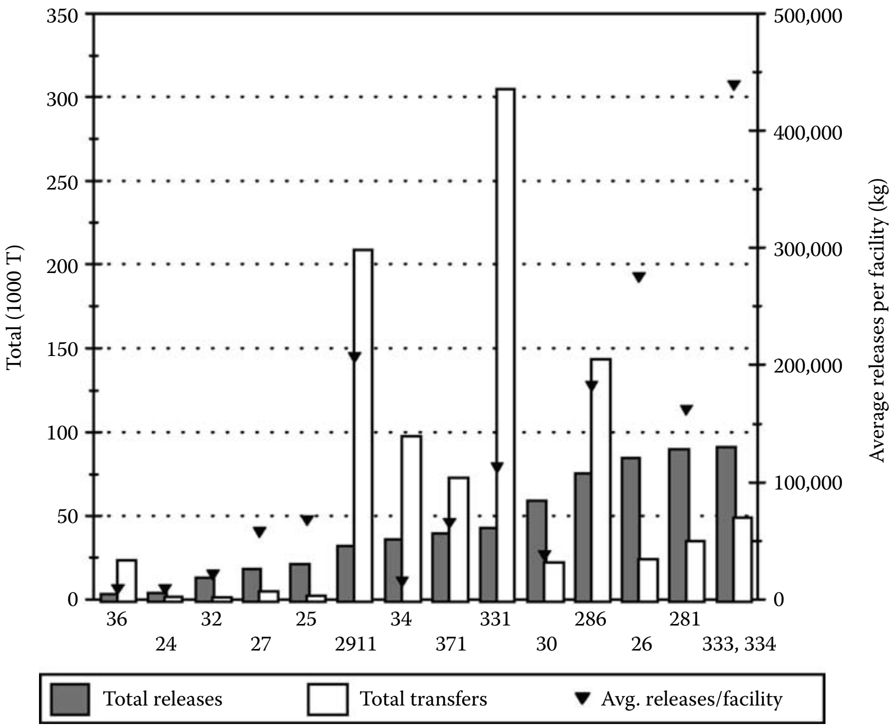
The best way to reduce pollution is to prevent it in the first place. Some companies have creatively implemented pollution prevention techniques that improve efficiency and increase profits while at the same time minimizing environmental impacts. This can be done in many ways, such as reducing material inputs, reengineering processes to reuse byproducts, improving management practices, and using substitution of toxic chemicals. Some smaller facilities are able to get below regulatory thresholds just by reducing pollutant releases through aggressive pollution prevention including a discussion of associated costs, time frames, and policies.

There are great efforts all around the world for improving recycling and waste reduction, including in Hong Kong[29] and Japan.[30] In Japan,[30] the following targets were set in 1998 for recycling and the reduction of final quantities of nonferrous metal industrial wastes by 2010:

1. Japan Mining Industry Association: reduction by 41%
2. Japan Brass Maker's Association: reduction by 13%
3. Japan Aluminum Association: reduction by 14%
4. Japan Electric Wire and Cable Maker's Association: reduction by 25%

Pollution prevention in the U.S., whether through source material reduction/reuse, or waste recycling, is practiced in various sectors of the nonferrous metals industry. Pollution prevention techniques and processes currently used by the nonferrous metals industry can be grouped into the following general categories[1]:

1. Process equipment modification
2. Raw materials substitution or elimination
3. Solvent recycling
4. Precious metals recovery



SIC number	Industry sector	SIC number	Industry sector	SIC number	Industry sector
36	Electronic equipment and components	2911	Petroleum refining	286	Organic chemical mfg.
24	Lumber and wood products	34	Fabricated metals	26	Pulp and paper
32	Stone, clay, and concrete	371	Motor vehicles, bodies	281	Inorganic chemical mfg.
27	Printing	331	Iron and steel	333,334	Nonferrous metals
25	Wood furniture and fixtures	30	Rubber and misc. plastics		

FIGURE 3.5 Releases and transfers by industry. (From U.S. EPA, Profile of the Nonferrous Metals Industry, publication EPA/310-R-95-010, U.S. EPA, Washington, DC, September 1995.)

3.5.4.1 Process Equipment Modification

Process equipment modification is used to reduce the amount of waste generated. Many copper, lead, and zinc refiners have modified their production processes by installing sulfur fixation equipment. This equipment not only captures the sulfur before it enters the atmosphere (helping the refining plant meet CAA sulfur standards), but processes it so that a marketable sulfuric acid is produced. Another example is the use of prebaked anodes in primary aluminum refining. When a prebaked anode is used, the electrolytic cell, or pot, can be closed, thereby increasing the efficiency of the collection of fluoride emissions. In addition, new carbon liners have been developed that significantly increase the life of the aluminum reduction cell. This has resulted in large reductions in the amount of spent potliner material generated by the aluminum industry.

3.5.4.2 Raw Materials Substitution or Elimination

Raw material substitution or elimination is the replacement of raw materials with other materials that produce less waste, or a nontoxic waste. Material substitution is inherent in the secondary nonferrous metals industry primarily by substituting scrap metal, slag, and baghouse dust for ore feedstock. All of these materials, whether in the form of aluminum beverage cans, copper scrap, or lead-acid batteries, are commonly added to other feedstock or charges (usually slag containing residual metals) to produce marketable grades of metal. Primary nonferrous metals refining also uses previously refined metals as feedstock, especially zinc-containing electric arc furnace dust (a byproduct of the iron and steel industry).

3.5.4.3 Precious Metals Recovery

Precious metals recovery is the modification of a refining process to allow the capture of marketable precious metals such as gold and silver. Like sulfur fixation, precious metals recovery is a common waste minimization practice. During primary copper smelting, appreciable amounts of silver and gold present in copper ore will be concentrated into the anode copper and can be recovered as a byproduct in the electrorefining process (as the copper anode is electrochemically dissolved and the copper attaches itself to the cathode, silver and gold drop out and are captured in the slime at the bottom of the tank). In the lead refining process the copper often present in lead ore is removed during the initial lead bullion smelting process as a constituent of dross. Silver and gold are removed from the lead bullion later in the process by adding certain fluxes that cause them to form an impure alloy. The alloy is then refined electrolytically and separated into gold and silver. Precious metals recovery also takes place during zinc refining to separate out copper, a frequent impurity in zinc ore. Copper is removed from the zinc ore during the zinc purification process (after zinc undergoes leaching, zinc dust is added, which forces many of the deleterious elements to drop out; copper is recovered in a cake form and sent for refining).

3.5.5 IMPORTANT POLLUTION PREVENTION CASE STUDIES

Various pollution prevention case histories have been documented for nonferrous metals refining industries. In particular, the actions of the AMPCO Metal Manufacturing Company, Inc., typify industry efforts to simultaneously lessen the impact of the industrial process on the environment, reduce energy consumption, and lower production costs.[1]

3.5.5.1 The Use of Electric Induction to Replace Fossil Fuel Combustion

AMPCO Metal Manufacturing Company, Inc. (Ohio) participated in the development of pollution prevention technologies. The project, sponsored by the U.S. DOE and U.S. EPA, consists of researching and developing the use of electric induction to replace fossil fuel combustion as is currently used to heat tundishes. Tundishes are used to contain the heated reservoir of molten alloy in the barstock casting process. The fossil fuel combustion process currently used requires huge amounts of energy and produces tremendous amounts of waste gases, including combustion bases and lead and nickel emissions.

Heating the tundish by electric induction instead of fossil fuel combustion will substantially improve the current process, saving energy and reducing pollution. Energy efficiency will jump to an estimated 98%, saving 16 billion chu (28.9 billion Btu)/yr/unit. Industry-wide energy savings in 2010 are estimated to be 114 billion chu (206 billion Btu)/yr, assuming a 70% adoption at U.S. foundries.

In addition to the energy savings, the new process also has substantial environmental benefits. Along with the elimination of lead and nickel gases, carbon dioxide, carbon monoxide, and nitrogen oxide emissions from combustion will decrease. The consumption of refractory (a heat-resisting ceramic material) will decline by 80%, resulting in a similar reduction of refractory waste disposal. In all, the prevention of various forms of pollution is estimated to be 66.7 million kg (147 million lb/yr) by 2010.

Economically, the elimination of lead and nickel emissions will result in an improved product because exposure of the metal to combustion gases in the current process results in porosity and entrainment of hydrogen gas in the metal. Overall, AMPCO estimates an annual savings in operations and maintenance expenses of USD 1.2 million with the use of this technology. Assuming the same 70% industry adoption, economic savings by 2010 could reach USD 5.8 million. Without the new electric induction heating process, the capital costs required for compliance could be USD 3 million.

3.5.5.2 Processing Nonferrous Metal Hydroxide Sludge Wastes

Nonferrous metal hydroxide sludge wastes contain a large quantity of water, and the content of valuable metals is too small to allow economical smelting of these wastes. However, the wastes are a burden on the environment and they can only be deposited in special garbage dumps, which are very costly. Therefore a method for processing and recovery of the valuable materials and metal in the waste is highly desirable.

Such a method has been patented in the U.S.[31] for processing the nonferrous metal hydroxide sludge wastes containing chromium, copper, zinc, and nickel for simultaneous recovery and separation of the individual nonferrous metals sequentially. In this method, the individual nonferrous metals, such as, chromium, copper, zinc, and nickel can be individually and economically separated from the collected nonferrous metal hydroxide sludge wastes. This is achieved by the combination of the following steps performed in sequence[31]:

1. Chlorinating the aqueous waste sludge suspension (to oxidize the chromium) at temperatures of 20 to 80°C and pH values between 4 and 13. The chlorinated sludge is then acidified with sulfuric acid to a pH of 1.0 to 3.0. The insoluble components are then separated, followed by the separation of the chromium(VI) from the solution using a fixed-bed anion exchanger (at pH values of <3).
2. Copper is separated from the remaining solution by means of known and conventional liquid–liquid-extraction procedures.
3. Zinc is separated from the remaining solution, which also contains chloride and sulfate by means of liquid–liquid extraction.
4. Aluminum is precipitated and separated from the remaining solution in the form of the hydroxide.
5. Nickel is separated from the filtrate by means of liquid–liquid-extraction.
6. The individual nonferrous metal fractions thus obtained are then processed in conventional ways.[32]

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4 Management, Minimization, and Recycling of Metal Casting Wastes

An Deng, Yung-Tse Hung, and Lawrence K. Wang

CONTENTS

4.1 INDUSTRY DESCRIPTION

The metal casting industry, also known as the foundry industry, is one of the largest recyclers in the world. For centuries, this industry has been converting a huge volume (e.g., 15 to 20 million tons in the U.S.) of scrap metal that would otherwise be disposed in landfills, into manufactured useful products. This scrap metal forms the raw material charged into furnaces of the foundry facility and converted into usable castings. The casting categories include many general ferrous and nonferrous metals and their alloys, including iron, steel, aluminum, copper, magnesium, and zinc. Major end-use markets cross all sectors of the global economy, examples being the automotive industry, transportation equipment, construction, mining and oil field machinery, and industrial machinery.

4.1.1 Casting Flow

4.1.1.1 Overview

Metal casting is a process in which molten metal is poured into a mold to produce metal products. In the mold, the molten metal cools and shapes into castings by filling the preset mold internal space. The most common metal casting process is sand casting, which uses sand as the major molding and core-making material. Besides sands, other materials can also be used as molding materials, such as ceramic mold for investment casting and metal mold for die casting.[1,2] A general metal casting flow diagram is shown in Figure 4.1. A schematic process is shown in Figure 4.2. The casting begins with the customer demands and material preparations, including metal product specification, sands, binders, and scraps. Manufactured molds and cores are assembled in the assembly area, and made ready for pouring.

As the assembled molds are being placed on the pour-off lines, the scrap metal is melted in the furnace. Molten metal from the furnace is brought to the molds on the pouring lines in a refractory lined pouring ladle. Once poured, the molds are allowed to cool before being sent to the shakeout processes. At the shakeout, the castings are separated from the sand mold. The sand is sent to a reclamation system so that it can be reused in the molding process.

The materials comprising the core and mold in the casting processes have the properties of porosity, cohesion, and refractoriness. Sand has globally been selected as one of the materials meeting the property requirements. Its aggregate porosity, connected as passages, allows air and steam to escape from the mold during casting. The sand particles can adhere together into all kinds of molding shapes. In particular, sands have the ability to withstand severe heat and resist penetration of the molten metal, and impart a smooth and desirable appearance to the casting.

4.1.1.2 Core Making

Cores are separate shapes that are placed in the mold to provide castings with contours, cavities, and passages that are not achievable by the mold alone. A core has to be fixed tightly in place while

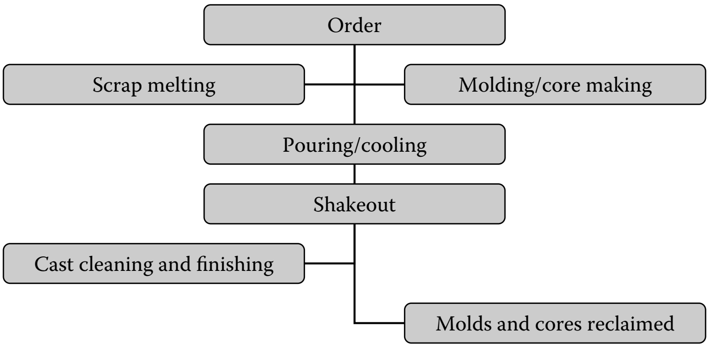

FIGURE 4.1 General metal casting flow chart. (From U.S. EPA, Summary of Factors Affecting Compliance by Ferrous Foundries, Vol. 1, EPA-340/1-80-020, U.S. EPA, Washington, DC, January 1981.)

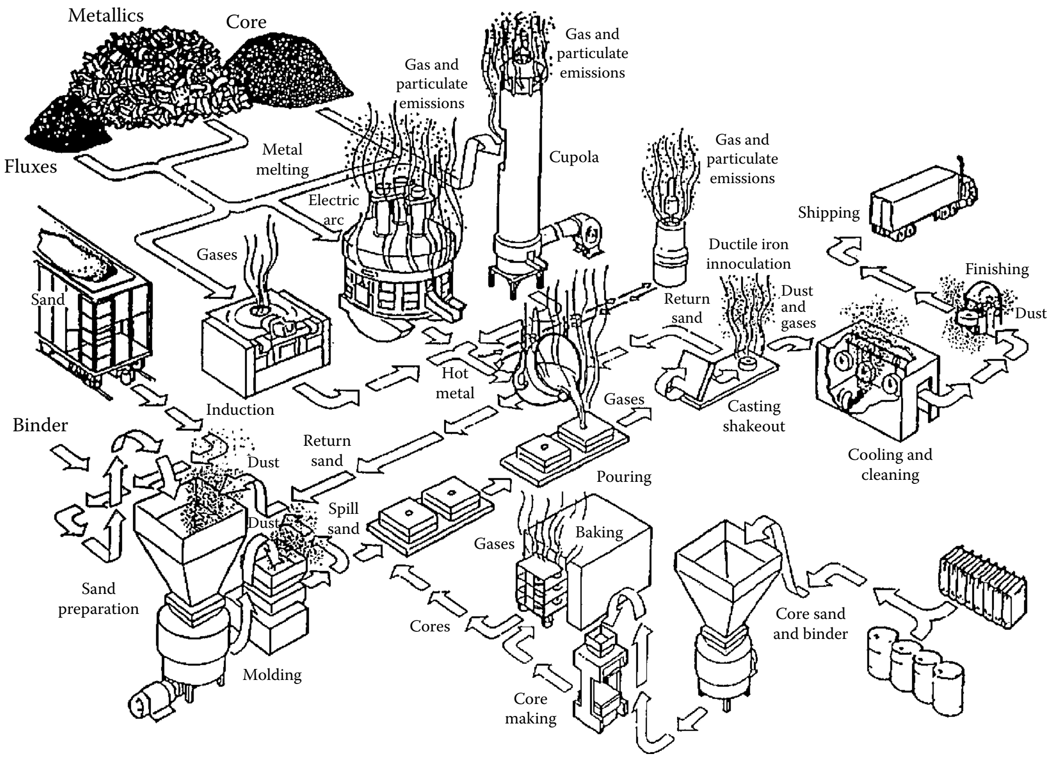

FIGURE 4.2 Metal casting process.

the metal flows around it. Cores are made by mixing sand with binders and catalysts, which are activated to bond sand into various shapes. Figure 4.3 demonstrates the typical core-making process. The sand and binders are blended uniformly in a mixer. The mixture is then discharged into a core machine, where continuous curing with a catalyst is applied. After the core is cured, it is removed and sent to a molding assembly area.

4.1.1.3 Molding

Molding is the process where a pattern is pressed or embedded into special sand to the desired shape or form. Alternatively, the pattern can be placed on a molding board, and the sand rammed or compressed around the pattern. Figure 4.4 shows the typical molding flow. The sand and binder are first

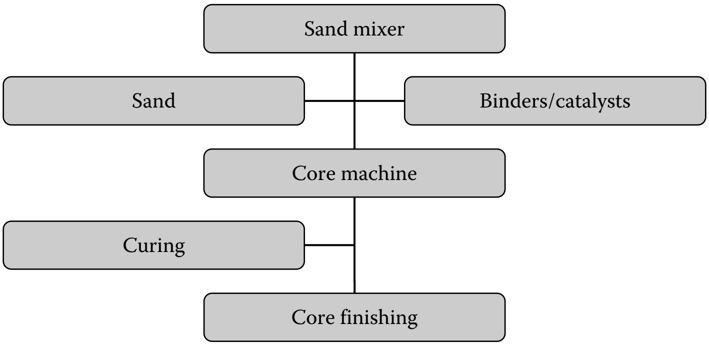

FIGURE 4.3 Core making flow chart.

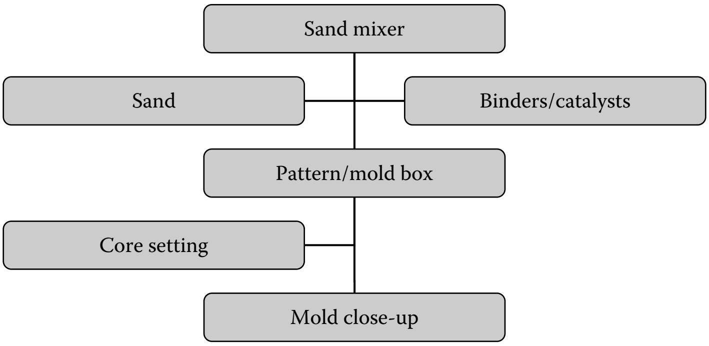

FIGURE 4.4 Typical molding flow chart.

mixed in a mixer. Then the mixed sand is discharged onto a pattern face mounted in a mold box. The sand in the box is compacted to its maximum density. Once the sand is set, the pattern is removed from the sand, and cores are placed in the mold. The mold is then closed up and moved to the pouring lines.

4.1.1.4 Melting and Pouring

Figure 4.5 describes the typical metal melting flow chart. At first, the customer's metal specification for the casting will determine what type of scrap metal will be used to feed the furnace. Once charged, the furnace uses multiple melting powers or burners (that is, electricity, kerosene, gas, coke, charcoal, and used engine oil) to melt the scrap metal. Scrap metals may be fully melted in tens of minutes, depending upon the size of the vessel used. Alloys are added according to the metal specification. The addition is determined by spectro analysis in the melting process. When the melting is complete, the molten metal is placed in a pouring shank and sent to the pouring line.

Furnace types include cupolas, electric arc, induction, hearth or reverberatory, and crucible. Because of the different characteristics of metals, different inputs are required and different pollution is released from each type. Table 4.1 summarizes the types of furnaces depending on the type of metal being used.

The molds are cast and allowed to cool for a suitable time, often 30 to 40 min, before shaking out the castings. The shakeout work may be supplied by a vibrating conveyor or a rotating drum, which cause the molds to be broken up by the vibration, exposing the casting for removal. The sand

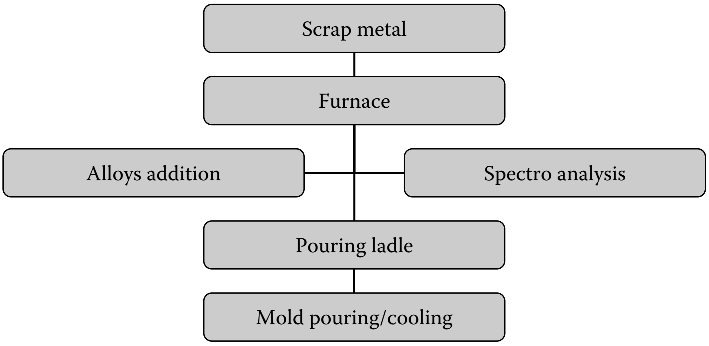

FIGURE 4.5 Typical melting flow chart.

TABLE 4.1
Common Types of Metal-Melting Furnaces

Furnace Type	Raw Materials	Outputs	Process
Cupola furnace	Iron ore, scrap iron, lime, coke	Molten iron	Alternative layers of metal and coke are fed into the top of the furnace. The metal is melted by hot gasses from the coke combustion. Impurities react with the lime and are separated.
Electric arc furnace	Scrap iron, flux	Molten iron and steel	Electric arcs from carbon electrodes melt the scrap metal. The flux reacts with impurities.
Induction furnace	Scrap iron or non-ferrous metals	Molten iron or nonferrous metals	Induction furnaces are the most common type used by both ferrous and nonferrous foundries. Copper coils heat the metal using alternating currents. The flux reacts with impurities.
Reverberatory, hearth, or crucible furnace	Nonferrous metals, flux	Molten nonferrous metals	Reverberatory furnaces melt metals in batches using a pot-shaped crucible that holds the metal over an electric heater or fuel-free burner. The flux reacts with impurities.

Source: From WMRC, Primary Metal, Illinois Waste Management and Research Centre, available at http://www.wmrc.uiuc.edu/info/library_docs/manuals/primmetals/chapter3.htm.

from the mold is separated and processed through a reclamation system for reuse in molding and core making.

4.1.1.5 Casting Cleaning and Inspection

The foundry cleaning room is a collection area where castings are finished to meet the casting specifications. A sample flow chart is shown Figure 4.6. When castings are removed from the shakeout, they are run through the shot blast to remove sand and expose the surface for inspection and further work. Castings are inspected for defects such as cracks, flashing, and inclusions. If none are found the castings are sent to the heat-treating department. If defects are present that require welding or grinding the castings are sent to the appropriate area to have the defect corrected. Once rework is completed, the castings are sent to the heat-treating department. After being heat treated, the castings are again sent through the shot blast before being sent to the final inspection area.

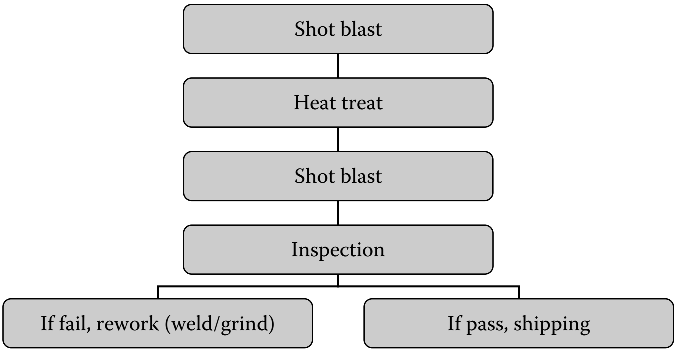

FIGURE 4.6 Casting, cleaning and inspection flow chart.

4.1.1.6 Reclamation of Molds and Cores

After shakeout, the return sand is reclaimed by a crushing process and by screening out core lumps, nonmagnetic metallics, and other unwanted material. Burnt binders (such as clay, resin, and other foreign fines) will excessively build up in the matrix of reclaimed molds and cores, and may reduce the gas/heat permeability within the molds and cores. This used molding sand will be put back through the sieve to have the correct amount of water added. Sometimes, the reclaim process may not be sufficient to recondition the technically acceptable or functional refractory materials, which eventually become excess foundry sand and is removed from the system. New sand, additional water, make-up binder, and additional catalysts are added to ensure molding and core-making quality.

4.1.2 CASTING PROCESSES

Casting processes can be divided according to the refractory materials used, that is, sand, ceramics, and metals. The principal sand casting processes used in the metal casting industry are sand mold casting, expendable pattern (lost foam) casting, shell mold casting, plaster mold casting, and vacuum (V-process) casting. Processes that use some form of disposable ceramic molds include the ceramic mold process and investment mold casting. Processes that use a reusable metal mold include die casting, permanent mold casting, and centrifugal casting.

4.1.2.1 Sand Casting

This is the earliest and the most commonly used casting process. It has the advantages of wide metal suitability, low cost, and simple operation. It uses sand as a refractory material. Many types of sand are utilized by the foundry industry. However, because of its wide availability and relatively low cost, silica sand is the one that makes most metal castings. Silica sand is composed of the mineral quartz (SiO_2), which has a fusion point of approximately 1670°C (3090°F), which is often lowered by the presence of appreciable quantities of minerals with lower fusion points.

4.1.2.2 Shell Casting

In this process, the mold cavity is formed by a shell of resin-bonded sand. The shell is built up in layers, starting with a very fine-grained dip-coat, which is then dusted with a fine powder (molochite or zircon). Once the first coat is set hard, the wax is dipped a second time. The third and successive coats are dusted with coarse stucco. This coarse aggregate builds up the strength of the shell. Shell mold castings surpass ordinary sand castings in surface finish and dimensional accuracy, and cool at slightly higher rates. In addition, equipment costs are higher, and the size and complexity of castings that can be produced are more limited.

4.1.2.3 Investment Casting

This process is used to produce intricate, thin-section parts with great dimensional accuracy, fine detail, and very smooth surfaces. All ferrous and nonferrous alloys can be cast in investment molds. Investment casting begins with expendable wax patterns that are assembled into clusters, then coated with a series of successively coarser ceramic slurries. The assembly is then fired in a furnace to dry and harden the ceramic shell and to melt out the wax, leaving a cavity into which molten metal is poured to form the casting.

4.1.2.4 Die Casting

A die is a reusable mold, usually made of steel, for the mass production of small parts in low-melting-point alloys—usually zinc or aluminum alloys. For the mass production of small parts that have no undercuts, the durability and excellent surface quality of the die, in addition to the saving in labor costs, make die casting a competitive and worthwhile process.

4.1.2.5 Permanent Mold Casting

Metal molds and cores are used in permanent mold casting. The process works best in continuous operation so that the mold temperature can be maintained within a fixed operating range. The operating temperature of the mold is one of the most important factors in successful permanent mold casting. Mold cavities are machined from solid blocks of graphite. Mold life is the major cost factor in permanent mold casting.

4.1.2.6 Centrifugal Casting

Centrifugal force is used to introduce molten metal into a mold cavity that is spinning around its axis. Cast iron pipe is produced in centrifugal molds, and copper-base alloy bearings are also commonly produced this way. Permanent metal molds are usually coated or lined to extend operating life.

4.1.3 SAND CASTING SYSTEMS

Of the many casting processes, sand casting is principally addressed in this section as this process not only prevails in the casting industry, but also generates a vast volume of solid wastes. Sand casting systems are possibly the most versatile foundry method, and are largely divided according to the binder and bonding manners into two categories, green sand and chemically bonded sand systems. The green sand system uses sand, clay, water, and additives as components, and bonds sand particles together by relying upon mechanical forces generated by mixing the clay and water. Chemically bonded sand systems use sand, resins, or inorganic binders, and sometimes water and catalysts, as components. The bonding forces are generated by chemical reactions (polymerization) between the resins/inorganic binders and catalysts.

4.1.3.1 Green Sand System

Green sand molding is the most widely used molding process in the world, accounting for up to 90% ferrous sand casting materials.[4] It is low in cost, high in performance, and the materials are reusable. Green, in this sense, does not refer to color, but is a technical point, indicating a natural bonding effect (with water, but without artificial binders, additives, or catalysts). Green sand consists of 85 to 95% high-quality silica sand, 4 to 10% bentonite clay (as a binder), 2 to 5% water, and 2 to 10% sea coal (a carbonaceous mold additive to improve casting surface finish). A machine, known as a muller, is used to coat the sand quickly and uniformly with a clay and water mixture (glue). A muller is capable of producing more than several tons of prepared molding sand in a few minutes.

Sand is composed of grains ranging from 0.05 to 2 mm in diameter. The physical properties of sand that can affect green sand system performance include grain shape, grain size distribution, grain fineness, permeability, density, and coefficient of thermal expansion. The chemical properties of sand that can affect green sand system performance include chemical composition, loss on ignition, pH value, and fusion point.

Clays used in foundries include hydrous alumina silicates, known as bentonites. Their properties provide cohesion and plasticity in the green state and also high strength when dried. There are three clays that are commonly used in foundries: western bentonite [sodium bentonite, burnout point 1290°C (2350°F)], southern bentonite [calcium bentonite, burnout point 1065°C (1950°F)], and fire clay [kaolinite, burnout point 1425°C (2600°F)].

The water used for a green sand system should be clean and it should be consistent. It should have a pH that is neutral to alkaline, not acidic, because acids prevent bentonite from swelling. In addition to sand, clay, and water, there are a number of other materials, or additives, that can enhance, control, and optimize the performance of green sand systems.

4.1.3.2 Chemically Bonded Sand Systems

Foundry cores and molds may be made using resin-coated sand prepared by a number of different bonding processes (e.g., no-bake, cold-box, warm-box, hot-box, shell) that use all sorts of different binders (resins) with unique chemistries. These binders can be triggered, based upon the processes, in two ways—self-setting and triggered setting. In the self-setting system (also known as a self-set, cold setting, cold-box, or no-bake process), sand, binder, and a hardening chemical are mixed together; the binder and hardener start to react immediately, but sufficiently slowly to allow the sand to be formed into a mold or core, which continues to harden further until strong enough to allow casting. In triggered setting system, sand and binder are mixed and blown or rammed into a core box. Little or no hardening reaction occurs until triggered by applying heat or a catalyst gas. Setting then takes place in seconds.

Self-setting systems

These include the following:

1. *Furanes*. Furane sands use a furane resin and an acid catalyst. The resins are urea-formaldehyde (UF), phenol-formaldehyde (PF), or UFPF resins with additions of furfuryl alcohol (FA). The speed of setting is controlled by the percentage of acid catalyst used and the strength of the acid. Ratios such as resin at 0.8 to 1.5% of base sand, catalyst at 40 to 60% of resin are normally used, depending on the sand temperature and the speed of setting required. The optimum ambient temperature is 20 to 30°C, resulting in a compressive strength of typically 4000 kPa (600 psi).
2. *Phenolic-isocyanates (phenolic-urethanes)*. The binder is supplied in three parts: a phenolic resin in an organic solvent (0.8%), methylene diphenyl diisocyanate (MDI) (0.5%), and a liquid amine catalyst. When mixed with sand, the amine causes a reaction between the resin and the MDI, forming urethane bonds, which rapidly set the mixture. The speed of setting is controlled by the type of catalyst. The optimum cure temperature is 25 to 30°C. Compression strength is typically over 4000 kPa (600 psi).
3. *Alkaline phenolic resin, ester hardened*. The binder is a low viscosity, highly alkaline phenolic resole resin (1.2 to 1.7%). The hardener is a liquid organic ester (18 to 25%). Sand is mixed with hardener and resin, usually in a continuous mixer. The speed of setting is controlled by the type of ester used. Low sand temperature slows the cure rate, but special hardeners are available for cold and warm sand. In 24 h compression strength can reach 4000 kPa (600 psi).
4. *Ester silicate process*. Sand is mixed with a suitable grade of sodium silicate (2.2 to 2.8% of sand weight), often incorporating a breakdown agent, together with 10 to 12% (based on silicate) of liquid organic ester hardener. The acid ester reacts with the sodium silicate, hardening the sand. The speed of hardening is controlled by the type of ester used. The final compression and tensile strength achieved are 2000 to 5000 kPa (300 to 700 psi) and 700 kPa (100 psi), respectively.
5. *Portland cement process*. Sand is mixed with portland cement (10% of sand weight) and water (5% of sand weight). Molds are air dried for 24 h and may then be dried out more rapidly.

Triggered setting systems

Triggered setting systems are used to make cores for repetition foundries. After the mixed sand is blown into the core box, the cores must be cured in the box until sufficient strength has been achieved to allow stripping without damage or distortion. Usually the core continues to harden after stripping.

Tensile strengths of 1000 to 2000 kPa (150 to 300 psi) are typical, equating roughly to transverse strengths of 1500 to 3000 kPa. Final strengths may be higher. Triggered setting systems are categorized into two groups, that is, heat triggered processes and gas triggered processes.

Heat triggered processes include the following bonding systems:

1. *Shell process*. Sand is precoated with a solid phenolic novolak resin and a catalyst to form a dry, free-flowing material. The coated sand is blown into a heated core box or dumped onto a heated pattern plate, causing the resin to melt and then harden. Shell molds are normally 20 to 25 mm thick. Resin additions are 2.5 to 4.5% of sand weight, and the catalyst hexamine is added at 11 to 14% of the resin content. The minimum curing time is 90 s but 2 min is common. A 3.5% resin content will give a tensile strength of 1400 kPa (200 psi).
2. *Hot-box process*. The binder is an aqueous PFUF or UFFA resin, and the catalyst is an aqueous solution of ammonium salts, usually chloride and bromide. Sand is mixed with the liquid resin (2.0 to 2.5% of sand weight) and catalyst (20 to 25% of resin weight) and blown into a heated core box. The heat liberates acid vapor from the catalyst, which triggers the hardening reaction. Hardening continues after removal of the core from the box. Thin section cores cure in 5 to 10 s. As cores increase in section size, curing time must be extended up to about 1 min for a 50-mm section. The final tensile strength is 1400 to 2800 kPa (200 to 400 psi).
3. *Warm-box process*. The binder, 1.3 to 1.5% of sand weight, is a reactive, high FA binder. The catalyst, 20% of sand weight, is usually a copper salt of sulfonic acid. Sand, binder, and catalyst are mixed and blown into a heated core box. The heat activates the catalyst, which causes the binder to cure. Curing time is 10 to 30 s depending on thickness. The final tensile strength can be 3000 to 4000 kPa (400 to 600 psi).
4. *Oil sand*. Certain natural oils, such as linseed oil, known as “drying oils,” polymerize and harden when exposed to air and heat. Silica sand is mixed with the drying oil (1 to 2% of sand weight), a cereal binder (1 to 2% of sand weight), and water (2 to 2.5% of sand weight). The resulting mixture is either manually packed or blown into a cold core box. Applied backing will harden the oil and the core becomes rigid. A recirculation air oven is needed because oxygen is necessary to harden the oil. The temperature is normally 230°C, allowing 1 h for each 25-mm section thickness. Correctly baked cores develop a tensile strength of 1340 kPa (200 psi).

Gas triggered processes include the following bonding systems:

1. *Phenolic-urethane-amine gassed (cold-box) process*. The binder is supplied in two parts: a solvent-based phenolic resin (0.8 to 1.5% of sand weight), a polyisocyanate (0.8 to 1.5% of sand weight), MDI (methylene diphenyl diisocyanate) in a solvent. The resins are mixed with sand and the mixture blown into a core box. An amine gas [TEA (triethylamine) or DMEA (dimethyl ethyl amine)] is blown into the core, catalyzing the reaction and causing almost instant hardening. The tensile strength immediately after curing is high at 2000 kPa (300 psi), and the transverse strength is 2700 kPa (400 psi).
2. *Alkaline phenolic resin gassed process*. Alkaline phenol-formaldehyde resin containing a coupling agent is used. The resin (2.0 to 2.5% of sand weight) is mixed with sand, and the mixture is blown into a core box. Carbon dioxide is passed through the mixture, lowering the pH and activating the coupling agent, which causes crosslinking and hardening of the resin. Strength continues to develop after the core is ejected as further crosslinking occurs and moisture dries out. The compression strength is 2000 to 3000 kPa (300 to 400 psi), and the tensile strength is 500 to 800 kPa (70 to 110 psi).
3. *The SO_2 process*. Sand is mixed with a furane polymer resin (1.2 to 1.4% of sand weight) and an organic peroxide (such as methyl ethyl ketone peroxide at 25 to 60% of resin

weight). The mixture is blown into the core box and hardened by passing sulfur dioxide gas through the compacted sand. The gas reacts with the peroxide-forming carbon trioxide and then H_2SO_4, which hardens the resin binder. The tensile strength is 1250 kPa (180 psi) after 6 h.

4. *SO_2-cured epoxy resin*. Modified epoxy/acrylic resins (1.2 to 1.4% of sand weight) are mixed with organic peroxide (26 to 60% of resin weight), the mixture is blown into the core box and a hardening mechanism similar to the SO_2 process takes place.
5. *Ester-cured alkaline phenolic system*. The resin is an alkaline phenolic resin (essentially the same as the self-hardening resins of this type). Sand is mixed with the resin and blown or manually packed into a core box. A vaporized ester, methyl formate, is passed through the sand, hardening the binder. The total resin and peroxide addition is 1.5%. Compression strengths of 5000 kPa (700 psi) are possible.
6. *Carbon dioxide–silica process*. Sand is mixed with sodium silicate (3.0 to 3.5% of sand volume), and the mixture is blown or hand-rammed into a core box or around a pattern. Carbon dioxide gas is passed through the compacted sand to harden the binder. The bonding strength eliminates the need for drying or baking the mold and metal can be poured into the mold immediately. Over-gassing should be avoided because it makes the mixture friable.

4.1.4 CASTING METALS

The metal casting industry conventionally divides casting products into ferrous and nonferrous metals, in particular, iron-based, steel-based, aluminum-based, and copper-based castings. The other castings of low fractions include magnesium, lead, zinc, and their alloys. In the U.S., the foundry industry currently produces 11 million tons of metal product per year, with a shipment value of $19 billion. Of them, iron and steel accounted for 84% of metals cast.[5] The remaining 15% of foundry operations are concerned with aluminum, copper, zinc, and lead production. Table 4.2 summarizes critical physical and thermal properties of aluminum, iron/steel, and cast iron.

4.1.4.1 Iron Castings

Iron is the world's most widely used metal. Iron castings encompass a family of ferrous alloys: gray iron, alloy iron, white iron, malleable iron, ductile iron, and compacted graphite iron. Wide variations in properties can be achieved by varying the balance between carbon and silicon, by alloying, and by applying various types of heat treatment. Iron castings have good fluidity and mold filling during the casting process, with low shrinkage on cooling.

TABLE 4.2
Physical and Mechanical Properties of Aluminum, Iron/Steel, and Cast Iron

Properties	Al	Fe	Gray Iron	Ductile Iron
Content (%)	Pure	Pure	10–40	40–70
Atomic weight (g/cm^3)	26.98	55.85	48.44	48.44
Density, solid (g/cm^3)	2.70	7.86	7.1–7.35	7.06–7.44
Density, liquid (g/cm^3)	2.38	7.01	7.1	7.1
Melting point (°C)	660.37	1536	1120–1180	1120–1180
Thermal expansion coefficient, 0°C (K^{-1} 10^{-6})	23.9	11.7	11.7	11.4–12.8
Heat conductivity, 25°C (W/m K)	237	74.4	45–52	25–42

4.1.4.2 Steel Castings

The most common types of steels used in castings are carbon steels, which contain only carbon as the major alloying element. Carbon steels are classified by their carbon content into three groups: low-carbon steel ($C < 0.20\%$), medium-carbon steel ($C = 0.20$ to 0.50%), and high-carbon steel ($C > 0.50\%$). Steel's hardness also depends upon the carbon content.

4.1.4.3 Aluminum Castings

Aluminum is a light metal with good tensile strength. It is easily cast, extruded, or pressed. At present, aluminum is the second most widely used metal after iron. Aluminum castings can be cast by virtually all of the common casting processes. It is common to add the alloying constituents as solids to molten aluminum: Al–Cu, Al–Mg, Al–Zn, Al–Sn. The potential for the use of aluminum in automotive applications is considerable, including engine blocks, heads, pistons, rocker covers, inlet manifolds, differential casings, steering boxes, brackets, wheels, and so on. Castings may also be used for household and hospital utensils, and machinery.

4.1.4.4 Copper Castings

Copper is a soft metal that is resistant to corrosion and is a good conductor of heat and electricity. It is most commonly used for electrical wiring and hot water pipes. Copper is second only to aluminum in importance among the nonferrous metals. Products include bushings and bearings, propellers, and other cast products. Copper-base alloys are grouped according to composition: pure copper, high-copper alloys, brasses, leaded brasses, bronzes, aluminum bronzes, silicon bronzes, copper–nickel alloys, and copper–nickel–zinc alloys. In brasses, zinc is the principal alloying element. Tin is the principal alloying element in cast bronze alloys. Copper castings are produced by several methods, including centrifugal molds, green sand molds, and die casting.

4.2 CHARACTERIZATION OF WASTES

Three major solid wastes—spent foundry sand, furnace slag, and baghouse dust—are discharged from metal casting facilities. In the U.S., the annual generation of foundry solid waste is believed to range from 9 to 13.6 million metric tons (10 to 15 million tons).[6] Of them, spent foundry sand can account for nearly 70% of a foundry's total wastestream.[1] In addition to solid waste, wastewater and air emissions are also discharged from a metal casting facility. Reliable quantification of physical properties and chemical characterization of the byproduct is important for the marketability of the materials. This section focuses on the characterization of the solid wastes of the metal casting industry. Characterization of air emission and wastewater shall also be addressed according to some limited documental data. Mainly four aspects of characterization for a solid wastestream are included: origin, physical properties, chemical properties, and mechanical properties.

4.2.1 GENERAL

Prior to their acceptance for beneficial treatment or reuse, foundry wastes discharged from casting processes are characterized and must comply with environmental protection laws and regulations. Countries vary significantly in constituting environmental protection laws. In the U.S., numerous federal environmental laws (or acts) and regulations have been promulgated to protect human health and the environment. Table 4.3 lists most of the federal laws or regulations involved in managing wastes of the metal casting industry. These acts are the unique measures assessing the environmental impact and reuse acceptance of foundry solid waste. Thus, detailed physical and chemical characterization of foundry waste materials is necessary in order to obtain permits for reusing foundry byproducts.

TABLE 4.3
Federal Legislation Related to Solid Waste Management

Title	Year of Promulgation or Amendment
Solid Waste Disposal Act (SWDA)	1965
National Environmental Policy Act (NEPA)	1969
Occupational Safety and Health Act (OSHA)	1970
Clean Air Act (CAA)	1970, 1977, 1990
Clean Water Act (CWA)	1977, 1981, 1987
Safe Drinking Water Act (SDWA)	1974, 1977, 1986
Toxic Substances Control Act (TSCA)	1976
Resource Conservation and Recovery Act (RCRA)	1976, 1980
Comprehensive Environmental Response, Compensation and Liabilities Act (CERCLA or Superfund)	1980
Hazardous and Solid Waste Amendments (HSWA)	1984
Superfund Amendments	1986
Pollution Prevention Act (PPA)	1990

4.2.2 AIR EMISSION

4.2.2.1 Origin

Air emission, known as a gaseous waste, is the largest waste source from foundries.[2] Emission sources include the binder systems used in mold making, vapors from metal melting, and airborne sand used in the pouring and shakeout steps. Very limited quantified data are available about the characterization of air emissions. They are thought containing metals dust, semivolatile and volatile organic compounds. They mainly come from the melting procedures. Pouring and cooling steps contribute about 16% of the total organic and semivolatile wastes from foundries.[7]

4.2.2.2 Characterization

Air emission composition is closely related to its form of generation or collection. Cupola furnaces produce more metallic air emissions than other furnace types. Lower metal emissions are released from induction furnaces and core- and mold-making processes. Emissions from the pouring process depend on the metal temperature. The hotter the metals, the higher the metal emissions.[7] Organic air emissions arise largely from vaporized resins, solvents, and catalysts, which are used extensively in core- and mold-making steps. With the promulgation of the Clean Air Act and its amendments, as well as increasingly stringent regulations from U.S. EPA, more air emissions studies are being conducted.

The principal gases produced were found to be hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen, oxygen, and water vapor. Volatile hydrocarbons, including ethane, ethylene, propane, propylene, acetylene, FA, methanol, and ethanol, constitute up to 5% of the gas volume. Benzene, toluene, nitrous oxide, and hydrogen cyanide were identified in the atmosphere near a pouring line in a foundry using alkyd isocyanate resin bonded molds. Concentrations detected in the foundry atmosphere were generally low.

4.2.3 WASTEWATER

4.2.3.1 Origin

Wastewater discharge, known as liquid pollution in a facility, makes up a small portion of the total wastestream from foundries.[2] Wastewater mainly comes from the noncontact cooling water used to cool metal and other work pieces or from wet scrubber air emission systems. Water runoff from floor cleaning and other maintenance procedures may also contribute to wastewater. However, the volumes of liquid waste are relatively small and do not pose a large pollution problem for foundries. Some plants have water treatment facilities to remove contaminants for water reuse.

U.S. EPA promulgated wastewater discharge regulations for the foundry industry in October 1985, which are published in the Code of Federal Regulations at 40 CFR Part 464.[8] The regulations cover 28 process segments (processes such as casting quench, grinding scrubber, mold cooling) in four subcategories: aluminum casting, copper casting, ferrous casting, and zinc casting. It is noted that the cast metals have unique properties that influence the way they are melted and processed and, thus, affect the process wastewater characteristics.

4.2.3.2 Characterization

Table 4.4 presents wastewater flow characterization for the foundry industry by casting metals. Also presented in this table is the level of process water recycle, and the number of plants surveyed with central wastewater treatment facilities for all of the processes at that plant. The discharge flow represents all processes within the specific metal casting facilities.

Many toxic pollutants were detected in the process wastewaters from metal molding and casting processes. The toxic pollutants detected most frequently in concentrations at or above 0.1 mg/L were phenolic compounds and heavy metals. The pollutants include 2,4,6-trichlorophenol, 2,4-dimethylphenol, phenol, 2-ethylhexyl, cadmium, chromium, copper, lead, nickel, and zinc. Each type of operation in the foundry industry can produce different types of pollutants in the wastewater stream. Also, because each subcategory operation often involves different processes, pollutant concentrations per casting metals may vary.

4.2.4 SPENT FOUNDRY SAND

4.2.4.1 Origin

Foundries purchase new, virgin sand to make casting molds, and the sand is reused numerous times within the foundry. However, heat and mechanical abrasion eventually render the sand unsuitable for use in casting molds, and a portion of the sand is continuously removed and replaced with virgin sand. The removed sand becomes spent foundry sand, which is discarded from the foundry facility.

In the U.S., the foundry industry produces roughly seven to eight million tons of spent sand each year,[1] which are available to be recycled into nonfoundry applications. However, less than 15% of

TABLE 4.4
Wastewater Flow Characterization by Casting Metals

	Iron/Steel Casting	Aluminum Casting	Copper and Alloy Casting	Magnesium Casting	Zinc Casting
Applied flow (ML/yr)	397,000	14,500	34,900	8.18	4040
Recycle flow (ML/yr)	317,000	7530	25,300	0	3430
Direct discharge flow (ML/yr)	69,300	5700	9610	8.18	5050
Indirect discharge flow (ML/yr)	11,600	1260	48	0	100
100% recycle flow (ML/yr)	189,000	408	3340	0	1010
Central treatment facilities (no. of plants)	109	12	10	0	13
Operation treatment facilities (no. of plants)	205	20	14	3	12

Note: ML/yr, million liters per year.

the spent foundry sand is recycled. It is believed that a greater percentage of spent foundry sand can be safely and economically recycled, as has been encouraged by many successful case studies. Concentrating energies on the largest volume stream first will have the greatest economic impact for the industry as a whole.

Spent material often contains casting residues, such as degraded binders, metals, and oversized mold/core materials. Spent foundry sand may also contain some leachable contaminants, including heavy metals and phenols that are absorbed by the sand during the molding process and casting operations.[9] The detection of heavy metals is of greater concern in nonferrous foundry sands generated from nonferrous foundries.[10] Spent foundry sand from the brass or bronze foundries, in particular, may contain high concentrations of cadmium, lead, copper, nickel, and zinc.[11]

4.2.4.2 Physical Properties

Spent foundry sand can be divided, based upon bonding processes, into two categories—spent green sand and spent chemically bonded sand. Spent green sand is black in color due to its carbon content, and has clay contents that result in a fraction of the material passing a No. 200 sieve (0.075 mm). Chemically bonded sands are generally yellowish in color and coarser in texture than clay bonded sands.

Physical properties involve tests of the physical index parameters of the materials. For spent foundry sand, these parameters include particle gradation, unit weight, specific density, moisture content, adsorption, hydraulic conductivity, clay content, plastic limit, and plastic index. These parameters determine the suitability of spent foundry sand for uses in potential applications. Typical physical properties of spent green foundry sand are listed in Table 4.5.

The grain size distribution of spent foundry sand is very uniform, with approximately 85 to 95% of the material between 0.6 mm and 0.15 mm (No. 30 and No. 100) sieve sizes. Five to twelve percent of foundry sand can be expected to be smaller than 0.075 mm (No. 200 sieve). The particle shape is typically subangular to round. Spent foundry sand gradations are too fine to satisfy the fine aggregate standard specified in specification ASTM C33 Standard Specification for Concrete Aggregates.

Spent foundry sand has low absorption and is nonplastic. Reported values of absorption were found to vary widely (0 to 5%), which can also be attributed to the presence of binders and

TABLE 4.5
Typical Physical Properties of Spent Green Foundry Sand

Property	Results	Test Methods
Specific gravity	2.39–2.55	ASTM D854
Bulk relative density, kg/m^3 (lb/ft^3)	2590 (160)	ASTM C48/AASHTO T84
Absorption (%)	0.45	ASTM C128
Moisture content (%)	0.1–10.1	ASTM D2216
Clay lumps and friable particles	1–44	ASTM C142/AASHTO T112
Coefficient of permeability (cm/s)	10^{-3}–10^{-6}	AASHTO T215/ASTM D2434
Plastic limit/plastic index	Nonplastic	AASHTO T90/ASTM D4318

Source: From AFS, Alternative Utilization of Foundry Waste Sand, final report (Phase I) for Illinois Department of Commerce and Community Affairs, American Foundrymen's Society, Des Plaines, IL, July 1991. Javed, S. and Lovell, C.W., Use of Foundry Sand in Highway Construction, Joint Highway Research Project No. C-36-50N, Purdue University, West Lafayette, IN, July 1994. Javed, S., Lovell, C. W., and Wood, L.E., Waste Foundry Sand in Asphalt Concrete, in *Transportation Research Record*, No 1437, Transportation Research Board, Washington, DC, 1994.

additives.[11,12] The content of organic impurities (particularly from sea coal binder systems) can vary widely and can be quite high. This may preclude its use in applications where organic impurities could be important (e.g., portland cement concrete aggregate).[9] The specific gravity of foundry sand has been found to vary from 2.39 to 2.55. This variability has been attributed to the variability in fines and additive contents in different samples.[11] In general, foundry sands are dry, with moisture contents less than 2%. A large fraction of clay lumps and friable particles have been reported, which are attributed to the lumps associated with the molded sand, which are easily disintegrated in the test procedure.[11] The variation in permeability listed in Table 4.5 is a direct result of the fraction of fines in the samples collected.

4.2.4.3 Chemical Compositions

The chemical compositions of materials are usually expressed in terms of simple oxides calculated from elemental analysis determined by x-ray fluorescence. For spent foundry sand, the chemical parameters include bulk oxides mass composition, loss on ignition, and total oxygen demand. Table 4.6 lists the general chemical properties of spend foundry sand. It is shown that spent foundry sand consists primarily of silica dioxide.

Depending on the binder and type of metal cast, the pH of spent foundry sand[12] can vary from approximately 4 to 8. As such, it has been reported that some spent foundry sands can be corrosive to metals.[14] Spent foundry sand must be monitored to assess the need to establish controls for potential phenol discharges.[9,15,16]

4.2.4.4 Trace Element Characterization

Trace element characterization represents concentrations of elements that are contaminated in materials or their leachates in a trace level, generally reported in units of mg/kg or mg/L. Although in minimum quantities, trace elements need to be characterized to assess the hazardous impact of the

TABLE 4.6
Foundry Sand Sample Chemical Oxide Composition

Constituent	Value (%)
SiO_2	87.91
Al_2O_3	4.70
Fe_2O_3	0.94
CaO	0.14
MgO	0.30
SO_3	0.09
Na_2O	0.19
K_2O	0.25
TiO_2	0.15
P_2O_5	0.00
Mn_2O_3	0.02
SrO	0.03
Loss on ignition	5.15, on average
Total	99.87

Source: From AFS, Alternative Utilization of Foundry Waste Sand, final report (Phase I) for Illinois Department of Commerce and Community Affairs, American Foundrymen's Society, Des Plaines, IL, July 1991.

materials and their compliance with environmental protection laws. Total analyses and leaching analyses are generally used. The former quantifies as a dry-basis the mass percentage of trace elements by following U.S. EPA standard environmental analytical methods or approved analytical chemistry methods, relying upon techniques of inductively coupled plasma atomic emission mass spectrometry (ICP-AES, ICP-MS) and gas chromatography interfaced with a mass spectrometer (GC-MS). Leaching analysis is often run as a simulation of the field extraction effect, in which materials are extracted into aqueous media by leachate fluid, groundwater, rainfall, or other fluids. Currently, three leaching protocols are frequently documented to simulate field extraction variation: the Toxicity Characteristic Leaching Procedure (TCLP, U.S. EPA Method 1311), the Synthetic Precipitation Leaching Procedure (SPLP, U.S. EPA Method 1312), and the Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM D3987). TCLP and SPLP are acidic toxicity tests, whereas ASTM D3987 is a neutral leaching procedure.

Many studies have been conducted on metal contaminants in foundry sands. Spent foundry sand segregated from the other wastestreams leaches regulated metals well below the toxicity characteristic levels.[12] It is also found that spent foundry sands produced by iron, steel, and aluminum foundries are rarely hazardous, whereas spent foundry sand collected from copper-based facilities may render leachate with regulated elements exceeding regulation threshold values.[12,14] Only iron and manganese, which are not regulated under RCRA, were recorded at increased leaching potentials on a number of occasions. Lead, chromium, copper, and zinc are reported to be of concern for mixed foundry wastes. There is no direct correlation between the total metal content and the leachability under TCLP. Quantities of total metal content in spent and virgin sands and in sandy soils are typically of the same order of magnitude, which suggests an opportunity for spent foundry sand replacing conventional sand and natural soil in many applications, without posing environmental threats.

Few studies have been conducted to determine organic residues in spent foundry sand and leachates from disposal sites. It is reported that several organic compounds are present in the spent foundry sand but have concentrations below the regulated toxicity characteristic limits. Organic compounds of concern include benzoic acid, naphthalene, methylnaphthalenes, phenol, methylenebisphenol, diethylphenol, and 3-methylbutanoic acids.[12] These compounds are thought to be derived from the decomposition of organic binders such as phenolic urethane, furan, and alkyd isocyanate.

4.2.4.5 Mechanical Properties

Typical mechanical properties of spent foundry sand are listed in Table 4.7. Spent foundry sand has good durability characteristics as measured by low microdeval abrasion and magnesium sulfate

TABLE 4.7
Typical Mechanical Properties of Spent Foundry Sand

Property	Results	Test Method
Microdeval abrasion loss (%)	<2	—
Magnesium sulfate soundness loss (%)	5–47	ASTM C88
Friction angle (°)	33–40	—
California bearing ratio (%)	4–20	ASTM D1883

Source: From MNR, Mineral Aggregate Conservation, Reuse and Recycling, report for Ontario Ministry of Natural Resources, Ontario, Canada, February 1992. Javed, S. and Lovell, C.W., Use of Foundry Sand in Highway Construction, Joint Highway Research Project No. C-36-50N, Purdue University, West Lafayette, IN, July 1994.

soundness loss tests.[17] Recent studies have reported relatively high soundness loss, which is attributed to samples of bound sand loss and not a breakdown of individual sand particles.[11] The angle of shearing resistance (friction angle) of foundry sand has been reported to be in the range of 33 to 40°, which is comparable to that of conventional sands.[11]

4.2.5 BAGHOUSE DUST

4.2.5.1 Origin

Baghouse dusts are fine particles that are captured from the gas collection and cleaning system (baghouse) installed in a metal casting facility. Baghouses consist of several rows or compartments of fabric filters that collect the dust during the operation of a metal casting facility. Most of these systems are preceded by cyclones, which are primary collection devices used to capture the coarser particles emitted from the casting processes. Metal casting facilities that do not have baghouse collection systems are equipped with wet scrubbers to control air emissions.

The primary sources of airborne dust are the vibrating shakeout and the sand carryover, as well as the sand that remains attached to castings after shakeout. When a green sand mold is placed onto a conventional vibrating shakeout, a large amount of fine silica dust is released into the plant. The amount is directly related to the sand temperature at shakeout. The higher the sand temperature at shakeout, the more dust is carried into the atmosphere and captured by the baghouse. The second source of dust is sand still attached to castings after shakeout (in pockets, cavities, and corners); this may be released into the atmosphere in the shot blasting process.

4.2.5.2 Physical Properties

As baghouse dust accounts for a minimum of the total foundry solid waste, less attention is placed on characterizing this wastestream. Few data are available giving its physical properties and chemical composition. Visually, it is a very fine powder, dark gray in color. The dust may demonstrate physical properties that are similar to clay soils.

4.2.5.3 Chemical Composition

The main mineral components of baghouse dust are silica, clay, some resin evaporation residue, and metal fines. Its composition is related to the way it is collected. Shake-out dust mainly contains silica and clay. Metal fines may be present in the dust collected from areas used for cleaning, grinding, and melting processes.

4.2.6 FURNACE SLAG

4.2.6.1 Origin

In the melting process, metal scraps and fluxes (limestone or dolomite) are charged into a furnace, sometimes along with coke for fuel if a blast furnace is used. Upon heating using electricity (arc furnace) or burning (blast furnace), scraps are melted into a molten phase. The metal is subsequently gravimetrically separated from the composite flux, leaving the residual slag. Flux is used to adequately render the slag fluid so that it can be separated from the molten iron, and it then flows freely from the cupola.

Furnace slag is a nonmetallic byproduct produced in the melting process. It consists primarily of silicates, alumina silicates, and calcium–alumina–silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises ~20% by mass of iron production. As a byproduct of the melting process, furnace slags vary considerably in form depending on the melted metals used, furnace types, and slag cooling method. Figure 4.7 demonstrates the major types of furnace slags.

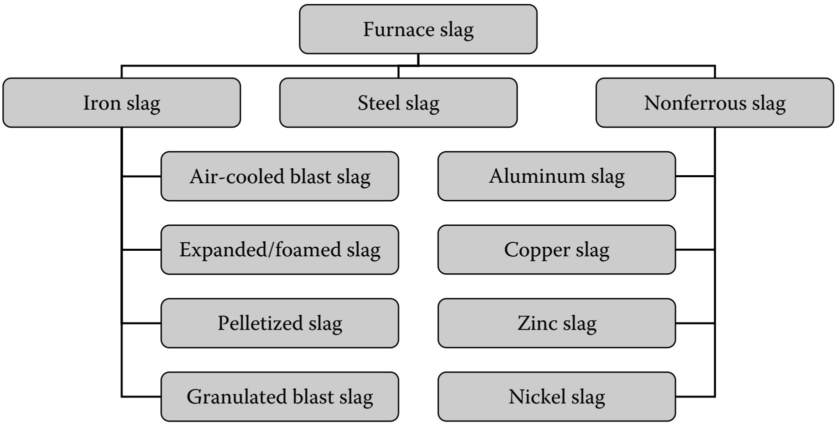

FIGURE 4.7 Furnace slag types.

For iron slag, subcategories include air-cooled blast furnace slag, expanded or foamed slag, pelletized slag, and granulated blast furnace slag. The generation of each slag is described below:

1. *Air-cooled blast furnace slag.* If the liquid slag is poured into beds and slowly cooled under ambient conditions, a crystalline structure is formed, and a hard, lump slag is generated, which can subsequently be crushed and screened.
2. *Expanded or foamed blast furnace slag.* If the molten slag is cooled and solidified by adding a controlled volume of water, air, or steam, the process of cooling and solidification can be accelerated, increasing the cellular nature of the slag and generating a lightweight expanded or foamed product. Foamed slag is distinguishable from air-cooled blast furnace slag by its relatively high porosity and low bulk density.
3. *Pelletized blast furnace slag.* If the molten slag is cooled and solidified with water and air quenched in a spinning drum, pellets, rather than a solid mass, can be produced. By controlling the process, the pellets can be made more crystalline, which is beneficial for aggregate use, or more vitrified (glassy), which is more desirable in cementitious applications. More rapid quenching results in greater vitrification and less crystallization.
4. *Granulated blast furnace slag.* If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs. This process results in the formation of sand-sized (or frit-like) fragments, usually with some friable clinker-like material. The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. When crushed or milled to very fine cement-sized particles, ground granulated blast furnace slag has cementitious properties, which makes it a suitable partial replacement for or additive to portland cement.

Steel slag, a byproduct of steel making, is a complex solution of silicates and oxides that solidifies upon cooling. The main components are consist of carbon, silicon, manganese, phosphorus, some iron as liquid oxides, lime, and dolime. There are several different types of steel slag produced during the steel-making process. These different types are referred to as furnace or tap slag, synthetic or ladle slags, and pit or cleanout slag.

Nonferrous slag is mostly formed by dumping it into a pit and simply allowing it to air cool, solidifying under ambient conditions. A small proportion is granulated, and by using rapid water and air quenching results in the production of a vitrified product. Similar to the generation of iron slag, the cooling rate has a strong influence on the mineralogy and, consequently, the physical and cementitious properties of the nonferrous slag. Slag generation is highly dependent on specific processes and sources. Consequently, slag properties can vary between plants and different ore sources, and must be investigated on a case-by-case basis.

4.2.6.2 Physical Properties

There can be considerable variability in the physical properties of blast furnace slag, depending on the slag generation method. Table 4.8 lists some typical physical properties of air-cooled, expanded, and pelletized blast furnace iron slags. Crushed air-cooled blast furnace slag is angular, roughly cubical, and has textures ranging from rough, vesicular (porous) surfaces to glassy (smooth) surfaces with fractures. Some air-cooled blast furnace slag has been reported to have a compacted unit weight as high as 1940kg/m^3 (120lb/ft^3). The water absorption of air-cooled blast furnace slag can be as high as 6%.

Crushed expanded slag is angular, roughly cubical in shape, and has a texture that is rougher than that of air-cooled slag. Its porosity is higher than that of air-cooled blast furnace slag aggregates. The bulk relative density of expanded slag is difficult to determine accurately, but it is ~70% that of air-cooled slag. Typical compacted unit weights for expanded blast furnace slag aggregates range from 800 kg/m^3 (50 lb/ft^3) to 1040 kg/m^3 (65 lb/ft^3).[19]

Unlike air-cooled and expanded blast furnace slag, pelletized blast furnace slag has a smooth texture and rounded shape. Consequently, its porosity and water absorption are much lower than those of air-cooled blast furnace slag or expanded blast furnace slag. Pellet sizes range from 13 mm (1/2 in.) to 0.1 mm (No. 140 sieve size), with the bulk of the product in the 9.5 mm (3/8 in.) to +1.0 mm (No. 18 sieve size) range. Pelletized blast furnace slag has a unit weight of about 840 kg/m^3 (52 lb/ft^3).[20]

Granulated blast furnace slag is a glassy granular material that varies, depending upon its chemical composition and mode of generation, from a coarse, popcorn-like friable structure greater than 4.75 mm (No. 4 sieve) in diameter to dense, sand-sized grains passing a 4.75 mm (No. 4) sieve. Grinding reduces the particle size to cement fineness, allowing its use as a supplementary cementitious material in portland cement concrete.

Steel slag aggregates are highly angular in shape and have a rough surface texture. They have high bulk specific gravity and moderate water absorption (<3%). Table 4.9 lists some typical physical properties of steel slag.

Table 4.10 lists some typical physical properties for nonferrous slags. Because they have similar properties, lead, lead–zinc, and zinc slags are grouped together.

TABLE 4.8
Typical Physical Properties of Blast Furnace Slag

	Slag Types		
Property	**Air-Cooled**	**Expanded**	**Pelletized**
Specific gravity	2.0–2.5	—	—
Compacted unit weight (kg/m^3) (lb/ft^3)	1120–1360 (70–85)	(800–1040) (50–65)	840 (52)
Absorption (%)	1–6	—	—

Source: From AASHTO, AASHTO Designation M240: Blended hydraulic cements, in *Standard Specification for Materials*, American Association of State Highway and Transportation Officials, 1986.

TABLE 4.9
Typical Physical Properties of Steel Slag

Property	Value
Specific gravity	3.2–3.6
Unit weight (kg/m^3) (lb/ft^3)	1600–1920 (100–120)
Absorption (%)	Up to 3

Air-cooled copper slag has a black color and glassy appearance. As a general rule, its specific gravity will vary with iron content, from a low of 2.8 to as high as 3.8.[21] The unit weight of copper slag is somewhat higher than that of conventional aggregate. The absorption of the material is typically very low (0.13%).[22]

Granulated copper slag is more porous and therefore has lower specific gravity and higher absorption than air-cooled copper slag. The granulated copper slag is made up of regularly shaped, angular particles, mostly between 4.75 mm (3/4 in.) and 0.075 mm (No. 200 sieve) in size.

Granulated nickel slag is essentially an angular, black, glassy slag, with most particles in the size range of −2 mm (No. 10 sieve) to +0.15 mm (No. 100 sieve).[21] It is more porous, with lower specific gravity and higher absorption than air-cooled nickel slag.

Slags from lead, lead–zinc, and zinc groups are often black to red in color and glassy. They have sharp, angular particles that are cubical in shape. The unit weights of lead, lead–zinc, and zinc slags are somewhat higher than conventional aggregate materials. Granulated lead, lead–zinc, and zinc slags tend to be porous, with up to 5% absorption.[23] The specific gravity can vary from less than 2.5 to as high as 3.6.[21,23] These slags are made up of regularly shaped, angular particles, mostly between 4.75 mm (3/4 in.) and 0.075 mm (No. 200 sieve) in size.

4.2.6.3 Chemical Compositions

Table 4.11 depicts the typical chemical composition of blast furnace iron slag. It is suggested that the chemical composition of blast furnace slags produced in North America has remained relatively consistent over the years.

TABLE 4.10
Typical Physical Properties of Nonferrous Slags

Property	Copper Slag	Nickel Slag	Lead, Lead–Zinc, and Zinc Slags
Appearance	Black, glassy, more vesicular when granulated	Reddish brown to brown-black, massive, angular, amorphous texture	Black to red, glassy, sharp angular (cubical) particles
Unit weight (kg/m^3)	2800–3800	3500	2500 or 3600
Absorption (%)	0.13	0.37	5.0

Source: From MNR, Mineral Aggregate Conservation, Reuse and Recycling, report for Ontario Ministry of Natural Resources, Ontario, Canada, February 1992. JEGEL, Manitoba Slags, Deposits, Characterization, Modifications, Potential Utilization, report, John Emery Geotechnical Engineering Limited, Toronto, Ontario, 1986. Hughes, M.L. and Haliburton, T.A., Use of zinc smelter waste as highway construction material, *Highway Research Record*, 430, 16–25, 1973. Mantell, C.L., *Solid Wastes*: *Origin, Collection, Processing and Disposal*, John Wiley & Sons, New York, 1975. With permission.

TABLE 4.11
Typical Composition of Blast Furnace Slag

	Percent							
	1949[a]		1957[a]		1968[a]		1985[a]	
Constituent	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**
CaO	41	34–48	41	31–47	39	32–44	39	34–43
SiO_2	36	31–45	36	31–44	36	32–40	36	27–38
Al_2O_3	13	10–17	13	8–18	12	8–20	10	7–12
MgO	7	1–15	7	2–16	11	2–19	12	7–15
FeO or Fe_2O_3	0.5	0.1–1.0	0.5	0.2–0.9	0.4	0.2–0.9	0.5	0.2–1.6
MnO	0.8	0.1–1.4	0.8	0.2–2.3	0.5	0.2–2.0	0.44	0.15–0.76
Sulfur	1.5	0.9–2.3	1.6	0.7–2.3	1.4	0.6–2.3	1.4	1.0–1.9

Source: From MNR, Mineral Aggregate Conservation, Reuse and Recycling, report for Ontario Ministry of Natural Resources, Ontario, Canada, February 1992.

[a] Data source is National Slag Association data: 1949 (22 sources); 1957 (29 sources); 1968 (30 sources), and 1985 (18 sources).

When ground to the proper fineness, the chemical composition and glassy (noncrystalline) nature of vitrified slags are such that when combined with water, these vitrified slags react to form cementitious hydration products. The magnitude of these cementitious reactions depends on the chemical composition, glass content, and fineness of the slag. The chemical reaction between ground granulated blast furnace slag and water is slow, but it is greatly enhanced by the presence of calcium hydroxide, alkalis, and gypsum ($CaSO_4$).

Because of these cementitious properties, ground granulated blast furnace slag can be used as a supplementary cementitious material either by premixing the slag with portland cement or hydrated lime to produce a blended cement (during the cement production process), or by adding the slag to portland cement concrete as a mineral admixture.

Blast furnace slag is mildly alkaline and exhibits a pH range of 8 to 10 in solution. Although blast furnace slag contains a small component of elemental sulfur (1 to 2%), the leachate tends to be slightly alkaline and does not present a corrosion risk to steel in pilings,[24] or to steel embedded in concrete made with blast furnace slag cement or aggregates.[25]

Table 4.12 lists the range of compounds present in steel slag from a typical base oxygen furnace. The predominant compounds are dicalcium silicate, tricalcium silicate, dicalcium ferrite, merwinite, calcium aluminate, calcium–magnesium iron oxide, and some free lime and free magnesia. The relative proportions of these compounds depend on the steel-making practice and the steel slag cooling rate. If the cooling rate of the steel slag is sufficiently low, crystalline compounds are generally formed. As a result, not all steel slags are suitable as aggregates.

Steel slag may expand when in contact with moisture. Free calcium and magnesium oxides are generally not completely consumed in the steel slag, and there is general agreement in the technical literature that the hydration of lime and magnesia is largely responsible for the expansive nature of most steel slags.[6,27] The free lime hydrates rapidly and can cause large volume changes over a relatively short period of time (weeks), whereas magnesia hydrates much more slowly and contributes to long-term expansion that may take years to develop.

Steel slag is mildly alkaline, with a solution pH value of 8 to 10. However, the pH of leachate from steel slag can exceed 11, a level that can be corrosive to aluminum or galvanized steel pipes placed in direct contact with the slag.

The chemical properties of copper, lead, lead–zinc, and zinc slags are essentially as ferrous silicates, whereas nickel slags are primarily calcium/magnesium silicates. Table 4.13 lists typical chemical compositions of these slags.

TABLE 4.12
Typical Steel Slag Chemical Composition

Constituent	Composition (%)
CaO	40–52
SiO_2	10–19
FeO	10–40 (70–80% FeO, 20–30% Fe_2O_3)
MnO	5–8
MgO	5–10
Al_2O_3	1–3
P_2O_5	0.5–1
S	<0.1
Metallic Fe	0.5–10

Source: From Emery, J.J., Slag Utilization in Pavement Construction, *Extending Aggregate Resources*, ASTM Special Technical Publication 774, American Society for Testing and Materials, 1982, pp. 95–118. With permission.

During slag production, the sudden cooling that results in the vitrification of nonferrous slags (typically in the granulating process) prevents the molecules from being locked up in crystals. In the presence of an activator (such as calcium hydroxide from hydrating portland cement), vitrified nonferrous slags react with water to form stable, cementitious, hydrated calcium silicates. The reactivity depends on the fineness to which the slag is ground (reactivity increases with fineness)[30] and the chemical composition of the slag and its glass content. These vitrified slags can be of such

TABLE 4.13
Typical Chemical Compositions of Nonferrous Slag

Element	Copper Slag (%)	Nickel Slag (%)	Lead Slag (%)	Lead–Zinc Slag (%)
SiO_2	36.6	29.0	35.0	17.6
Al_2O_3	8.1	Trace	—	6.1
Fe_2O_3	—	53.06	—	—
CaO	2.0	3.96	22.2	19.5
MgO	—	1.56	—	1.3
FeO	35.3	—	28.7	—
K_2O	—	—	—	—
F	—	—	—	—
MnO	—	Trace	—	2.0
P_2O_5	—	—	—	—
Cu	0.37	—	—	—
BaO	—	—	—	2.0
SO_3	—	0.36	—	—
Free CaO	—	—	—	—
S	0.7	—	1.1	2.8
PbO	—	—	—	0.8

Source: From OECD, *Use of Waste Materials and Byproducts in Road Construction*, Organization for Economic Co-operation and Development, Paris, 1977.

composition that when ground to proper fineness, they may also react directly with water to form hydration products that provide the slag with cementitious properties.

There is some evidence that nickel slag can be involved in the corrosion of iron and steel in the presence of moisture (probably galvanic corrosion). In Canada, where nickel slag is used in fill applications, it is common practice to provide a layer [typically 150 mm (6 in.) thick] of natural aggregate between ferrous materials and the slag.[21]

4.2.6.4 Mechanical Properties

Of all the slag types generated, air-cooled blast furnace is the type that is most commonly used as an aggregate material. Processed air-cooled blast furnace slag exhibits favorable mechanical properties for aggregate use, including good abrasion resistance, good soundness characteristics, and high bearing strength. Table 4.14 lists typical mechanical properties of air-cooled blast furnace slag aggregates.

Table 4.15 lists some typical mechanical properties of steel slag. Processed steel slag has favorable mechanical properties for aggregate use, including good abrasion resistance, good soundness characteristics, and high bearing strength.

TABLE 4.14
Typical Mechanical Properties of Air-Cooled Blast Furnace Slag

Property	Value
Los Angeles abrasion (%)	35–45
Sodium sulfate soundness loss (%)	12
Angle of internal friction (°)	40–45
Hardness[a]	5–6
California bearing ratio (CBR) (%), top size 19 mm (3/4 in.)[b]	Up to 250

Source: From Noureldin, A.S. and McDaniel, R.S., Evaluation of Steel Slag Asphalt Surface Mixtures, presented at the 69th annual meeting, Transportation Research Board, Washington, January 1990.

[a] Hardness of dolomite measured on same scale is 3 to 4.

[b] Typical CBR value for crushed limestone is 100%.

TABLE 4.15
Typical Mechanical Properties of Steel Slag

Property	Value
Los Angeles abrasion (%)	20–25
Sodium sulfate soundness loss (%)	<12
Angle of internal friction (°)	40–50
Hardness[a]	6–7
California bearing ratio (CBR), (%), top size 19 mm (3/4 in.)[b]	Up to 300

Source: From Noureldin, A.S. and McDaniel, R.S., Evaluation of Steel Slag Asphalt Surface Mixtures, presented at the 69th annual meeting, Transportation Research Board, Washington, January 1990.

[a] Hardness of dolomite measured on same scale is 3 to 4.

[b] Typical CBR value for crushed limestone is 100%.

TABLE 4.16
Typical Mechanical Properties of Nonferrous Slags

Test	Nickel Slag	Copper Slag	Lead, Lead–Zinc, and Zinc Slags
Los Angeles abrasion loss (%)	22.1	24.1	No data
Sodium sulfate soundness loss (%)	0.40	0.90	No data
Angle of internal friction (°)	~40	40–53	No data
Hardness	6–7	6–7	No data

Source: From Hughes, M.L. and Haliburton, T.A., Use of zinc smelter waste as highway construction material, Highway Research Record, 430, 16–25, 1973. Das, B.M., Tarquin A.J., and Jones, A.Q., Geotechnical properties of copper slag, *Transportation Research Record*, 941, National Research Board, Washington, DC, 1993.

Table 4.16 presents typical mechanical properties for nonferrous slags. Processed air-cooled and granulated copper and nickel slags have a number of favorable mechanical properties for aggregate use, including excellent soundness characteristics, good abrasion resistance, and good stability (high friction angle due to sharp, angular shape). However, nonferrous slags tend to be vitreous, or glassy, which adversely affects their frictional properties (skid resistance), a potential problem if used in pavement surfaces.

4.2.6.5 Thermal Properties

Thermal property is another critical property for furnace slag. Because of their more porous structure, blast furnace slag aggregates have lower thermal conductivities than conventional aggregates. Their insulating value is of particular advantage in applications such as frost tapers (transition treatments in pavement subgrades between frost-susceptible and nonfrost-susceptible soils) or pavement base courses over frost-susceptible soils.

Owing to their high heat capacity, steel slag aggregates have been observed to retain heat considerably longer than conventional natural aggregates. The heat retention characteristics of steel slag aggregates can be advantageous in hot mix asphalt repair work in cold weather.

4.3 SOURCE REDUCTION

The Pollution Prevention Act (PPA, 1990) set a priority for reducing the amount of manufacturing waste through "source reduction"—preventing the generation of waste on the factory floor. The second-best option is to recycle wastes for other uses. The next option in the priority list is to recover the energy content of any wastes that are generated. The last resort is to treat the wastestream. This solid waste management hierarchy also applies to foundry solid waste. In this section, following waste characterization and preceding waste reuse, source reduction regarding solid waste generation and pollution emission is addressed. Effective measures include chemical substitution, in-plant reclamation, waste segregation, and process modifications to reduce emission.

4.3.1 CHEMICAL SUBSTITUTION OR MINIMIZATION

Regulated chemicals are of particular concern to foundrymen, waste recyclers, and decision-makers. An increasingly applied measure is to substitute or at least minimize the use of these chemicals in the plant, and basically eliminate the source of the environmental threat. For instance, all resin manufacturers are reducing the free-phenol content of their products to mitigate the discharge of phenol. Water-based refractory coatings are replacing solvent-based products, leading to casting improvements, such as a reduction in the number of scrap pieces and improved cycle times, and most importantly, a lighter environmental impact.[32]

Targeted chemicals can also be heavy metals. Nonleaded brass castings (also described as very-low-lead alloys, because no lead is intentionally added to them) are an important new approach to reducing lead in drinking water. A variety of other approaches to meeting lead release requirements have been tried or are currently being used, including the use of organic and inorganic coatings, the chemical removal of interior surface lead, and the reduction of internal surface areas of devices by implementing design changes. Most of the lead-free alloys contain bismuth as the major alloying element. Bismuth replaces lead in copper alloys and contributes to the machinability and pressure tightness of the alloys. Bismuth, like lead, is almost completely insoluble in copper and has a low melting point. It is not known to be toxic to humans and is used as a chemical compound in a popular remedy for upset stomachs.

Chemical substitution or minimization may bring great benefits through a managed scrap charge process. Metal scraps are carefully charged, screening out heavy metal-rich scraps and avoiding a mixed metal scrap charge. Scraps containing toxic polymer materials shall be treated before being charged.

4.3.2 IN-PLANT RECLAMATION

In-plant reclamation refers to the sand reclamation process in a foundry facility, which directly minimizes the generation of spent foundry sand. Sand reclamation includes physical, chemical, or thermal treatment of foundry sands so they may be safely substituted for new sand in molding and core-making mixes.

Mechanical attrition is used to remove most of the spent binder. First, dry attrition or abrasion processes crush lumps to grain size. Mechanical abrasion is then used to separate the binder from the sand grains. Sometimes, sand is pneumatically propelled against a metal target plate. The impact of the sand on the plate scrubs off the clay and resin coating from the sand grains. Fines are separated and removed by dry classification.

Depending on the binder system used, 60 to 80% of the mechanically reclaimed sand can be reconditioned satisfactorily for molding, with the addition of clean sand. The remaining 20 to 40% of the mechanically treated sand may then be thermally treated to remove the residual organic binder, restoring the sand to a clean condition. Mechanical attrition has the lowest cost. It allows lump breaking, removes and segregate metal scraps, mechanically scrubs as much binder as possible while avoiding breakage of grains, and removes dust, fines and binder residue by air classification.

In some cases, particularly for resin bonded sand, thermal treatment is used to burn the resin binder and carbonaceous residues. Thermal treatments are usually gas heated, but electric or oil heating can also be used. Sand is heated to approximately 500 to 800°C (930 to 1475°F), at which temperature sand bonded with an entirely organic binder system can be reclaimed up to 100%. The sand is then cooled and crushed to grain size by mechanical scrubbing. Binder systems containing inorganic chemicals, for example, silicate-based systems, cement systems, and phosphoric acid systems, are difficult to reclaim at high percentages because no burnout of the inorganic material occurs. Thermal reclamation is costly because of the large amount of heat and relatively expensive equipment needed. The ensured reclamation quality (sand thermal stabilization and clean up) and the need to remove resin residue, however, has led to its increasing use.

Wet reclamation, although being phased out in the U.S., has been used for silicate bonded sand. After the sand is crushed to grain size, water scrubbing using mechanical agitation is used to wash off the silicate residues, then dried. This process requires a large amount of water and also the treatment and clarification of the water before its recirculation and disposal. In addition, the capital cost of the equipment is high and it requires a large amount of floor space.

Whatever method of reclamation is used, there is always some loss of sand so that 100% reclamation can never be achieved. Sand losses include burn-on, spillage, and inefficiency in the sand system and the need to remove fines. Total sand losses of up to 10% may be expected.

4.3.3 WASTE SEGREGATION

Waste segregation helps separate hazardous materials from nonhazardous materials, divide recyclable materials from nonrecyclable materials, make materials largely "pure" and then consistent in physical and chemical property, and leads to managed waste disposal. There are up to 40 wastestreams covering spent sand, slag, and dust, inclusive of spent molding sand, core sand waste, cupola slag, scrubber sludge, baghouse dusts, shotblast fines, buffing wastes, and others.[32] In a facility, workers tend to group several wastestreams and discard them as a composite.[12] As a result, complex properties with wide variation are identified, either rendering an assessment that the materials are hazardous, although only a minimum stream deserves the classification, or impeding the recycling program by worsening the materials' consistency.

Besides the segregation of generated wastestreams, in-plant reclamation also considers material division. In typical foundry processes, sand from collapsed molds or cores are subjected to reclamation. However, it is well known that reclamation of sand is easiest when only one type of chemical binder is used. If more than one binder is used, care must be taken to ensure that the binder systems are compatible. Shaken-out green sand and chemical bonded sand are better separated from each other to ensure their rebonding and casting quality. Waste segregation, such as separating fresh casting mixtures and core sand that have not been in contact with hot metal from the other wastestreams, also mitigates the organic compounds identified in the wastestreams.

4.3.4 PROCESS MODIFICATIONS TO REDUCE EMISSION

Toxins, such as benzene, naphthalene, phenol, toluene, xylene, formaldehyde, and mercury, are found in resins and scraps and released as a result of evaporation and solvent processes and during combustion. Respiration of these emissions affects the brain and central nervous system, causes irritation to the skin, eyes, nose, and throat, breathing difficulties, lung problems, impaired memory, stomach discomfort, liver, and kidney changes. Clean-air regulations as well as workplace safety and health standards, however, have forced operators to address the issue. To meet the challenge of providing environmentally friendly core binders and melting processes, a number of suppliers have introduced technologies that are a promising step towards a new generation of binders that both reduce the amount of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) released and yet do not compromise casting quality.

There is a large amount of development work going on worldwide to improve the performance of core binders and to make them more environmentally friendly. The inorganic binder system is a green and relatively environmentally safe bonding process. For example, for silicate-based processes, there is very little in the way of fumes or smells during core manufacture, storage, or casting. A recently improved resin/CO_2 process involves a water-based alkaline phenolic resin. Both the binder and sand are gas-cured with CO_2 to activate the coupling agent, with low emission. Protein-based foundry sand binders are an entirely new class of sand core binders. They are made from high strength collagens with an additive to promote rapid thermal breakdown of the binder coating. This binder essentially has zero odor, contains no hazardous chemicals, and offers excellent sand reclamation. More improvements come from renewed sodium silicate, modifications of the PUCB and alkaline phenolic resins, and the introduction of new binders. The ultimate industry goal is to develop bonding systems that provide an equally good casting surface, improve the shakeout behavior, and eliminate the use of noxious gaseous catalysts and scrubbers.

The dry ice blaster is an effective and mess-free method for in-place cleaning that eliminates the need to disassemble machinery before it is cleaned. Compressed air propels tiny dry ice pellets at supersonic speeds so they flash freeze and then lift grime, paint, rust, mold, and other contaminants from metal surfaces. Pellets vaporize quickly into the air, leaving no wastewater or solvents, only the soiled contaminant to be swept up.

Special baghouse filters are designed for high-efficiency filtration with a unique three-layer construction. The dust filtration is effective for a wide range of particle sizes. The layered design includes a polypropylene prefilter layer, a melt-blown polypropylene microfiber final filter layer, and a polypropylene outer migration barrier layer, resulting in a cost-effective filter bag.

The volume of sand carried over and adhering to the castings is the biggest factor relating to shot blast costs. By stopping the sand from going into the casting cleaning department, and keeping it in the sand system where it belongs, the benefits go right to the bottom line. In addition to saving on all the shot blasting costs, other savings include less wear on the dust collectors, reduced wastestreams, no airborne silica dust, and reduced cleanup time.

4.4 SOLID WASTES REUSE TECHNOLOGIES

As the volume of solid wastes generated out of the metal casting industry and the cost of waste disposal continue to increase, there is increased pressure and incentive to divert valuable materials from the wastestreams, recover and recycle these materials for use in secondary applications, which in turn reduces the burden on landfills and minimizes the need for virgin materials. Many examples show that it is not only better for the environment but is profitable for the metal casting industry to deliver or even sell waste materials, for instance, spent foundry sand, to an alternative user. These foundries have significantly reduced the volume of byproduct materials going to landfill and actually offset the total cost of transporting the byproduct “in” and “out.” This section summarizes reuse technologies of solid wastes from the metal casting industry.

4.4.1 General

The beneficial reuse of foundry solid waste has long been carried out informally, particularly in the U.S. Foundry solid waste has always been used as fills around the foundry or nearby neighborhood. With the promulgation of strict environmental protection laws, foundry solid waste is now required to be landfilled. Later, spent foundry sand was selected as a daily cover for landfills that are “cover short.” However, many recyclers believe that foundry solid waste should not necessarily be disposed of in landfills where other hazardous industrial waste belongs, simply because the main fraction of foundry solid waste is nonhazardous and has value in fully or partially substituting for currently in-use materials, for example, construction aggregates, soils, and minerals. Thus, reuse of foundry solid waste is marketable.

All reuse options of foundry solid waste are largely categorized into two domains: uses in civil engineering and uses in agricultural applications. In the civil engineering domain, the solid wastes can be used as aggregate materials in asphalt concrete, portlant cement concrete, flowable fill, and highway embankment fills, as raw feed for portland cement production, and as barrier materials in hydraulic cutoff wall or permeable reactive wall. In the agricultural domain, spent foundry sand has alternative uses, such as in manufactured soil and agricultural amendments. In addition to reuse technologies, requisite qualification inspections of waste materials, mainly technical evaluation, environmental concerns, and economic consideration, should be addressed.

4.4.2 Reuse Evaluation Framework

Any proposal to incorporate an unconventional material, and particularly a waste or byproduct material, into a functional product, requires the rendered product to provide reliable, safe, and cost-effective service during its useful life. Such requirements necessitate qualification evaluations to be performed on wastes before their acceptance as alternative materials. At least three evaluation aspects shall be included in an evaluation framework, that is, technical implementability, environmental safety, and economic benefits.

4.4.2.1 Technical Implementability

As they are unconventional materials, foundry solid waste lacks documented procedures qualifying its substitution for conventional materials, which is a primary barrier in the reuse program. Necessary procedures therefore include evaluation tests, assessment procedures, and criteria to address the technical performance and characteristics that a functional material shall present. A procedural framework needs to be outlined with which one can decide if a waste or byproduct material can be used fully or partially in replacing a conventional material.

There are seven major steps, as shown in Figure 4.8, in an unconventional material technical evaluation process that should be considered:

1. *Address key issues*. Identify all relevant engineering, environmental, occupational health and safety, recyclability, and economic issues that will arise when assessing the use of unconventional materials in functional products. Efforts should be concentrated on compiling and assessing existing data, which include previous laboratory testing, field demonstrations, and the performance history from previous projects that have made use of the proposed material in the proposed application. Incorporating existing data into this process can be of great assistance in the task of defining all relevant technical issues and avoiding any unnecessary duplication of prior efforts.
2. *Establish tests and criteria*. Establish laboratory testing and assessment procedures and criteria that the material and the product should meet prior to accepting solid waste incorporation. Although at the present time, there is an absence of generally accepted test methods and criteria to address all of the proposed key issues, solid waste has generally undergone significant laboratory and field demonstration testing, by referring to suitable specifications, to ensure an equivalent or better performance criteria defined so that the material and application is met. In some cases, such as blast furnace slag, formal specifications have eventually been developed.
3. *Performance tests*. This step is to implement testing and assessment procedures, at a bench-scale, to determine whether the material will meet the criteria established.
4. *Modify material or product*. If a material is not capable of meeting established material or product criteria, it is useful to consider whether additional or alternative material processing or product modification could achieve the desired results.
5. *Implementation factors*. There are always some nontechnical issues that could prevent widespread implementation of the unconventional materials. These nontechnical issues involve institutional acceptability, political acceptability, and public acceptability.

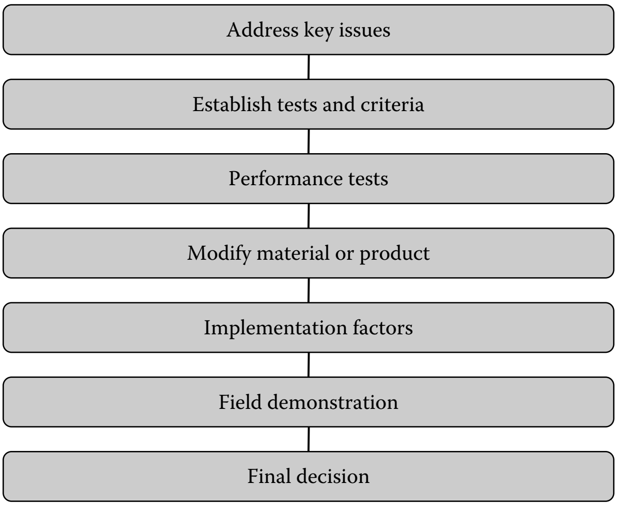

FIGURE 4.8 Technical evaluation of foundry solid waste reuse program.

6. *Field demonstration.* A field demonstration is always necessary to supplement a bench-scale evaluation, as some technical issues cannot be undertaken in a laboratory environment. In addition, field data help address nontechnical issues. Proper planning is critical for the implementation of a successful demonstration to ensure that all monitoring equipment, construction, and quality control procedures are in place.
7. *Final decision.* The ability to arrive at a final decision regarding the acceptability of a material for use will depend on the degree to which each of the aforementioned steps were planned and implemented. The establishment of a stepwise framework with specific objectives, procedures, and criteria is critical to implementing an evaluation approach that will address all necessary issues.

4.4.2.2 Environmental Issues

In the U.S., three pieces of federal legislation that were passed from 1969 to 1980, and the implementing rules and regulations that followed, initiated a series of fundamental changes in the management of waste and byproduct materials. They presently affect the way in which regulatory agencies address waste and byproduct material use. These acts include the National Environmental Policy Act (NEPA, 1969), the Resource Conservation and Recovery Act (RCRA, 1976, 1980), and the Comprehensive Environmental Response, Compensation, and Liabilities Act (CERCLA) or Superfund (1980).

NEPA was the major environmental legislation representing the nation's commitment to protect and maintain environmental quality. This act introduced the requirement that environmental impact statements be prepared on all federal actions.

RCRA was passed to manage nonhazardous and hazardous wastes and underground storage tanks, with an emphasis placed on the recovery of reusable materials as an alternative to their disposal. This act introduced the concept of the separate management of hazardous and nonhazardous wastes, and defined procedures to identify whether a waste is hazardous or nonhazardous. A waste exhibits the characteristic of toxicity, classified as a hazardous material, if the concentration of any of 39 selected analytes in the Toxicity Characteristic Leaching Procedure (TCLP) extract exceed regulatory action levels.

CERCLA was promulgated to address the release or imminent release of hazardous substances into the environment and established the mechanisms for responding to those releases and assessing liability. Regulations and procedures that evolved from CERCLA introduced the concept of human health risk assessments. CERCLA also provided the legal framework for assigning liability and assessing monetary damages for environmental impairment.

Although none of the three laws or their implementing regulations directly addressed the reuse of waste materials, they necessitate a series of evaluations in the reuse program of solid waste, which include the preparation of an environmental assessment, a human health risk assessment, or an ecosystem risk assessment.

4.4.3 REUSE IN CIVIL ENGINEERING

One of the largest opportunities to recycle foundry solid waste lies in the construction industry. Eight of the most researched civil applications are described in this section, where vast foundry solid waste was and is being consumed. These applications or products include asphalt concrete, portland cement concrete, granular base, embankment or fill, stabilized base, cement, flowable fill, and landfill liner and cover. A waste material (such as spent foundry sand, dust, or slag) may partially or fully suit these applications, depending their generation form and characteristics. A general overview of each application or product is provided, which includes a description of the application or product (components, material properties, test standards), and documented research work and case studies on reusing foundry solid wastes.

4.4.3.1 Asphalt Concrete

Description

Asphalt concrete is primarily used as a structural pavement surface constructed over a subgrade and a subbase. It is designed to support the traffic load and distribute the load over the roadbed. Asphalt concrete pavements can be constructed using hot mix or cold mix asphalt. Hot mix asphalt is a mixture of fine and coarse aggregate with asphalt cement binder that is mixed, placed, and compacted in a heated condition. Cold mix asphalt is a mixture of emulsified asphalt and aggregate, produced, placed, and compacted at ambient air temperature. Cold mix asphalt pavement usually requires an overlay of hot mix asphalt or surface treatment to resist traffic action.

Aggregates used in asphalt concrete mixtures comprise ~95% of the mix by mass and ~80% by volume. Thus, the aggregate material(s) used in asphalt concrete have a profound influence on the properties and performance of the mixture. Proper aggregate grading, strength, toughness, and shape are needed for improving final product uses. Table 4.17 provides a list of standard test methods that are used to assess the suitability of aggregates for use in asphalt paving applications.

TABLE 4.17
Asphalt Concrete Aggregate Test Procedures

	Test Method	Specification
General specifications	Coarse aggregate for bituminous paving mixtures	ASTM D692
	Fine aggregates for bituminous paving mixtures	ASTM D1073/AASHTO M29
	Steel slag aggregates for bituminous paving mixtures	ASTM D5106
	Aggregate for single or multiple surface treatments	ASTM D1139
	Crushed aggregate for macadam pavements	ASTM D693
Gradation	Sieve analysis of fine and coarse aggregates	ASTM C136/AASHTO T27
	Sizes of aggregate for road and bridge construction	ASTM D448/AASHTO M43
Particle shape	Index of aggregate particle shape and texture	ASTM D3398
	Flat and elongated particles in coarse aggregate	ASTM D4791
	Uncompacted void content of fine aggregate (as influenced by particle shape, surface texture, and grading)	ASTM C1252/AASHTO TP33
Particle texture	Accelerated polishing of aggregates using the British wheel	ASTM D3319/T279
	Insoluble residue in carbonate aggregates	ASTM D3042
	Centrifuge kerosene equivalent	ASTM D5148
Particle strength	Resistance to degradation of large-size coarse aggregate by abrasion and impact in the Los Angeles machine	ASTM C535
	Resistance to degradation of small-size coarse aggregate by abrasion and impact in the Los Angeles machine	ASTM C131/AASHTO T96
	Degradation of fine aggregate due to attrition	ASTM C1137
Durability	Aggregate durability index	ASTM D3744/AASHTO T210
	Soundness of aggregates by use of sodium sulfate or magnesium sulfate	ASTM C88/AASHTO T104
	Soundness of aggregates by freezing and thawing	AASHTO T103
Specific gravity and adsorption	Specific gravity and absorption of coarse aggregate	ASTM C127/AASHTO T85
	Specific gravity and absorption of fine aggregate	ASTM C128/AASHTO T84
Unit weight	Unit weight and voids in aggregate	ASTM C29/C29M/AASHTO T19
Volume stability	Potential expansion of aggregates from hydration reactions	ASTM D4792
Deleterious components	Sand equivalent value of soils and fine aggregate	ASTM D2419
	Clay lumps and friable particles in aggregates	ASTM C142

Source: From Federal Highway Administration, available at http://www.tfhrc.gov/hnr20/recycle/waste/app.htm.

TABLE 4.18
Asphalt Concrete Test Procedures

Property	Test Method	Specification
Stability and flow characteristics	Marshall method	AASHTO T245
	Hveem method	AASHTO T246, T247
	Asphalt Institute recommended cold mix method	Asphalt Institute Cold Mix Manual
	Resistance to plastic flow of bituminous mixtures using Marshall Apparatus	ASTM D1559
Stripping resistance	Immersion—Marshall method	ASTM D4867
	Immersion—Marshall method	AASHTO T283
Resilient modulus	Superpave mix design	Asphalt Institute Superpave Series No. 1 (SP-1), No. 2 (SP-2)
Unit weight	Theoretical maximum specific gravity and density of bituminous paving mixtures	ASTM D2041
Compacted density	In-place density of compacted bituminous paving mixtures	ASTM D2950

Source: From Federal Highway Administration, available at http://www.tfhrc.gov/hnr20/recycle/waste/app.htm.

Asphalt concrete is properly proportioned to resist the potentially damaging effects in the road. Asphalt concrete paving mixtures should be evaluated for the following properties: stability, flow, air voids, stripping resistance, resilient modulus, compacted density, and unit weight. Table 4.18 provides a list of standard laboratory tests that are presently used to evaluate the mix design or expected performance of fresh and hardened asphalt concrete.

Use of spent foundry sands

Spent foundry sand has been used as a substitute for fine aggregate in asphalt paving materials.[6,11,13] As spent foundry sand is a poorly graded fine sand [largely sized between 0.3 mm and 0.15 mm, 5 to 15% fines content passing 0.075 mm openings (No. 200 sieve)], which essentially excludes it as a solid substitution for conventional fine aggregate. To satisfy the gradation requirements for hot mix asphalt fine aggregates specified in AASHTO M29, the spent foundry sand must be blended with natural sand at selected percentages. Satisfactory performance has been obtained from hot mix pavements incorporating up to 15% spent foundry sand.

The properties of spent foundry sand that are of particular interest when foundry sand is used in asphalt paving applications include particle shape, gradation, durability, and plasticity. With the exception of gradation, clean, processed foundry sands can generally satisfy the physical requirements for hot mix asphalt fine aggregate (AASHTO M29). Round to subangular shapes facilitate the work consistency of asphalt mixture. The hydrophilic nature of the (primarily silica) foundry sand, however, can result in stripping of the asphalt cement coating surrounding the aggregate grains, when over 15% spent foundry sand of total aggregate is blended with the conventional fine sand. This problem can be mitigated by using an antistripping additive.[13]

Use of furnace slag

Air-cooled furnace (ferrous and nonferrous) slag is considered to be a conventional aggregate and can replace both coarse and fine aggregates in asphalt paving applications. Surface-treated pavements incorporating air-cooled furnace slag aggregate demonstrate a number of favorable mechanical properties for use as aggregate, including good friction resistance, good resistance to stripping, fair wear resistance, good soundness characteristics, or good resistance to freeze–thaw weathering.[35]

Air-cooled blast furnace iron slag, however, is more absorptive than conventional aggregate and therefore has a higher asphalt cement demand. It also has a lower compacted unit weight than conventional mineral aggregates, which results in a higher asphalt pavement yield (greater volume for the same weight). This is offset somewhat by the higher yield (volume per mass) of air-cooled furnace slag paving mixtures.[19]

The resistance of air-cooled blast furnace slag to impact is not very high and the material can break down under heavy traffic conditions. Such aggregate is better suited to surface treatment applications on light traffic pavements. Some nonferrous slags are vitreous or "glassy," which can adversely affect their frictional resistance properties. Some glassy nonferrous slags may also be susceptible to moisture-related damage (stripping).

Variability in the production process can result in poor consistency in the physical properties (gradation, specific gravity, absorption, and angularity) of air-cooled furnace slag. This lack of consistency has occasionally contributed to hot mix asphalt performance problems, such as flushing due to high binder content (too rich), raveling due to low binder content, and high fines-to-asphalt ratios (too lean).[10] To minimize problems associated with the variable properties of some air-cooled furnace slag aggregates, a comprehensive scout testing program may be necessary to monitor the gradation, specific gravity, absorption, and angularity of air-cooled blast furnace slag used in asphalt concrete.[26]

The potential for expansion because of free lime or magnesia in the steel slag is of particular concern, which could result in pavement cracking if ignored. It is recommended that no detectable soft lime particles or lime-oxide agglomerations be present.[36]

Some of the engineering properties of air-cooled furnace slag that are of particular interest when air-cooled furnace slag is used as an aggregate in asphalt concrete include gradation, grain shape and texture, bulk and compacted density, absorption, abrasion, stability, friction properties, and freeze–thaw resistance. Blast furnace slag should be crushed and screened to produce aggregate that satisfies the gradation requirements for hot mix asphalt as specified in ASTM D692 for coarse aggregate and AASHTO M29 for fine aggregate. For surface treatments, air-cooled furnace slag aggregate should satisfy gradation specification requirements in ASTM D1139.

Specific physical, chemical, and mineralogical properties of furnace slags depend in great part on the type of slag, method of production, type of furnace, and cooling procedures associated with their respective production processes. Consequently, each slag aggregate must be considered by mineralogical type on a source-specific and cooling (air-cooled or granulated) basis, with recognition of the inherent variability of the slag composition and the presence of potentially foreign materials.

Conventional asphalt mix design methods (e.g., Marshall, Hveem, SHRP) are applicable for the design of hot mix asphalt containing furnace slag aggregates. No special procedures are required for aggregate gradations. Both coarse and fine slag aggregates can be incorporated in hot mix asphalt, provided that the physical requirements of ASTM D692 and/or AASHTO M29 are satisfied. No special provisions are required for furnace slag, and conventional hot mix gradations specifications may be used. Blending with other suitable hot mix asphalt aggregates may be necessary to achieve gradation specifications compliance. Owing to the difference in unit weights, mix designs are usually calculated on a volumetric basis.

4.4.3.2 Portland Cement Concrete

Description

Portland cement concrete is perhaps the most popular and highest use volume construction material. It has the technical advantages of high strength, long durability, solid hardness, and reliable bearing capacity, making it globally favored for various structures. Basic components of portland cement concrete include coarse aggregate (gravel at 40 to 50% mass percentage), fine aggregate (sand at 20 to 25% mass percentage), portland cement (at 10 to 15% mass percentage), and water (at 15 to 20% mass percentage). Concrete can be either cast-in-place, or precast into concrete products such as bricks, pipes, and blocks. The aggregate functions as a filler material, which is bound together by hardened portland cement paste formed by chemical reactions (hydration) between the portland cement and water. In addition to these basic components, supplementary cementitious materials and chemical admixtures are often used to enhance or modify the properties of the fresh or hardened concrete. The coarse and fine aggregates comprise about 80 to 85% of the mix by mass (60 to 75% of the mix by volume). Proper aggregate grading, strength, durability, toughness, shape, and chemical properties are needed for concrete mixture strength and performance.

As aggregates used in concrete mixtures comprise the major components in the mixture, the aggregate materials used have a profound influence on the properties and performance of the mixture in both the plastic and hardened states. Important properties for aggregates that are used in concrete paving mixtures include gradation, absorption, particle shape and surface texture, abrasion resistance, durability, deleterious materials, and particle strength. Table 4.19 provides a list of standard test methods that are used to assess the suitability of conventional mineral aggregates in portland cement concrete paving applications.

The mix proportions for concrete paving mixtures are determined by attaining optimum characteristics of the mix in both the plastic and hardened states. The designed mixture can be properly placed and consolidated, finished to the required texture and smoothness, and will have the desired properties necessary for pavement performance. Concrete paving mixtures should be

TABLE 4.19
Concrete Aggregate Test Procedures

Property	Test Method	Specification
General	Concrete aggregates	ASTM C33
	Ready-mixed concrete	ASTM C94/AASHTO M157M
	Concrete made by volumetric batching and continuous mixing	ASTM C685/AASHTO M241
	Terminology related to concrete and concrete aggregates	ASTM C125
Gradation	Sizes of aggregate for road and bridge construction	ASTM D448/AASHTO M43
	Sieve analysis of fine and coarse aggregate	ASTM C136/AASHTO T27
Absorption	Specific gravity and absorption of coarse aggregate	ASTM C127/AASHTO T85
	Specific gravity and absorption of fine aggregate	ASTM C128/AASHTO T84
Particle shape and surface texture	Flat and elongated particles in coarse aggregate	ASTM D4791
	Uncompacted voids content of fine aggregate	ASTM C1252/AASHTO TP33
	Index of aggregate particle shape and texture	ASTM D3398
Abrasion resistance	Resistance to degradation of large-size coarse aggregate by abrasion and impact in the Los Angeles machine	ASTM C535
	Resistance to degradation of small-size coarse aggregate by abrasion and impact in the Los Angeles machine	ASTM C131/AASHTO T96
Durability	Aggregate durability index	ASTM D3744/AASHTO T210
	Soundness of aggregates by use of sodium sulfate or magnesium sulfate	ASTM C88/AASHTO T104
	Soundness of aggregates by freezing and thawing	AASHTO T103
Deleterious components	Petrographic examination of aggregates for concrete	ASTM C295
	Organic impurities in fine aggregate for concrete	ASTM C40
	Clay lumps and friable particles in aggregates	ASTM C142
	Plastic fines in graded aggregates and soils by use of the sand equivalent test	ASTM D2419
Volume stability	Potential volume change of cement–aggregate combinations	ASTM C342
	Accelerated detection of potentially deleterious expansion of mortar bars due to alkali–silica reaction	ASTM C227

Source: From Federal Highway Administration, available at http://www.tfhrc.gov/hnr20/recycle/waste/app2.htm.

evaluated for the following properties: slump, workability, setting time and air content at the fresh state, strength, density, durability, air content, frictional resistance, and volume stability at the hardened state. Table 4.20 provides a list of standard laboratory tests that are presently used to evaluate these properties.

Use of spent foundry sand

Spent foundry sand is thought of as a beneficial substitute for fine sand for use in portland cement concrete. Prior to acceptance of inclusion, test standards applied on conventional fine sand shall be referred to as the standards for spent foundry sand to compare the physical properties of conventional sand and spent foundry sand. The most important parameters are particle size distribution, fineness modulus, dust content, density, organics content, deleterious materials content, and grain shape. Although no spent foundry sand satisfies all of the specifications, foundry sand can be blended with conventional sand to be incorporated into the concrete matrix. The replacing ratio normally starts at one-third.

In the production of foundry sand concrete, conventional mixing, placing, and curing are easily referable.

TABLE 4.20
Concrete Paving Materials Test Procedures

Property	Test Method	Specification
General	Ready-mixed concrete	ASTM C94/AASHTO M157
	Concrete made by volumetric batching and continuous mixing	ASTM C685/AASHTO M241
	Concrete aggregates	ASTM C33
	Terminology related to concrete and concrete aggregates	ASTM C125
	Pozzolan use as a mineral admixture	ASTM C618
	Ground blast furnace slag specifications	ASTM C989
	Chemical admixtures for concrete	ASTM C494
	Air entraining agents	ASTM C260
	Silica fume specifications	ASTM C1240
Slump	Slump of hydraulic cement concrete	ASTM C143/AASHTO T119
Workability	Bleeding of concrete	ASTM C232/AASHTO T158
Hydration and setting	Time of setting of concrete mixtures by penetration resistance	ASTM C403
Strength	Compressive strength of cylindrical concrete specimens	ASTM C39/AASHTO T22
	Flexural strength of concrete (using simple beam with third-point loading)	ASTM C78/AASHTO T96
	Splitting tensile strength of cylindrical concrete specimens	ASTM C496/AASHTO T198
Air content	Microscopic determination of parameters of the air-void system in hardened concrete	ASTM C457
	Air content of freshly mixed concrete by the pressure method	ASTM C231/AASHTO T152
	Air content of freshly mixed concrete by the volumetric method	ASTM C173/AASHTO T196
	Unit weight, yield, and air content of concrete	ASTM C138
Density	Specific gravity, absorption, and voids in hardened concrete	ASTM C642
Durability	Resistance of concrete to rapid freezing and thawing	ASTM C666
	Scaling resistance of concrete surfaces exposed to deicing chemicals	ASTM C131/AASHTO T96
Volume stability	Length change of hardened hydraulic-cement mortar and concrete	ASTM C157
	Length change of concrete due to alkali–carbonate rock reaction	ASTM C1105

Source: From Federal Highway Administration, available at http://www.tfhrc.gov/hnr20/recycle/waste/app2.htm.

Use of furnace slag

Ground granulated blast furnace slag has been used for many years as a supplementary cementitious material in portland cement concrete, as a mineral admixture. The use of ground granulated blast furnace slag as a partial portland cement replacement takes advantage of the energy invested in the slag-making process and its corresponding benefits with respect to the enhanced cementitious properties of the slag. Rapid quenching is important if cementitious properties are to be achieved. The chemical composition of ground granulated blast furnace slag use in portland cement concrete must also conform to sulfur and sulfate content limitations outlined in AASHTO M302.

Granulated blast furnace slag is a glassy granular material, and its particle distribution, shape, and grain size vary, depending on the chemical composition and method of production, from popcorn-like friable particles to dense, sand-sized grains. Processing for use as a supplementary cementitious material requires grinding of the slag, typically using the same or similar plant and equipment as for portland cement production.

The properties of concrete mixes containing ground granulated blast furnace slag that are of particular interest when it is used as partial cement replacement include strength development, workability, heat of hydration, resistance to alkali–aggregate reactivity, resistance to sulfate attack, and salt scaling. Special production characteristics and performance may be exhibited when ground granulated blast furnace slag is incorporated, such as a slower strength development, longer-lasting workability, low slump loss, lower heat of hydration, reduced alkali–aggregate reaction, improved resistance to sulfate attack, and susceptibility to salt scaling.[38,39]

The most frequently used proportioning recommendations for ground granulated blast furnace slag use in concrete mix designs are covered in ACI 226.1R, Ground Granulated Blast-Furnace Slag as a Cementitious Constituent in Concrete. Some agencies require that a salt scaling test also be completed for selected concrete mixes subjected to deicing salts.[38] The same equipment and procedures as used for conventional portland cement concrete may be used to batch, mix, transport, place, and finish concrete containing ground granulated blast furnace slag.

4.4.3.3 Portland Cement

Description

Portland cement is a fine, soft, powdery substance that acts as a critical component in producing portland cement concrete. When mixed in contact with water, the cement will hydrate and generate complex chemicals that eventually bind the sand and gravel into a hard, solid mass, known as concrete.

There are eight types of portland cement as specified in standard ASTM C150 Standard Specification for Portland Cement. Each cement is manufactured with special use and chemical requirements. Their manufacturing process, however, is basically the same. Portland cement is a chemical product of a kiln process, where blended ground raw materials undergo chemical transformation. Raw materials must comprise a selected ratio of calcium oxide, silica, alumina, and iron oxide. Most of these ingredients are usually contained in shale, dolomite, and limestone, known as the prevailing raw materials. As sand is a good source of silica, alumina, and iron oxides, it is often used in as one of the raw minerals in manufacturing cement.

Use of spent foundry sand

Spent foundry sand can be used as a good source of silica in manufacturing portland cement. Also, the clay fraction of foundry sand is an additional source of iron and aluminum oxides. According to the portland cement industry, spent foundry sand can be beneficially used in the manufacture of portland cement, as sand possesses the following characteristics:

1. Silica content $>80\%$
2. Low alkali level
3. Uniform particle size

Manufacturers also request that spent foundry sand should be cleaned from other foundry byproducts. Core butts should be ground to a uniform grain size to improve the kiln process. In addition, adequate supplies of spent foundry sand are viable in the manufacturing process.

Use of furnace slag

Furnace slag can be used as a source of aluminum oxide and magnesia in manufacturing portland cement. Furnace slag is used as a component of blended cement. The use of ground granulated blast furnace slag in portland cement is governed by AASHTO M302. Three types of ground granulated slag cements are typically manufactured: portland cement is covered by AASHTO M85, portland blast furnace slag cement and slag cement by AASHTO M240.

Use of baghouse dust

Although low in volume compared with other foundry solid waste, baghouse dust may still be used beneficially in the production of portland cement. This opportunity arises from its attractive mineral composition: silica, clay, and metal fines, which are needed in the cement kiln. Also, special efforts may be undertaken to characterize its chemical composition and purity.

4.4.3.4 Embankment or Fill Material

Description

An embankment refers to a volume of longitudinal earthen material that is placed and compacted for the purpose of raising the level of a roadway (or railway) above the level of the existing ground surface. A fill refers to a volume of earthen material that is placed and compacted for the purpose of filling in a hole, cavity, or excavation. Embankments or fills are constructed of materials that usually consist of soil, but may also include aggregate, rock, or crushed paving material.

Soils range from granular soils (sand and gravel), which are highly desirable, to the more finely sized soils (silt and clay). Well-graded soils are preferred as they are readily compacted and give firm bearing capacity. Concerns in selecting soils are the presence of unsuitable or deleterious materials, such as tree roots, branches, stumps, sludge, metal, or trash. Other oversized materials, such as rocks, large stones, reclaimed paving materials, or air-cooled slags, can be used for the construction of embankment bases. Although the use of oversized materials can result in a stable embankment base, the oversized materials should have strong particles that do not readily break down under the action of construction machinery, but have a range of sizes so that void spaces are at least partially filled.

Some of the more important properties of materials that are used for the construction of embankments or fills include gradation, unit weight, specific gravity, moisture–density characteristics, shear strength, compressibility, bearing capacity, permeability, and corrosion resistance. Table 4.21 provides a list of the standard test methods usually used to assess the suitability of conventional earthen fill materials for use in embankment or fill construction.

Use of spent foundry sand

Embankment and fill applications are the biggest end-user of spent foundry sand. Natural soils are often composed primarily of sand, clay, and water. Most spent foundry sands have these same constituents, which suggests spent foundry sand as a good fill material. The immediate benefits include saving virgin soil materials and reduce the bottom line of the foundry industry. It is also reported that foundry sand as a fill material may present better performance then conventional materials, including better resistance to freeze–thaw distress.

The physical properties of concern for construction fill applications are the relationship between moisture and density, plasticity, the liquid limit, and particle size distribution. The same set of construction machinery for conventional fills, such as bulldozers, compactors, and grabbers, is suitable for fill earth works containing spent foundry sand.

Use of furnace slag

Both air-cooled blast furnace slag and expanded blast furnace slag can be used as a conventional aggregate in embankment or fill. They are generally considered by many specifying agencies to be

TABLE 4.21
Embankment or Fill Material Test Procedures

Property	Test Method	Specification
Gradation	Particle size analysis of soils	ASTM D422
	Sieve analysis of fine and coarse aggregate	ASTM D136
Unit weight and specific gravity	Unit weight and voids in aggregate	ASTM D29
	Specific gravity of soils	ASTM D854
	Relative density of cohesionless soils	ASTM D2049
	Maximum index density of soils using a vibratory table	ASTM D4253
	Minimum index density of soils and calculation of relative density	ASTM D4254
Moisture–density characteristics	Moisture–density relations of soils and soil–aggregate mixtures using 5.5 lb (2.49 kg) rammer and 12 in. (305 mm) drop	ASTM D698 (Standard)
	Moisture–density relations of soils and soil–aggregate mixtures using 10 lb (4.54 kg) rammer and 18 in. (457 mm) drop	ASTM D1557 (Modified)
Compacted density (in-place density)	Density of soil in place by the sand-cone method	ASTM D1556
	Density and unit weight of soil in place by the rubber balloon method	ASTM D2167
	Density of soil and soil–aggregate in place by nuclear methods (shallow-depth)	ASTM D2922
	Density of soil in place by the sleeve method	ASTM D4564
Shear strength	Unconsolidated undrained compressive strength of cohesive soils in triaxial compression	ASTM D2850
	Direct shear test of soils under consolidated drained conditions	ASTM D3080
	Consolidated-undrained triaxial compression test on cohesive soils	ASTM D4767
Compressibility	One-dimensional consolidation properties of soils	ASTM D2435
	One-dimensional consolidation properties of soils using controlled-strain loading	ASTM D4186
	One-dimensional swell or settlement potential of cohesive soils	ASTM D4546
Bearing capacity	California Bearing Ratio (CBR) of laboratory-compacted soils	ASTM D1883
	Bearing ratio of soils in place	ASTM D4429
Permeability	Permeability of granular soils by constant head	ASTM D2434
Corrosion resistance	pH of soil for use in corrosion testing	ASTM G51
	Field measurement of soil resistivity using the Wenner four-electrode method	ASTM G57
	Pore water extraction and determination of the soluble salt content of soils by refractometer	ASTM D4542

Source: From Federal Highway Administration, available at http://www.tfhrc.gov/hnr20/recycle/waste/app4.htm.

conventional aggregates and require minimal processing to satisfy conventional soil and aggregate engineering requirements. Although there is little documented use of nonferrous slags as aggregate in embankments or fill, both air-cooled and granulated nonferrous slags are potentially useful for these applications. Nonferrous slag that is suitable for use as a granular base will generally exceed specifications for embankment and fill construction. The high stability of nonferrous slag aggregates can be used advantageously to provide good load transfer to weaker subgrades.

Critical properties qualifying slag use in embankment and fills include gradation, stability, compacted density, drainage characteristics, and corrosivity. Blast furnace slag requires crushing processes to satisfy the physical requirements for use in embankments. Air-cooled nonferrous slags are fine enough to save crushing processes. If necessary, nonferrous slag aggregates can be blended with conventional embankment or fill materials (rock, soil, aggregates) to meet required gradation specifications. In addition, if used as materials for embankment and fills, air-cooled blast furnace takes advantages of high shear strength, reduced post-compaction settlement, slightly lighter weight, good drainage characteristics, no frost susceptibility, and no corrosion risk to steel.

Design procedures for embankments or fill containing blast furnace slag are the same as design procedures for embankments or fills using conventional materials. The same equipment and procedures used for handling, stockpiling, placing, and compacting conventional aggregates may be used for air-cooled blast furnace slag.

4.4.3.5 Flowable Fill

Description

Flowable fill refers to cementitious slurry created by blending fine aggregate or filler, water, and cementitious material(s), and is used primarily as a backfill in lieu of compacted soil. This mixture is capable of filling all voids in irregular excavations (such as utility trenches) and inaccessible places (such as narrow cavities), is self-leveling, self-setting, and hardens in a matter of a few hours without the need for compaction in layers. Flowable fill is sometimes referred to as controlled density fill (CDF), controlled low strength material (CLSM), lean concrete slurry, and unshrinkable fill. The applications of flowable fill are numerous and include restoration of utility cuts in county roads, backfilling structures, filling abandoned wells, filling voids under existing pavements, and pipe embedments.[41–46]

Flowable fill is defined by the American Concrete Institute[47] as a self-compacting cementitious material that is in a flowable state at placement and has a compressive strength of 8.3 MPa (1200 psi) or less at 28 days. Most current applications for flowable fill involve unconfined compressive strengths of 2.1 MPa (300 psi) or less, which makes possible its excavation at a later date.

Fine aggregate or filler material are important components in the mixture, which provides the solids to develop compressive strength. The aggregates must be sufficiently finely graded to enhance the flowability of the mix, but also granular enough to be able to drain some of the excess water from the mix prior to initial hardening. Sand is the most commonly used flowable fill material, although other materials (such as coal bottom ash, fly ash, and quarry fines) have also been used. Important properties include gradation and unit weight, which have a direct effect on the flow characteristics and yield of fresh flowable fills.

The most important physical characteristics of fresh and hardened flowable fill mixtures are its strength development, flowability, hardening time, bleeding and shrinkage, unit weight, bearing capacity, shear strength, and corrosion resistance. Table 4.22 lists the standard test methods usually used to evaluate flowable fill materials.

Use of spent foundry sand

Natural sand is a major component of most flowable fill mixes. Ferrous spent foundry sand can be used as substitute for natural sand (fine aggregate) in flowable fill.[48,49] Spent sands from nonferrous foundries and foundry baghouse dust can contain high concentrations of heavy metals that may preclude their use in flowable fill applications. Some of the engineering properties of spent foundry sand that are of particular interest when foundry sand is used in flowable fill applications include particle shape, gradation, strength characteristics, soundness, deleterious substances, and corrosivity.

Flowable fill mixes are usually designed on the basis of compressive strength, generally after 28 days of ambient temperature curing, but sometimes on the basis of longer term (90 days or more) strength. They are designed to have high fluidity during placement [typical slump of 150 to 200 mm (6 to 8 in.)] and to develop limited strength [typically between 340 and 1400 kPa (50 and 200 psi)], which is sufficient to support traffic without settling, yet can be readily excavated. The mix design shown in Table 4.23 could be referred to as a starting point for mixing formulation for a flowable fill containing spent foundry sand.

Construction procedures for flowable fill materials are no different than those for conventional earth backfill materials. The same methods and equipment used to mix, transport, and place flowable fill made with conventional aggregates may be used for flowable fill incorporating spent foundry

TABLE 4.22
Flowable Fill Test Procedures

Property	Test Method	Specification
Strength development	Unconfined compressive strength of cohesive soil	ASTM D2166
	Unconfined compressive strength index of chemical-grouted soils	ASTM D4219
Flowability	Slump of portland cement concrete	ASTM C143
	Flow of grout for preplaced aggregate (flow cone method)	ASTM C939
Hardening time	Time of setting of concrete mixtures by penetration resistance	ASTM C403
Bleeding and shrinkage	Change in height at early ages of cylindrical specimens from cementitious mixtures	ASTM C827
Unit weight	Unit weight, yield, and air content of concrete	ASTM C138
Bearing strength	California Bearing Ratio (CBR) of laboratory-compactive soils	ASTM D1883
Shear strength	Unconsolidated undrained compressive strength of cohesive soils in triaxial compression	ASTM D2850
	Direct shear test of soils under consolidated drained conditions	ASTM D3080
Corrosion resistance	pH of soil for use in corrosion testing	ASTM G51
	Field measurement of soil resistivity using the Wenner four-electrode method	ASTM G57
	Optimum SO_3 in portland cement	ASTM C563

sand. Special measures may be required to control the early contact water leachate (containing phenols) from spent foundry sand stockpiles. The construction of an impervious pad (to collect surface moisture or precipitation passing through the stockpile) and subsequent filtration (through an activated carbon filter) of the leachate has reportedly been effective in limiting the phenol concentration of the discharge.

4.4.3.6 Landfill Liner, Cover, and Hydraulic Barrier

Description

The landfill liner, cover, and hydraulic barrier all belong to the subsurface pollutant engineered containment system. The liner is designed at the bottom of a landfill to contain downward leachate. The cover is designed at the top of a landfill to prevent precipitation from infiltrating into the landfill. The hydraulic barrier, or cutoff walls, is a vertical compacted earthen system to contain horizontal flow of plume. The ultimate purpose of these barriers is to isolate contaminants from the environment and, therefore, to protect the soil and groundwater from pollution originating in the landfill or polluted site.

TABLE 4.23
Mixing Proportions of Flowable Fill with Spend Foundry Sand (kg/m^3)

	Cement	Fly Ash	Spend Foundry Sand	Water
Minimum	25	334	818	291
Maximum	94	463	1264	504
Average	57	383	1075	399

Source: From Deng, A., *Excess Foundry Sand Characterization and Experimental Investigation in Controlled Low-Strength Material*, PhD Dissertation of the Pennsylvania State University, University Park, PA, August 2004.

The primary characteristic necessary for a liner, cover, or cutoff wall is low permeability, which essentially enables them to slow down the seepage or diffusion of chemicals. Clay is therefore the main material used to construct these containment systems. The thickness and chemical compatibility of containment systems are of concern in assessing the performance of a system. For example, clay liners are constructed as a simple liner that is 2 to 5 ft thick. In composite and double liners, the compacted clay layers are usually between 2 and 5 ft thick, depending on the characteristics of the underlying geology and the type of liner to be installed. Regulations specify that the clay used can only allow water to penetrate at a rate of less than 1.2 in./yr. However, the effectiveness of clay liners can be reduced by fractures induced by freeze–thaw cycles, drying out, and the presence of some chemicals.

Use of spent foundry sand

Most spent foundry sand discarded is green sand. The primary components of green sand are silica and bentonite. Thus, green sands are essentially a sand–bentonite mixture, which makes them potentially useful as a liner and cover materials, that is, for hydraulic barrier layers.

The critical properties of green sand affecting its performance as a hydraulic barrier material include grain size distribution, compaction curves, and hydraulic conductivity when compacted. In general, hydraulic conductivity in use should be less than 1×10^{-7} cm/s, which is the criterion for a conventional clay barrier. Sometimes, if aggressive leachate might penetrate through the barrier, the chemical compatibility and durability of a green sand barrier must be researched. As zero-valence iron, clay, and carbonaceous materials help the containment of chemicals, green sand is thought to be an active containment media in the subsurface cleaning domain.

4.4.4 AGRICULTURAL APPLICATIONS

An emerging domain for some spent foundry sand reuse is as a component in the manufacture of topsoil and growing amendments or composites. In many parts of the globe, high-quality topsoils for landscaping are not available in urban areas. Commercial landscapers and nursery growers frequently manufacture topsoil and composite by blending composted materials and low-quality soils, which not only exhausts natural resource, but also increases manufacture cost. Spent foundry sand has been reported to be amended into a product matching the characteristics of topsoil and amendments; this could be another competitive and vast market for both the metal casting industry and horticultural professionals.

4.4.4.1 Topsoil

Description

Topsoil is the uppermost layer of the Earth's surface, ranging in depth from a few inches to many feet. Topsoil has been created over long time by the physical and chemical action of climate, weather on the Earth's parent rock materials, and decay of plants. As a result, a considerable accumulation of decaying organic matter is found in topsoil. Topsoil is the base for gardening and landscaping activities, where plants are grown by gardening efforts. Unfortunately, genuine topsoil created by natural forces is often unavailable because it is so scarce, and when it can be obtained it is often very expensive.

Topsoil should have a loose and open structure so that it drains fast to keep the ground surface dry. At the same time, it must be able to retain enough moisture in order that plants growing in it are not constantly subjected to drought stress. The properties of interest include particle gradation, clay content, nutrient content, and retention capacity.

Use of spent foundry sand

Spent foundry green sand is of particular interest to soil blending companies that produce topsoil, because of its dark color, clay content, moisture retention, and consistency. A high sand content is required in topsoil, so spent foundry sand could be a major component. Spent sand reduces the formation of clumps and prevents the mix from compacting, which allows air to circulate within the topsoil and to stimulate decomposition. The U.S. Agricultural Research Service is leading some pilot studies conducted to investigate the feasibility of beneficially using foundry sand as a topsoil replacement.

4.4.4.2 Growing Amendments

Description

Very similar in growing function to topsoil, growing amendments are also manufactured for agronomic purposes. They are specifically designed as a composite for serving gardening, greenhouse, nursery, or horticultural industries.

The growing amendments should be porous and well drained, yet retentive of sufficient moisture to supply adequate water volume for plants. A relatively low level of soluble salts is necessary to maintain a mild environment for plants. However, an adequate exchange capacity is preferred to retain and supply the elements necessary for plant growth. The media should be free from harmful pests, pathogenic organisms, insects, nematodes, and weed seeds. In use, it should present stable biological and chemical characteristics. For sand-based growing amendments, the components generally include peat, bark, and sand. The former two components account for 60 to 80% in weight.

Use of spent foundry sand

Replacing natural soil/sand with spent foundry sand in agronomic applications represents an excellent market for the beneficial reuse of foundry byproduct. The presence of clay in foundry sand is beneficial because clay increases the capacity of soils to retain nutrients and therefore reduce the amount of additional nutrient required for plant growth.[50] A pilot study[51] has indicated that spent foundry sand can be incorporated into growing mixes for the nursery industry. The pilot study[51] used the mixing formulation of 50% manufactured growing mix and 50% foundry sand. The materials should avoid the complexity of a wide carbon: nitrogen ratio, high pH, and high water holding capacity, which leads to the easy development of successful growing amendments containing spend foundry sand. The nursery industry and the greenhouse industry represent an excellent market for local small and large foundries.

4.4.5 GENERAL PROCESSES

4.4.5.1 Crushing, Screening, and Storage

For solid wastes to be suitable as a full or partial replacement for components in other applications, it should be free of objectionable material such as wood, garbage, and metal that can be introduced at the foundry. It should be free of foreign material and thick coatings of burnt carbon, binders, and mold additives that could inhibit product manufacture, such as cement hydration. It may be necessary to crush the solid waste to reduce the size of oversized core butts or unclasped molds. Magnetic separation is a good solution to producing a suitable coarse or fine aggregate product.

Aggregates should exhibit consistent physical and chemical characteristics to quality for most of the aforementioned applications. However, current practices often lead to a composite of various foundry wastestreams. Special attention is required to set up a rigorous quality control system with waste supply on a source-specific basis.

Stockpiles of a sufficient volume of solid wastes should be supplied for reuse requirements.

4.4.5.2 Design and Construction

Conventional structural design and construction procedures for a construction are generally applicable to a construction incorporating foundry solid wastes. The same production methods and equipment used for conventional manufacture can be used for production of manufacture using foundry solid waste.

4.4.6 UNRESOLVED ISSUES

From an engineering perspective, recycled materials should be used in such a manner that the expected performance of the product will not be compromised. Waste and byproduct materials, however, differ vastly in their types and properties and, as a result, in the end-use applications for which they may be suited. Experience and knowledge regarding the use of these materials vary from material to material as well as from facility to facility. To recover these materials for potential use, engineers, researchers, generators, and regulators need to be aware of the properties of the materials, how they can be used, and what limitations may be associated with their use.

Most foundries have installed sand reclamation systems that screen the metal and debris out of the sand so that a good, clean product is available for reuse in a variety of applications and industries. This is a good start in the strategy of reusing foundry solid waste. Depending on the projected end-use, it may be important to segregate wastestreams at the foundry, as each stream can have different characteristics. Additionally, some waste materials, such as bulk spent sand, are typically unrecoverable during the "shakeout" and finishing processes. These sands may be contaminated with metal or very large chunks of burned cores (referred to as core "butts") and will need to undergo some type of segregation, crushing, and screening before recycling. Some hard chunks may not even be crushable, and have to be landfilled.

4.5 BARRIERS TO SOLID WASTE REUSE

Besides technical aspects, wide acceptance of reusing foundry solid wastes as marketable materials will only be achieved by removing barriers or limitations arising from public perception (education or training), environmental regulation, engineering guidelines and procedures, economics, and market potentials. These barriers are basically nontechnical but take considerable efforts to address. Unlike the technical aspects of a reuse program, many parties are involved, such as the government, the public, academics, and industrial and commercial departments. A coordinated and consistent framework needs to be constructed among these parties, aiming at eliminating barriers to the foundry solid waste reuse program.

4.5.1 EDUCATION

Public acceptance of foundry waste reuse significantly depends upon their understanding of nature and the performance of foundry waste materials and generated products. In general, negative descriptions, such as its black appearance, the presence of casting byproducts and heavy metals, high melting temperature and sometimes odor, may automatically bring objections into the public mind. It is unfair. The public should be well educated to understand the generation and characterization of foundry solid waste. Documented technical data and environmental regulations are to be presented to convince people that foundry solid waste (at least not all) is not hazardous or as bad as they thought.

Communication channels shall be set up between industry and academics. There has been inconsistency with regards to the characterization of foundry solid waste between industry and academics. The former cares about the workability and efficiency of materials in generating products. The latter concentrate on the technical behavior of materials if reused. The way that metal casters define the characteristics of their sands is completely different from what the contractor wants to know. For example, metal casters talk about ground fineness number, whereas contractors want to know fine and clay contents. At the point of reusing their solid waste, metal casters should divert their attention from regulators and customers to researchers, working within a well channeled system.

4.5.2 ENVIRONMENTAL REGULATION

Solid waste regulations are frequently cited as barriers for metal industrial byproduct recycling. Research indicates that most ferrous spent foundry sand meets nonhazardous standards under the

RCRA. Competing granular materials, such as sands, gravels, and native soils, are not regulated materials although their environmental profiles may be similar to spent sands.

In some case, experts may debate the reuse of nonhazardous materials, which, they insist, should still be dumped to general landfill sites where nonhazardous materials belong, like municipal solid waste. It is also insisted that there is no documented regulation requiring the reuse of nonhazardous materials. Therefore, to defend the beneficial reuse program of foundry solid waste, regulations should specifically permit their marketing.

Environmental regulation should be complied with to legally validate a reuse program. It is critical that recyclers become familiar with the federal and state regulations relative to their materials. Before reuse starts, materials should be tested according to these environmental regulations to determine whether they are hazardous or nonhazardous. Knowing and understanding the rules and regulations will lead to a better reuse program.

4.5.3 Guidelines, Procedures, and Specifications

Conventional materials have been approved to enter the market, supported by many standalone guidelines, procedures, and specifications. As such, suppliers and users favor the selection of conventional materials. Foundry solid waste is being put to a competitive disadvantage against conventional materials, just because no standalone guidelines and procedures are universally documented for their potential markets. This barrier could be eliminated by showing data demonstrating that foundry solid waste is at least as good as, if not better than, conventional materials for target end-uses. A trial and error procedure is normally used in bench-scale tests, where guidelines, procedures, and specifications are developed by referring to documented ones. Successful experimental and field demonstration then further modifies and finalizes guidelines, procedures, and specifications.

4.5.4 Economics

Economical factors, such as disposal costs, the availability of conventional materials, and transportation costs, are critical considerations. As with any material, transportation costs are generally the highest cost factor in recycling solid waste. The most economically sustainable options for recycling foundry solid waste will generally match the volume and characteristics of the materials with nearby businesses and construction projects. Small foundries may not generate enough material on a weekly or monthly basis to satisfy the need for construction sands. In this case, it may be necessary to collect similar wastestreams from multiple sources or to partially substitute for conventional materials in order to meet volume requirements.

Some end-use applications may prefer the characteristics of foundry solid waste. For instance, spent foundry sand is a uniformly graded fine aggregate containing chemically active iron and organics. Spent foundry sand can be superior to other types of granular materials, such as compacted soils or clays, for hydraulic barriers. In this case, spent foundry sand provides better performance at lower cost.

4.5.5 Market Potential

One particular mistake that foundries make is improperly defining the market potential of their byproducts. Competitive material availability and transportation costs will dictate market acceptance in most cases. They must study the landscape before attempting to enter the market. Active marketing efforts will always get paid back. Keep in mind that many potential customers are cost-conscious, and that is an advantage to the foundry byproducts process. Aiming low to establish a market is a great strategy for getting in the door. Foundries need to value market sustainability and cost reduction over the best short-term deal. Build partnerships with end-users and long-term progress will be established.

Before entering the market, the following questions should be addressed in order to have a good start. The ultimate goal is that the bottom line of reuse is well understood, making sure the materials are characterized properly, and then marketing them according to the appropriate regulations.

1. Is the volume of material supplies adequate for the quantity expectations of a potential customer?
2. Will the properties and variability of the materials satisfy the quality expectations of a potential customer?
3. Will any processing be required to consistently guarantee the expected quality level?
4. Is all cost taken into account?
5. What is the cost of the material the byproduct is to replace?
6. Are all permits obtained for the actions?

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5 Waste Treatment in the Aluminum Forming Industry

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CONTENTS

5.1 INDUSTRY AND PROCESS DESCRIPTION

The aluminum forming industry is a manufacturing industry in which aluminum or aluminum alloys are made into semifinished aluminum products using hot or cold working processes. The aluminum forming manufacturing operations include the rolling, drawing, extruding, and forging of aluminum. In the U.S., the industry consists of about 300 plants owned by about 150 companies. The industry employs about 30,000 workers.

As well as the aluminum forming manufacturing operations of rolling, drawing, extruding, and forging, there are associated processes, such as the casting of aluminum alloys for subsequent forming, heat treatment, cleaning, etching, and solvent degreasing.[1–6]

Surface treatment of aluminum (such as cleaning, etching, and solvent degreasing) is any chemical or electrochemical treatment applied to the surface of aluminum. Such surface treatment is considered to be an important part of aluminum forming. For the purposes of government regulation, surface treatment of aluminum is considered to be an integral part of aluminum forming whenever it is performed at the same plant site at which aluminum is formed, and such operations are not considered for government regulation under the Electroplating and Metal Finishing provisions of U.S. 40 CFR parts 413 and 433.

Casting aluminum when performed as an integral part of aluminum forming and located on site at an aluminum forming plant is considered an aluminum forming operation and hence is covered under these government guidelines.

When aluminum forming is performed on the same site as primary aluminum reduction the casting shall be regulated by the nonferrous metals guidelines if there is no cooling of the aluminum prior to casting. If the aluminum is cooled prior to casting then the casting shall be regulated by the aluminum forming guidelines. The major aluminum forming processes are briefly described in the narrative below.

5.1.1 CASTING

Before aluminum alloys can be used for rolling or extrusion and subsequently for other aluminum forming operations, they are usually cast into ingots of suitable size and shape.

The aluminum alloys used as the raw materials for casting operations are sometimes purchased from nearby smelters and transported to the forming plants in a molten state. Usually, however, purchased aluminum ingots are charged together with alloying elements into melting furnaces at the casting plants. Several types of furnaces can be used, but reverberatory furnaces are the most common.

At many plants, fluxes are added to the metal to reduce hydrogen contamination, remove oxides, and eliminate undesirable trace elements. Solid fluxes such as hexachloroethane, aluminum chloride, and anhydrous magnesium chloride may be used, but it is more common to bubble gases such as chlorine, nitrogen, argon, helium, and mixtures of chlorine and inert gases through the molten metal.

The casting methods used in aluminum forming can be divided into three classes: direct chill casting, continuous casting, and stationary casting.

5.1.1.1 Direct Chill Casting

Vertical direct chill casting is the most widely used method of casting aluminum for subsequent forming. Direct chill casting is characterized by continuous solidification of the metal while it is being poured. The length of an ingot cast using this method is determined by the vertical distance it is allowed to drop rather than by mold dimensions. Molten aluminum is tapped from the melting furnace and flows through a distributor channel into a shallow mold. Noncontact cooling water circulates within this mold, causing solidification of the aluminum. The base of the mold is attached to a hydraulic cylinder that is gradually lowered as pouring continues. As the solidified aluminum leaves the mold it is sprayed with contact cooling water, reducing the temperature of the forming ingot. The cylinder continues to lower into a tank of water, causing cooling of the ingot as it is immersed. When the cylinder has reached its lowest position, pouring stops and the ingot is lifted from the pit. The hydraulic cylinder is then raised and positioned for another casting cycle. Lubrication of the mold is required to ensure proper ingot quality. Lard or castor oil is usually applied before casting begins and may be reapplied during the drop.

5.1.1.2 Continuous Casting

Unlike direct chill casting, no restrictions are placed on the length of the casting as it is not necessary to interrupt production to remove the cast product. Continuous casting eliminates or reduces the degree of subsequent rolling required. Because continuous casting affects the mechanical properties of the aluminum cast, the use of continuous casting is limited by the alloys used, the nature of subsequent forming operations, and the desired properties of the finished product. Continuous casting techniques have been found to significantly reduce or eliminate the use of contact cooling water and oil lubricants.

5.1.1.3 Stationary Casting

Molten aluminum is poured into cast-iron molds and allowed to air cool. Lubricants and cooling water are not required. Melting and casting procedures are dictated by the intended use of the ingots produced. Frequently the ingots are used as raw material for subsequent aluminum forming operations at the plant. Other plants sell these ingots for reprocessing.

5.1.2 ROLLING

The rolling process is used to transform cast aluminum ingot into any one of a number of intermediate or final products. Pressure exerted by the rollers as aluminum is passed between them flattens the metal and may cause work hardening.

Heat treatment is usually required before and between stages of the rolling process. Ingots are usually made homogeneous in grain structure prior to hot rolling in order to remove the effects of casting on the aluminum's mechanical properties. Annealing is typically required during cold rolling to keep the metal ductile and remove the effects of work hardening. The kind and degree of heat treatment applied depends on the alloy involved, the nature of the rolling operation, and the properties desired in the product.

It is necessary to use a cooling and lubricating compound during rolling to prevent excessive wear on the rolls, to prevent adhesion of aluminum to the rolls, and to maintain a suitable and uniform rolling temperature. Oil-in-water emulsions, stabilized with emulsifying agents such as soaps and other polar organic materials, are used for this purpose in hot rolling operations.

5.1.3 EXTRUSION

In the extrusion process, high pressures are applied to a cast billet of aluminum, forcing the metal to flow through a die orifice. The resulting product is an elongated shape or tube of uniform cross-sectional area.

Extrusions are manufactured using either a mechanical or a hydraulic extrusion press. A heated cylindrical billet is placed into the ingot chamber and the dummy block and ram are placed into position behind it. Pressure is exerted on the ram by hydraulic or mechanical means, forcing the metal to flow through the die opening. The extrusion is sawed off next to the die, and the dummy block and ingot butt are released. Hollow shapes are produced with the use of a mandrel positioned in the die opening so that the aluminum is forced to flow around it. A less common technique, indirect extrusion, is similar except that in this method the die is forced against the billet, extruding the metal in the opposite direction through the tam stem. A dummy block is not used in indirect extrusion.

Although aluminum can be extruded cold, it is usually first heated to a temperature ranging from 375 to 525°C, so that little work hardening will be imposed on the product. Heat treatment is frequently used after extrusion to achieve the desired mechanical properties.

The extrusion process requires the use of a lubricant to prevent adhesion of the aluminum to the die and ingot container walls. In hot extrusion, limited amounts of lubricant are applied to the ram and die face or to the billet ends. For cold extrusion, the container walls, billet surfaces, and die orifice must be lubricated with a thin film of viscous or solid lubricant. The lubricant most commonly used in extrusion is graphite in an oil or water base. A less common technique, spraying liquid nitrogen on the billet prior to extrusion, is also used. The nitrogen vaporizes during the extrusion process and acts as a lubricant.

5.1.4 FORGING

Closed die forging, the most prevalent method, is accomplished by hammering or squeezing the aluminum between two steel dies, one fixed to the hammer or press ram and the other to the anvil. Forging hammers, mechanical presses, and hydraulic presses can be used for the closed die forging of aluminum alloys. The heated stock is placed in the lower die and, by one or more blows of the ram, forced to take the shape of the die set. In closed die forging, aluminum is shaped entirely within the cavity created by these two dies. The die set comes together to completely enclose the forging, giving lateral restraint to the flow of the metal.

The process of open die forging is similar to that described above but in this method the shape of the forging is determined by manually turning the stock and regulating the blows of the hammer or strokes of the press. Open die forging requires a great deal of skill and only simple, roughly shaped forgings can be produced. Its use is usually restricted to items produced in small quantities and to development work where the cost of making closed-type dies is prohibitive.

The process of rolled ring forging is used in the manufacture of seamless rings. A hollow cylindrical billet is rotated between a mandrel and pressure roll to reduce its thickness and increase its diameter.

Proper lubrication of the dies is essential in forging aluminum alloys. Colloidal graphite in either water or an oil medium is usually sprayed onto the dies for this purpose.

5.1.5 DRAWING

The term drawing, when it applies to the manufacture of tube, rod, bar, or wire, refers to the pulling of metal through a die or succession of dies to reduce its diameter, alter the cross-sectional shape, or increases its hardness. In the drawing of aluminum tubing, one end of the extruded tube is swaged to form a solid point and then passed through the die. A clamp, known as a bogie, grips the swaged end of tubing. A mandrel is inserted into the die orifice, and the tubing is pulled between the mandrel and die, reducing the outside diameter and the wall thickness of the tubing. Wire, rod, and bar drawing is accomplished in a similar manner but the aluminum is drawn through a simple die orifice without using a mandrel.

In order to ensure uniform drawing temperatures and avoid excessive wear on the dies and mandrels used, it is essential that a suitable lubricant be applied during drawing. A wide variety of lubricants are used for this purpose. Heavier draws may require oil-based lubricants, but oil-in-water emulsions are used for many applications. Soap solutions may also be used for some of the lighter draws. Drawing oils are usually recycled until their lubricating properties are exhausted.

Intermediate annealing is frequently required between draws in order to restore the ductility lost by cold working of the drawn product. Degreasing of the aluminum may be required to prevent burning of heavy lubricating oils in the annealing furnaces.

5.1.6 Heat Treatment

Heat treatment is an integral part of aluminum forming and is practiced at nearly every plant in the category. It is frequently used both in-process and as a final step in forming to give the aluminum alloy the desired mechanical properties. The general types of heat treatment applied are as follows:

1. *Homogenizing*. This increases the workability and helps control recrystallization and grain growth following casting.
2. *Annealing*. This softens work-hardened and heat-treated alloys, relieves stress, and stabilizes properties and dimensions.
3. *Solution heat treatment*. This improves mechanical properties by maximizing the concentration of hardening constituents in the solid solution.
4. *Artificial aging*. This provides hardening by precipitation of constituents from the solid solution.

Homogenizing, annealing, and aging are dry processes whereas solution heat treatment typically involves significant quantities of contact cooling water.

5.1.7 Surface Treatment

A number of chemical or electrochemical treatments may be applied after the forming of aluminum or aluminum alloy products. Solvent, acid and alkaline solutions, and detergents can be used to clean soils such as oil and grease from the aluminum surface. Acid and alkaline solutions can be used to etch the product or brighten its surface. Acid solutions are also used for deoxidizing and desmutting.

Surface treatments and their associated rinses are usually combined in a single line of successive tanks. Wastewater discharges from these lines are typically commingled before treatment or discharge. In some cases, rinsewater from one treatment is reused in the rinse of another. These treatments may be used for cleaning purposes, to provide the desired finish for an aluminum formed product, or to prepare the aluminum surface for subsequent coating by processes such as anodizing, conversion coating, electroplating, painting, and porcelain enameling.

A number of different terms are commonly used in referring to sequences of surface treatments, for example, pickling lines, cleaning lines, etch lines, preparation lines, and pretreatment lines. The terminology depends, to some degree, on the purpose of the lines, but usage varies within the industry. In addition, the characteristics of wastewater generated by surface treatment are determined by the unit components of the treatment lines rather than the specific purpose of its application. Cleaning and etch line is used in this section to refer to any surface treatment processes other than solvent cleaning.

5.2 ALUMINUM FORMING INDUSTRY SUBCATEGORY DESCRIPTION

Division of the industry into subcategories provides a mechanism for addressing processes, products, and other variations that result in distinct wastewater characteristics. The aluminum forming industry is comprised of separate and distinct processes with enough variability in products and wastes to require categorization into a number of discrete subcategories. The individual processes, wastewater characteristics, and treatability comprise the most significant factors in the subcategorization of this complex industry. Other factors either served to support and substantiate the subcategorization or were shown to be inappropriate bases for subcategorization. From this evaluation, the following are the established subcategories:

1. Rolling with neat oils
2. Rolling with emulsions
3. Extrusion

4. Forging
5. Drawing with neat oils
6. Drawing with emulsions

Each industrial subcategory is broken into "core" and "additional allocation" operations. The core is defined as those operations that always occur in the subcategory or do not affect the wastewater characteristics from the subcategory facilities (e.g., dry operations, zero-pollutant-allocation operations, or operations that contribute insignificant pollutants and wastewater volume in comparison with other streams). These operations that do not contribute to the wastewater characteristics will not occur at every plant, which should not affect wastewater treatment.

Operations that may affect wastewater characteristics but are not included in the core are classified as additional allocation operations. These are ancillary operations involving discharged wastewater streams of significant pollutant concentrations and flows that may or may not be present at any one facility. If an additional allocation operation occurs at a facility, the wastewater from the operation would occur in addition to the core wastewater, with a subsequent modification to the performance expected from a treatment facility. The most common additional allocation operations are as follows:

1. Cooling water from direct chill casting
2. Quench water from heat treatment
3. Rinsewater from cleaning and etch lines

The designation of core and additional allocation operations is listed by subcategory in Table 5.1. More than one subcategory may be associated with a specific facility. A brief description of the subcategories follows.

TABLE 5.1
Summary of Core and Additional Allocation Operations Associated with Aluminum Forming Industry Subcategories

Core	Additional Allocation
Subcategory 1: Rolling with Neat Oils	
Rolling using neat oils	Solution heat treating
Roll grinding	Cleaning or etching
Degassing	Annealing
Stationary casting	
Continuous sheet casting	
Homogenizing	
Artificial aging	
Degreasing	
Cleaning or etching	
Sawing	
Stamping	
Subcategory 2: Rolling with Emulsions	
Rolling with emulsified lubricants	Direct chill casting or continuous rod casting
Roll grinding	Solution heat treatment
Degassing	Cleaning or etching
Stationary casting	

Continued

TABLE 5.1 (continued)

Core	Additional Allocation
Homogenizing	
Artificial aging	
Cleaning or etching	
Subcategory 3: Extrusion	
Extrusion die cleaning	Direct chill or continuous rod casting
Extrusion dummy block cooling	Press and solution heat treatment
Degassing	Cleaning or etching
Stationary casting	Extrusion die cleaning
Artificial aging	Annealing
Annealing	
Degreasing	
Cleaning or etching	
Subcategory 4: Forging	
Artificial aging	Forging
Annealing	Solution heat treatment
Degreasing	Cleaning or etching
Cleaning or etching	
Sawing	
Subcategory 5: Drawing with Neat Oils	
Drawing with neat oils	Continuous rod casting
Continuous rod casting	Solution heat treatment
Stationary casting	Cleaning or etching
Artificial aging	
Annealing	
Degreasing	
Cleaning or etching	
Sawing	
Stamping	
Swaging	
Subcategory 6: Drawing with Emulsions or Soaps	
Drawing with emulsions or soaps	Continuous rod casting
Continuous sheet casting	Solution heat treatment
Stationary casting	Cleaning or etching
Artificial aging	
Annealing	
Degreasing	
Cleaning or etching	

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

5.2.1 ROLLING WITH NEAT OILS

This subcategory is applicable to all wastewater discharges resulting from or associated with aluminum rolling operations in which neat oils are used as a lubricant. The rolling with neat oils subcategory consists of approximately 45 plants, 22 of which use only this process. Half of the plants (23 of 45) associated with this subcategory were also associated with one or more additional subcategories.

5.2.2 ROLLING WITH EMULSIONS

This subcategory is applicable to all wastewater discharges resulting from or associated with aluminum rolling operations in which oil-in-water emulsions are used as lubricants. The rolling with emulsions subcategory consists of approximately 23 plants, of which only one uses this process exclusively. Thus, 96% of the plants in this subcategory were also included in one or more other subcategories.

5.2.3 EXTRUSION

All wastewater discharges resulting from or associated with extrusion are applicable to this subcategory. The extrusion subcategory consists of approximately 157 plants, more than in any other subcategory. Of these plants, 140 use the extrusion process exclusively. Although most of the plants in this subcategory (89%) are not associated with any other subcategories, some overlap does occur.

5.2.4 FORGING

This subcategory is applicable to all wastewater discharges resulting from or associated with forging of aluminum or aluminum alloy products. The forging subcategory consists of approximately 15 plants, 12 of which use only this process. Thus, only 20% of the plants have operations that overlap with one or more other subcategories.

5.2.5 DRAWING WITH NEAT OILS

All wastewater discharges resulting from or associated with drawing operations that use neat oil lubricants are applicable to this subcategory. Fifty of the sixty-two plants that comprise the drawing with neat oils subcategory use this process exclusively. The remaining 12 plants in this subcategory were also associated with one or more additional subcategories.

5.2.6 DRAWING WITH EMULSIONS OR SOAPS

This subcategory is applicable to all wastewater discharges resulting from or associated with the drawing of aluminum products using oil-in-water emulsion or soap solution lubricants. Eight of the eleven plants that comprise this subcategory use the drawing with emulsions or soaps process exclusively. Overlap with other subcategories occurs at the remaining three plants.

5.3 ALUMINUM FORMING INDUSTRY WASTE CHARACTERIZATION

Wastewater characterization for the aluminum forming industry has been developed on a wastestream basis, rather than on a subcategory basis. Table 5.2 summarizes the wastewater sources reported for this industry. Wastewater flow rates identified for these sources are presented in Table 5.3.

The pollutants characteristic of the industry wastewaters are summarized in Table 5.4 through Table 5.11, for both classical and toxic pollutants. The toxic pollutant data have been developed using a verification protocol established by U.S. EPA, with the exception of the following: selenium, silver, thallium, and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCCD). Table 5.12 presents the minimum detection limit for the toxic pollutants. Any value below the minimum limit is listed in the summary tables as below detection limit (BDL).

5.3.1 DIRECT CHILL CASTING

Of the approximately 266 plants in the aluminum forming industry, 57 cast aluminum or aluminum alloys using the direct chill method. Because the ingot or billet produced by direct chill casting is used as stock for subsequent rolling or extrusion, this wastewater stream is associated with both rolling with emulsions and extrusion categories. Table 5.4 summarizes the classical and toxic pollutant data associated with the contact cooling water wastestream from direct chill casting.

TABLE 5.2
Wastewater Sources Reported in Aluminum Forming Industry Processes

Wastewater Source	Plants Known to Have Process Wastewater
Direct chill cooling	29
Continuous rod casting cooling	3
Continuous rod casting lubricant	2
Continuous sheet casting	3
Stationary mold casting	0
Air pollution control for metal treatment	5
Rolling with neat oils	45
Rolling with emulsions	27
Roll grinding emulsions	4
Extrusion die cleaning bath	11
Extrusion die cleaning rinse	5
Air pollution control for extrusion die cleaning	2
Extrusion dummy block cooling	3
Air pollution control for forging	3
Drawing with neat oils	55
Drawing with emulsions or soaps	5
Heat treatment quench	43
Air pollution control for annealing furnace	1
Annealing furnace seal	1
Degreasing solvents	2
Cleaning and etch line baths	12
Cleaning and etch line rinses	20
Air pollution control for etch lines	4
Saw oil	3
Swaging and stamping	0

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

5.3.2 ROLLING WITH EMULSIONS

Rolling operations that use oil-in-water emulsions as coolants and lubricants are found in 27 plants of the aluminum forming industry. Table 5.5 summarizes the classical and toxic pollutant data for the rolling with emulsions subcategory.

5.3.3 EXTRUSION

The wastewater characterization data for the extrusion die cleaning rinse are summarized by classical and toxic pollutants in Table 5.6.

5.3.4 FORGING

Of the approximately 15 aluminum forging plants, three use wet scrubbers to control particulates and smoke generated from the partial combustion of oil-based lubricants in the forging process.

TABLE 5.3
Summary of Wastewater Flows Reported for Aluminum Forming Industry Processes

			Wastewater Flows							
			Minimum		Mean		Median		Maximum	
Operation	Number of Plants	Number with Zero Discharges	(cu m/Mg)[a]	(gal/ton)	(cu m/Mg)	(gal/ton)	(cu m/Mg)	(gal/ton)	(cu m/Mg)	(gal/ton)
Direct chill cooling (no recycle)	16	0	0.0003	0.08	7.9	1900	0.96	230	92	22,000
Direct chill cooling (recycle)	24	6	0.0003	0.08	0.96	230	0.43	104	5.8	1400
Continuous rod casting cooling	1	0	—	—	1.0	250	—	—	—	—
Continuous sheet casting	4	2	0.001	0.24	0.0009	0.22	0.0005	0.12	0.003	0.64
Rolling with emulsions	20	0	0.0003	0.08	0.035	8.4	0.005	1.2	0.3	73
Extrusion die cleaning										
Caustic bath	11	0	0.0002	0.06	0.014	3.3	0.008	1.9	0.054	13
Rinse	5	0	0.001	0.31	0.018	4.4	0.012	2.8	0.054	13
Extrusion dummy block cooling	2	0	2.1	500	2.1	510	—	—	2.2	520
Drawing with emulsions or soaps	6	1	0.003	0.81	1700	400,000	0.67	160	10,000	2,400,000
Heat treatment quench	52	9	0.021	5	5.8	1400	2.3	560	32	7700
Annealing furnace, air pollution control	1	0	—	—	0.026	6.3	—	—	—	—
Cleaning and etch line, rinse	20	0	0.001	0.34	22	5300	5.0	1200	150	36,000
Cleaning and etch line, air pollution control	3	0	0.54	130	2.0	490	1.0	240	4.6	1100
Saw oil lubricants	6	1	0.0004	0.10	0.0018	0.42	0.001	0.25	0.006	1.5

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

[a] cu m/Mg = $m^3/10^6$ g.

TABLE 5.4
Summary of Pollutant Data for the Direct Chill Casting Subcategory Verification Data

Pollutant	Number of Samples/ Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Classical Pollutants (mg/L)				
COD	12/12	<5–420	72	<170
Suspended solids	12/12	<1–220	26	<39
Oil and grease	13/13	<5–210	68	<74
TOC	12/12	1–150	16	47
pH (pH units)	12/12	6.0–8.4	7.4	7.4
Phenols, total	12/12	<0.001–0.12	0.01	0.024
Toxic Pollutants (μg/L)				
Toxic metals				
Lead	12/12	BDL–100	<20	27
Mercury	12/12	BDL–20	1.2	3.2
Zinc	12/12	BDL–1000	100	200
Toxic organics				
Bis(2-ethylhexyl) phthalate	12/9	BDL–280	46	70
Butyl benzyl phthalate	12/4	BDL–360	130	160
Di-n-butyl phthalate	12/7	BDL–43	20	20
Di-n-octyl phthalate	12/3	BDL–94	40	46
Phenol	12/5	BDL–56	50	33
2-Chlorophenol	12/2	BDL–12	—	BDL
Benzene	12/8	BDL–13	BDL	BDL
Chloroform	12/11	BDL–96	14	22
Methylene chloride	12/12	BDL– <240	95	<98
Polychlorinated biphenyls				
PCB 1232, 1248, 1260, 1016	12/5	BDL–32	BDL	12

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, 1, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit.

The summaries of the classical and toxic pollutant data on the air pollution controls for the forging subcategory are contained in Table 5.7.

5.3.5 Drawing with Emulsions or Soaps

Eight of the 266 plants in the aluminum forming industry draw aluminum products using oil-in-water emulsions and three use soap solutions as drawing lubricants. These solutions are frequently recycled and discharged periodically after their lubrication properties are exhausted. Table 5.8 summarizes the classical and toxic pollutant data for the drawing with emulsions subcategory.

5.3.6 Heat Treatment

Heat treatment of aluminum products frequently involves the use of a water quench in order to achieve the desired metallic properties. Of the 266 aluminum forming plants, 84 use heat treatment processes that involve water quenching. The sampling data for classical and toxic pollutants from

TABLE 5.5
Summary of Pollutant Data for the Rolling with Emulsions Subcategory Verification Data

Pollutant	Number of Samples/ Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Classical Pollutants (mg/L)				
Dissolved solids	2/2	27,000–34,000	—	30,000
Suspended solids	3/3	890–3900	2400	2400
TOC	3/3	1800–23,000	6800	11,000
Phenols, total	1/1	0.24	—	—
Oil and grease	4/4	1300–31,000	19,000	11,000
Aluminum	3/3	44–210,000	20,000	77,000
Calcium	3/3	22–27,000	18,000	15,000
Magnesium	3/3	11–17,000	12,000	9400
pH (pH units)	1/1	7.0	—	—
Toxic Pollutants (μg/L)				
Metals and inorganics				
Arsenic	3/3	BDL–16	BDL	BDL
Cadmium	3/3	15–180	65	87
Chromium	3/3	41–120	120	93
Copper	3/3	630–7400	4100	4100
Cyanide	3/3	BDL–940	BDL	350
Lead	3/3	2000–57,000	12,000	24,000
Nickel	3/3	86–210	130	140
Zinc	3/3	1400–4200	2200	2600
Toxic organics				
Bis(2-ethylhexyl) phthalate	4/1	1900	—	—
Butyl benzyl phthalate	4/1	190	—	—
Di-n-butyl phthalate	4/1	19,000	—	—
2,4,6-Trichlorophenol	4/1	22	—	—
Phenol	4/2	60–9900	—	5000
Toluene	3/3	BDL–130	40	58
Ethylbenzene	3/2	40–40	—	—
Acenaphthene	4/1	95	—	—
Naphthalene	4/3	10–380	150	180
Chrysene	4/2	<10–360	—	<180
Anthracene	4/3	90–<1100	200	<460
Fluorene	4/3	40–450	70	190
Phenanthrene	4/3	90–<1100	200	<460
Pyrene	4/2	20–98	—	59
Methylene chloride	3/3	BDL–1200	BDL	400
Tetrachloroethylene	3/3	BDL–3600	10	1200
Polychlorinated biphenyls				
PCB 1242, 1254, 1221, total	3/1	63	—	—
PCB 1232, 1248, 1260, 1016, total	3/1	65	—	—
Pesticides				
4,4-DDE	3/1	BDL	—	—
Alpha-endosulfan	3/1	BDL	—	—
Endrin aldehyde	3/1	58	—	—
Alpha-BHC	3/1	BDL	—	—
Beta-BHC	3/1	18	—	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit.

TABLE 5.6
Summary of Pollutant Data for the Extrusion Subcategory Verification Data

Pollutant	Number of Samples/ Number of Detections	Range of Detections
Classical Pollutants (mg/L)		
COD	1/1	12
TOC	1/1	19
Dissolved solids	1/1	3200
Suspended solids	1/1	28
Oil and grease	1/1	8
Phenol, total	1/1	0.005
Aluminum	1/1	400
Calcium	1/1	<1
Magnesium	1/1	<1
Sulfate	1/1	60
pH (pH units)	1/1	11
Toxic Pollutants (μg/L)		
Metals and inorganics		
Cadmium	1/1	20
Chromium	1/1	90
Copper	1/1	200
Lead	1/1	600
Mercury	1/1	0.7
Zinc	1/1	100
Toxic organics		
Bis(2-ethylhexyl) phthalate	1/1	27
Methylene chloride	1/1	36

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit.

TABLE 5.7
Summary of Pollutant Data for the Forging Subcategory Verification Data

Pollutant	Number of Samples/ Number of Detections	Range of Detections
Classical Pollutants (mg/L)		
COD	1/1	350
TOC	1/1	98
Dissolved solids	1/1	390
Suspended solids	1/1	2
Oil and grease	1/1	160
Phenols, total	1/1	0.07
Aluminum	1/1	0.5
Calcium	1/1	59
Magnesium	1/1	10
Sulfate	1/1	95

Continued

TABLE 5.7 (continued)

Pollutant	Number of Samples/ Number of Detections	Range of Detections
Toxic Pollutants (μg/L)		
Toxic metals		
Lead	1/1	2000
Zinc	1/1	300
Toxic organics		
2,4-Dichlorophenol	1/1	38
Fluoranthene	1/1	18
Methylene chloride	1/1	950
2,4-Dinitrophenol	1/1	23
4,6-Dinitro-o-cresol	1/1	24
N-Nitrosodiphenylamine	1/1	17
Benzo(a)anthracene	1/1	19
Chrysene	1/1	19
Anthracene/phenanthrene	1/1	28
Pyrene	1/1	21
Polychlorinated biphenyls		
PCB 1242, 1254, 1221	1/1	1.3

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

TABLE 5.8
Summary of Pollutant Data for fhe Drawing Oil Emulsion-Soap Subcategory Verification Data

Pollutant	Number of Samples/ Number of Detections	Range of Detections
Classical Pollutants (mg/L)		
Oil and grease	1/1	1500
pH (pH units)	1/1	7.2
Aluminum	1/1	340
Calcium	1/1	130
Magnesium	1/1	37
Toxic Pollutants (μg/L)		
Toxic organics		
1,1,1-Trichloroethane	1/1	530
1,1-Dichloroethane	1/1	97
p-Chloro-m-cresol	2/1	28
2-Chlorophenol	2/1	130
2,4-Dinitrotoluene	2/1	77
Ethylbenzene	1/1	15
Methylene chloride	1/1	3

Continued

TABLE 5.8 (continued)

Pollutant	Number of Samples/ Number of Detections	Range of Detections
Isophorone	2/1	39
Bis(2-ethylhexyl) phthalate	1/1	34
Di-n-butyl phthalate	1/1	23
Di-n-octyl phthalate	1/1	23
Toluene	1/1	200
Pesticides		
Alpha-endosulfan	2/1	BDL
Polychlorinated biphenyls		
PCB 1254	2/1	BDL
PCB 1248	2/1	BDL
Metals and inorganics		
Arsenic	1/1	37
Cadmium	1/1	11
Chromium	1/1	8000
Copper	1/1	480
Lead	1/1	140
Nickel	1/1	34
Zinc	1/1	46,000

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit.

TABLE 5.9
Summary of Pollutant Data for the Rolling Heat Treatment Quench Subcategory Verification Data

Pollutant	Number of Samples/Number of Detections	Range of Detections	Mean of Detections
Classical Pollutants (mg/L)			
Oil and grease	2/2	12–13	12
Suspended solids	2/1	3	—
pH (pH units)	2/2	7.1–7.9	7.5
Aluminum	2/2	<0.2–0.4	<0.3
Calcium	2/2	41–51	46
Iron	2/2	<0.1–<0.1	—
Magnesium	2/2	11–20	16
COD	2/2	<5–7	<6
Dissolved solids	2/2	110–410	260
Sulfate	2/2	<3–70	<36
TOC	2/2	<1–2	<2
Phenols, total	2/2	0.01–0.01	—

Continued

TABLE 5.9 (continued)

Pollutant	Number of Samples/ Number of Detections	Range of Detections	Mean of Detections
Toxic Pollutants (μg/L)			
Toxic organics			
Chloroform	2/2	BDL–20	12
Methylene chloride	2/2	38–<40	<39
Metals and inorganics			
Nickel	2/2	BDL–20	12

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit.

TABLE 5.10
Summary of Pollutant Data for the Heat Treatment Quench Forging Subcategory Verification Data

Pollutant	Number of Samples/ Number of Detections	Range of Detections	Median of Detections	Mean of Detections
	Wastestream: Forging			
Classical Pollutants (mg/L)				
Oil and grease	3/3	4–87	14	35
Suspended solids	3/3	4–240	22	88
pH (pH units)	3/3	7.7–8.2	—	8.0
Aluminum	4/4	<1–9	<1.1	<3
Calcium	4/4	38–80	58	58
Magnesium	4/4	8–35	21	21
COD	3/3	<5–56	18	<26
Dissolved solids	4/4	190–1400	690	740
Sulfate	4/4	30–330	130	160
TOC	3/3	<2–14	3	<6.3
Phenols, total	3/3	0.003–0.8	0.02	0.27
Toxic Pollutants (μg/L)				
Toxic organics				
Bis (2-ethylhexyl) phthalate	4/4	BDL–890	BDL	240
Metals and inorganics				
Cadmium	4/4	BDL–12	<10	<6
Chromium	4/4	7–72,000	23,000	30,000
Copper	4/4	<50–380	85	<150
Lead	4/3	<50–17,000	60	<5700
Mercury	4/4	BDL–0.5	<0.2	0.24
Nickel	4/4	BDL–<20	<7	<9.1
Zinc	4/4	50–5200	120	1400

Continued

TABLE 5.10 (continued)

Pollutant	Number of Samples/ Number of Detections	Range of Detections	Median of Detections	Mean of Detections
		Wastestream: Drawing		
Classical Pollutants (mg/L)				
Oil and grease	1/1	20	—	—
Suspended solids	1/1	19	—	—
pH (pH units)	1/1	8.2	—	—
COD	1/1	92,000	—	—
Phenols, total	1/1	0.005	—	—
TOC	1/1	19,000	—	—
Toxic Pollutants (µg/L)				
Toxic organics				
Benzene	1/1	2100	—	—
Chloroform	1/1	12,000	—	—
Methylene chloride	1/1	31,000	—	—
Bis(2-ethylhexyl) phthalate	1/1	310	—	—
Di-n-butyl phthalate	1/1	330	—	—
Diethyl phthalate	1/1	160	—	—
Dimethyl phthalate	1/1	20	—	—
Tetrachloroethylene	1/1	<4000	—	—
Toluene	1/1	320	—	—
Trichloroethylene	1/1	430	—	—
Polychlorinated biphenyls				
PCB 1242, 1254, 1221	1/1	4.5	—	—
PCB 1232, 1248, 1260, 1016	1/1	3.2	—	—
Metals and inorganics				
Antimony	1/1	<100	—	—
Copper	1/1	<16	—	—
Cyanide	1/1	1300	—	—
Mercury	1/1	10	—	—
		Wastestream: Extrusion Press		
Classical Pollutants (mg/L)				
Oil and grease	5/5	8–130	17	37
Suspended solids	5/5	<1–59	3	<19
pH (pH units)	5/5	7.4–9.2	7.8	8.1
COD	5/5	<5–210	74	<74
TOC	5/5	<1–88	27	<33
Phenols, total	4/4	0.001–0.015	0.012	0.01
Toxic Pollutants (µg/L)				
Toxic organics				
2-Chlorophenol	5/1	20	—	—
1,2-*trans*-Dichloroethylene	5/2	BDL–13	—	9
Methylene chloride	5/5	49–210,000	100	42,000
Bis(2-ethylhexyl)phthalate	5/4	BDL–100	18	36
Butyl benzyl phthalate	5/5	BDL–67	BDL	20

Continued

TABLE 5.10 (continued)

Pollutant	Number of Samples/ Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Metals and inorganics				
Copper	4/4	BDL–100	36	44
Nickel	4/4	BDL–<17	BDL	<6.1
		Wastestream: Extrusion Solution		
Classical Pollutants (mg/L)				
Oil and grease	1/1	41	—	—
Suspended solids	2/2	<2–2	—	<2
pH	2/2	7.3–7.3	—	—
Aluminum	2/2	<0.5–0.54	—	<0.5
Calcium	2/2	38–58	—	48
Magnesium	2/2	5.3–25	—	15
COD	2/2	7–20	—	14
Dissolved solids	2/2	160–580	—	370
Sulfate	2/2	7–120	—	64
TOC	2/2	1.8–2.7	—	2.2
Phenols, total	2/2	0.001–0.01	—	0.005
Toxic Pollutants (μg/L)				
Toxic organics				
Methylene chloride	2/2	10–630	—	320
Metals and inorganics				
Chromium	2/2	18–5100	—	2600
Nickel	2/2	BDL–18	—	10

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

BDL, below detection limit.

heat treatment quenching processes are presented in Tables 5.9 and 5.10 by the aluminum forming operation that it follows.

5.3.7 ETCH OR CLEANING

Thirty plants in the aluminum forming industry use etch or cleaning lines. Rinsing is usually required following successive chemical treatments within these etch or cleaning lines. Wastewater discharge values tend to increase as the number of rinses increase. Table 5.11 summarizes the classical and toxic pollutant data for etch line rinses.

5.4 PLANT-SPECIFIC DESCRIPTION OF CASE HISTORIES

5.4.1 PLANT A: CASE HISTORY

A very limited amount of individual plant specific data for the aluminum forming industry is available. Data available on the influent and effluent streams are discussed briefly in the following subsections for specific plants. This aluminum processing plant uses lime precipitation (pH adjustment) followed by coagulant addition and sedimentation as its treatment system. Data

TABLE 5.11
Summary of Pollutant Data for the Etch Line Rinses Subcategory Verification Data

Pollutant	Number of Samples/Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Classical Pollutants (mg/L)				
Oil and grease	18/16	2–47	11	16
Suspended solids	18/18	<1–2700	95	<300
pH (pH units)	16/16	1.1–12	7.0	6.4
Aluminum	19/19	0.9–1200	100	300
Calcium	19/18	0.03–1200	26	90
Iron	18/15	0.1–200	1.9	20
Magnesium	1/1	10	—	—
COD	17/17	<5–280	35	<90
Dissolved solids	19/19	20–48,000	660	4600
Sulfate	19/19	1–9400	40	600
TOC	18/18	<1–180	10	<31
Phenols, total	18/18	0.003–0.04	0.008	0.01
Toxic Pollutants (µg/L)				
Toxic organics				
Acenaphthene	19/5	BDL–17	BDL	10
Benzene	19/9	BDL–34	BDL	12
Chloroform	19/18	BDL–75	16	24
1,2-*trans*-Dichloroethyl	19/5	BDL–110	BDL	22
2,4-Dimethyl phenol	19/2	BDL–19	—	12
Methylene chloride	19/18	BDL–2100	120	380
Isophorone	19/2	BDL–16	—	10
4-Nitrophenol	19/1	18	—	—
Phenol	19/9	BDL–63	BDL	12
Bis(2-ethylhexyl) phthalate	19/18	BDL–120	BDL	26
Butyl benzyl phthalate	19/9	BDL–66	BDL	11
Di-n-butyl phthalate	19/14	BDL–68	BDL	10
Di-n-octyl phthalate	19/5	BDL–38	BDL	12
Diethyl phthalate	19/9	BDL–22	BDL	BDL
Chlordane	19/12	BDL–BDL	—	—
Polychlorinated biphenyls				
PCB 1242, 1254, 1221	19/11	BDL–16	BDL	BDL
PCB 1232, 1248, 1260, 101	19/12	BDL–20	BDL	BDL
Metals and inorganics				
Arsenic	19/17	BDL–200	BDL	17
Beryllium	19/15	BDL–<20	BDL	<10
Cadmium	19/15	BDL–210	<10	<23
Chromium	19/15	7–860,000	110	52,000
Copper	19/15	9–2,400,000	200	160,000
Lead	19/16	BDL–10,000	250	1100
Mercury	19/15	BDL–21	0.5	2.0
Nickel	19/15	BDL–2800	<6	220
Zinc	19/15	BDL–2,100,000	300	140,000

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

BDL, below detection limit.

TABLE 5.12
Minimum Detection Limits for Toxic Pollutants

Toxic Pollutant	Concentration (μg/L)
Organic pollutants	10
Pesticides	5
Metals	
Antimony	100
Arsenic	10
Asbestos	1×10^7 fibers/L
Beryllium	10
Cadmium	2
Chromium	5
Copper	9
Cyanide	100
Lead	20
Mercury	0.1
Nickel	5
Selenium	10
Silver	20
Thallium	100
Zinc	50

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

on the pollutant removal efficiency at Plant A are summarized in Table 5.13. No production or water usage data are available for this plant.

5.4.2 PLANT B: CASE HISTORY

No plant-specific identification number was available for this facility. The wastewater from Plant B contains pollutants from both metals processing and finishing operations. It is treated by precipitation–settling followed by filtration with a rapid sand filter. A clarifier is used to remove much of the solids load. Table 5.14 summarizes the data on pollutant removal efficiency at Plant B.

5.4.3 U.S. EPA DATA ON FULL-SCALE TREATMENT OF ALUMINUM FORMING WASTEWATERS

U.S. EPA has documented case histories of full-scale treatment of aluminum forming wastewaters, which are included in Appendixes A, B, C, and D of this chapter for reference. The detailed theories and principles of the full-scale treatment processes can be found in the literature.[8–10]

Appendix A presents the actual data on a full-scale treatment of aluminum forming wastewater by emulsion breaking and oil–water separation. Either chemical emulsion breaking (CEB) or thermal emulsion breaking (TEB) can be used for breaking the emulsified oil in wastewater. Once the emulsified oil is freed as oil drops, it can be easily removed by an API oil–water separator (Figure 5.1), a parallel plate separator (Figure 5.2), an ultrafiltration unit, or a dissolved air flotation clarifier.[8–10] It is very encouraging to note that over 94% of TSS, COD, TOC, O&G (oil and grease), cadmium, chromium, copper, lead, nickel, zinc, acenaphthene, phenol, bis-(2-ethylhexyl)-phthalate, bi-n-butyl phthalate, anthracene, fluorine, phenanthrene, pyrene, endrin-aldehyde, and PCB can be successfully removed by these preliminary treatment processes.

Appendix B presents the U.S. EPA data on a full-scale treatment of aluminum forming wastewater by emulsion breaking and ultrafiltration. After emulsion breaking, various oil–water separation

TABLE 5.13
Removal of Pollutants by Lime Precipitation at Metal Processing Plant A[a]

Pollutant (mg/L)	Raw Wastewater	Treated Effluent	Percent Removal
pH (pH units)	2.8	7.1	—
TSS	24	11	54
Copper	180,000	2000	99
Zinc	110,000	8700	92

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

[a] Data are based on the average of three influent/effluent samples.

TABLE 5.14
Removal of Pollutants by a Combination of Lime Precipitation, Sedimentation, and Filtration at Plant B[a]

Pollutant (μg/L)	Raw Wastewater	Treated Effluent	Percent Removal
Chromium	5900	38	99
Copper	170	11	94
Nickel	3300	180	95
Zinc	2900	35	99
Iron	22900	400	98

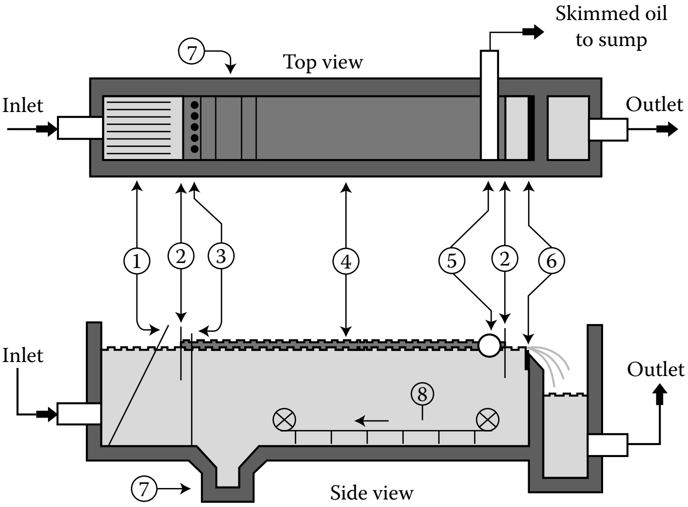
Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

[a] Treated effluent performance reported for the period 1974–1979.

processes can be used for separation of the freed oil together with other pollutants from the wastewater. This specific set of treatment data documents the efficiency of the emulsion breaking and ultrafiltration treatment system. Again, Appendix B shows that the preliminary treatment system of emulsion breaking and ultrafiltration can achieve over 90% of O&G, TSS, COD, TOC, benzene, 2,4,6-trichlorophenol, bis-(2-ethylhexyl) phthalate, diethyl phythalate, tetrachloroethylene, and PCB.

Appendix C documents the U.S. EPA data on full-scale treatment of aluminum forming wastewater by chemical precipitation and clarification. It is important to note that Appendixes A and B present the preliminary treatment performance by which main organics are removed. The preliminary treatment step will not remove heavy metals in a significant amount. Accordingly, the system presented in Appendix C is a secondary treatment system following the preliminary treatment step. Appendix C shows that in the secondary treatment system consisting of chemical precipitation, sedimentation clarification can further achieve over 90% removal of oil and grease, and total toxic organics (TTO), such as fluoranthene, methylene chloride, 2,4-dinitrophenol, n-nitrosodiphenylamine, chrysene, and pyrene. Although lead was removed by 69%, the removal of other major heavy metals (chromium, copper, mercury, nickel, and zinc) was insignificant.

Appendix D presents the U.S. EPA data on a full-scale treatment of aluminum forming wastewater by chromium reduction, chemical precipitation, and sedimentation clarification. Chromium reduction, as described in detail by Wang, Hung and Shammas,[9] is an important step prior to



1 Trash trap (inclined rods)
2 Oil retention baffles
3 Flow distributors (vertical rods)
4 Oil layer
5 Slotted pipe skimmer
6 Adjustable overflow weir
7 Sludge sump
8 Chain and flight scraper

FIGURE 5.1 Typical gravimetric API oil–water separator. (*Source:* Wikipedia Encyclopedia, API Oil–Water Separator, http://en.wikipedia.org/wiki/API_oil-water_Separator.)

chemical precipitation and clarification. The treatment system documented in Appendix D consists of the following:

1. Chromium reduction using sulfuric acid
2. Neutralization and chemical precipitation using lime and/or sodium hydroxide
3. Sedimentation for clarification

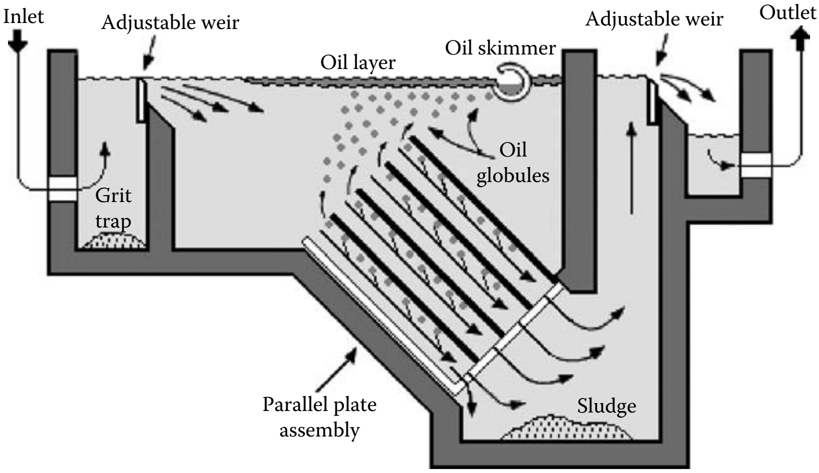


FIGURE 5.2 Typical parallel plate oil–water separator. (*Source:* Wikipedia Encyclopedia, API Oil–Water Separator, http://en.wikipedia.org/wiki/API_oil-water_Separator.)

TABLE 5.15
Removal of Pollutants by Sodium Hydroxide Precipitation

Pollutant (μg/L)	Raw Wastewater	Treated Effluent	Percent Removal
pH (pH units)	2.3	9	—
Chromium	74	BDL	93[a]
Copper	65	17	74
Iron	11,000	880	92
Lead	1300	120	91
Manganese	0.11	0.05	55
Nickel	61	31	49
Zinc	120	12	90
TSS	—	12,000	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

BDL, below detection limit.

[a] Approximate value.

It should be noted that dissolved air flotation (DAF) is a more effective process for clarification.[8–10] As shown in Appendix D, with an additional step of chromium reduction, the secondary treatment system effectively removed chromium (over 99%), copper (89%), cadmium (64%), lead (67%), and zinc (77%).

5.5 POLLUTANT REMOVABILITY

This section describes the treatment techniques currently used or available to remove or recover wastewater pollutants normally generated by aluminum forming facilities. In general, these pollutants are removed by oil removal (skimming, emulsion breaking, and flotation), chemical precipitation and sedimentation, or filtration.[6–13]

TABLE 5.16
Removal of Pollutants by Lime and Sodium Hydroxide Precipitations

Pollutant	Raw Wastewater	Treated Effluent	Percent Removal
pH (pH units)	9.4	8.3	—
Aluminum (mg/L)	35	0.35	99
Copper (mg/L)	670	BDL	99[a]
Iron (mg/L)	150	0.55	>99
Manganese (mg/L)	210	0.12	>99
Nickel (mg/L)	6100	BDL	>99[a]
Selenium (mg/L)	29,000	BDL	>99[a]
Titanium (mg/L)	130	BDL	>99[a]
Zinc (mg/L)	17,000	27	>99
TSS (mg/L)	3600	12	>99

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

BDL, below detection limit.

[a] Approximate value.

TABLE 5.17
Removal of Pollutants by Sulfide Precipitation at Three Plants

Pollutant	Raw Wastewater	Treated Effluent	Percent Removal
Plant 1			
pH (pH units)	5.9	8.5	—
Chromium, hexavalent (mg/L)	26,000	<14	>99
Chromium (mg/L)	32,000	<40	>99
Iron (mg/L)	0.52	0.10	81
Zinc (mg/L)	40,000	<70	>99
Plant 2			
pH (pH units)	7.7	7.4	—
Chromium, hexavalent (mg/L)	22	<20	>9
Chromium (mg/L)	2400	<100	>99
Iron (mg/L)	110	0.6	>99
Nickel (mg/L)	680	100	>85
Zinc (mg/L)	34,000	100	>99
Plant 3			
Chromium, hexavalent (mg/L)	11,000	BDL	>99[a]
Chromium (mg/L)	18,000	BDL	>99[a]
Copper (mg/L)	29	BDL	83[a]
Zinc (mg/L)	60	BDL	92[a]

Source: U.S. EPA, References 1, 2, and 5.

BDL, below detection limit.

[a] Approximate value.

Most of the pollutants may be effectively removed by precipitation of metal hydroxides or carbonates using a reaction with lime, sodium hydroxide, or sodium carbonate. For some, improved removals are provided by the use of sodium sulfide or ferrous sulfide to precipitate the pollutants as sulfide compounds with very low solubilities. After soluble metals are precipitated as insoluble flocs, one of the water–solid separators (such as dissolved air flotation, sedimentation, centrifugation, membrane filtration, and so on) can be used for flocs removal.[9–11] The effectiveness of pollutant removal by several different precipitation methods is summarized in Tables 5.15–5.17.

Table 5.18 presents the removability of pollutants by two types of skimming systems:

1. The API system
2. The TEB system

API stands for the American Petroleum Institute and TEB stands for Thermal Emulsion Breaking. Figures 5.1 and 5.2 show two typical types of oil–water separators, gravimetric and parallel plate.[7] A dissolved air flotation (DAF) clarifier is commonly used for polishing the effluent from an oil–water separator.[8–10,13]

5.6 TREATMENT TECHNOLOGY COSTS

The investment cost, operating, and maintenance costs, and energy costs for the application of control technologies to the wastewaters of the Aluminum Forming Industry have been analyzed.

TABLE 5.18
Removal of Pollutants by Two Types of Skimming Systems

Pollutant	Raw Wastewater	Treated Effluent	Percent Removal
API System[a]			
Oil and grease (mg/L)	230,000	15	>99
Chloroform (mg/L)	23	BDL	78[c]
Methylene chloride (μg/L)	13	12	8
Naphthalene (μg/L)	2300	BDL	>99[c]
N-nitrosodiphenylamine (μg/L)	59,000	180	>99
Bis(2-ethylhexyl) phthalate (μg/L)	11,000	27	>99
Butylbenzyl phthalate (μg/L)	BDL	BDL	NM
Di-n-octyl phthalate (μg/L)	19	BDL	74[c]
Anthracene-phenanthrene (μg/L)	16,000	14	>99
Toluene (μg/L)	20	12	40
TEB System[b]			
Oil and grease (mg/L)	2600	10	>99
Chloroform (μg/L)	BDL	BDL	NM
Methylene chloride (μg/L)	BDL	BDL	NM
Naphthalene (μg/L)	1800	BDL	>99[c]
Bis (2-ethylhexyl) phthalate (μg/L)	1600	18	99
Diethyl phthalate (μg/L)	17	BDL	71[c]
Anthracene-phenanthrene (μg/L)	140	BDL	96[c]

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

BDL, below detection limits; NM, not meaningful.

[a] API, American Petroleum Institute oil–water separator.

[b] TEB, thermal emulsion breaker.

[c] Approximate value.

These costs were developed to reflect the conventional use of technologies in this industry. Several unit operation/unit process configurations have been analyzed for the cost of application of technologies and to select the best practicable control technology (BPT) and best applicable technology (BAT) level of treatment. The detailed presentation of the applicable treatment technologies, cost methodology, and cost data are available in the literature.[1–4] Specifically the U.S. EPA Report W-83-13, "Cost Effectiveness Analysis of Effluent Guidelines and Standards for the Aluminum Forming Category" reports the results of a cost-effectiveness (CE) analysis of alternative water pollution control technologies for the aluminum forming category.[4] The primary cost of interest in the U.S. EPA report is the total annualized cost in complying with the regulations incurred by industry. The 1983 costs can be easily updated to the current cost,[12,13] or any future costs using the cost indexes announced periodically by the U.S. Army Corps of Engineers (U.S. ACE)[14] or *Engineering News Record* of McGraw-Hill Book Company, NY.

5.7 ALUMINUM FORMING INDUSTRIAL EFFLUENT LIMITATIONS

The effluent limitations of all aluminum forming operations representing (a) the degree of effluent reduction attainable by the application of the BPT currently available; and (b) the degree of effluent reduction attainable by the application of the BAT economically achievable, can be found from the

TABLE 5.19
U.S. EPA Aluminum Forming Industry Effluent Guidelines and Categorical Regulations Summary (April 6, 2001)

Industrial Category Category Description	40 CFR Reference	SIC Codes (Partial List)	Subparts	Promulgation Date	New Source Date	Regulated Parameters for Pretreatment
Aluminum Forming Processes by which aluminum or aluminum alloys are changed in size and shape. Processes include rolling, extrusion, forging, and drawing.	467	3353 3354 3355 3357 3463	A. Rolling with neat oils B. Rolling with emulsions C. Extrusion D. Forging E. Drawing with neat oils F. Drawing with emulsions or soaps	10/24/83	11/22/82	Cr, CN, Zn, TTO

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Aluminum Forming Point Source Category*, Vols. 1 & 2, U.S. EPA, Washington, DC, 1984; U.S. EPA, *Aluminum Forming Point Source Category*, 2008.

U.S. Code of Federal Register 40CFR–Chapter I, Part 467, p. 615, Aluminum Forming Point Source Category, available at http://www.access.gpo.gov.[5] Table 5.19 indicates that the regulated parameters for pretreatment of aluminum forming industrial wastewater are chromium, cyanide, zinc, and total toxic organics (TTO).

5.8 TECHNICAL TERMINOLOGIES OF ALUMINUM FORMING OPERATIONS AND POLLUTION CONTROL

1. Aluminum forming is a set of manufacturing operations in which aluminum and aluminum alloys are made into semifinished products by hot or cold working.
2. Ancillary operation is a manufacturing operation that has a large flow, discharges significant amounts of pollutants, and may not be present at every plant in a subcategory, but when present is an integral part of the aluminum forming process.
3. Contact cooling water is any wastewater that contacts the aluminum workpiece or the raw materials used in forming aluminum.
4. Continuous casting is the production of sheet, rod, or other long shapes by solidifying the metal while it is being poured through an open-ended mold using little or no contact cooling water. Continuous casting of rod and sheet generates spent lubricants, and rod casting also generates contact cooling water.
5. Degassing is the removal of dissolved hydrogen from the molten aluminum prior to casting. Chemicals are added and gases are bubbled through the molten aluminum. Sometimes a wet scrubber is used to remove excess chlorine gas.
6. Direct chill casting is the pouring of molten aluminum into a water-cooled mold. Contact cooling water is sprayed onto the aluminum as it is dropped into the mold, and the aluminum ingot falls into a water bath at the end of the casting process.
7. Drawing is the process of pulling metal through a die or succession of dies to reduce the metal's diameter or alter its shape. There are two aluminum forming subcategories based

on the drawing process. In the drawing with neat oils subcategory, the drawing process uses pure or neat oil as a lubricant. In the drawing with emulsions or soaps subcategory, the drawing process uses an emulsion or soap solution as a lubricant.

8. Emulsions are stable dispersions of two immiscible liquids. In the aluminum forming category this is usually an oil and water mixture.
9. Cleaning or etching is a chemical solution bath and a rinse or series of rinses designed to produce a desired surface finish on the workpiece. This term includes air pollution control scrubbers, which are sometimes used to control fumes from chemical solution baths. Conversion coating and anodizing when performed as an integral part of the aluminum forming operations are considered cleaning or etching operations. When conversion coating or anodizing are covered here they are not subject to regulation under the provisions of the U.S. 40 CFR Part 433, Metal Finishing.
10. Extrusion is the application of pressure to a billet of aluminum, forcing the aluminum to flow through a die orifice. The extrusion subcategory is based on the extrusion process.
11. Forging is the exertion of pressure on dies or rolls surrounding heated aluminum stock, forcing the stock to change shape and in the case where dies are used to take the shape of the die. The forging subcategory is based on the forging process.
12. Heat treatment is the application of heat of specified temperature and duration to change the physical properties of the metal.
13. Hot water seal is a heated water bath (heated to approximately 180°F) used to seal the surface coating on formed aluminum that has been anodized and coated. In establishing an effluent allowance for this operation, the hot water seal shall be classified as a cleaning or etching rinse.
14. In-process control technology is the conservation of chemicals and water throughout the production operations to reduce the amount of wastewater to be discharged.
15. Neat oil is pure oil with no or few impurities added. In aluminum forming its use is mostly as a lubricant.
16. Rolling is the reduction in thickness or diameter of a workpiece by passing it between lubricated steel rollers. There are two subcategories based on the rolling process. In the rolling with neat oils subcategory, pure or neat oils are used as lubricants for the rolling process. In the rolling with emulsions subcategory, emulsions are used as lubricants for the rolling process.
17. The term Total Toxic Organics (TTO) means the sum of the masses or concentrations of each of the following toxic organic compounds, which is found in the discharge at a concentration greater than 0.010 mg/L:
    i. p-Chloro-m-cresol
    ii. 2-Chlorophenol
    iii. 2,4-Dinitrotoluene
    iv. 1,2-Diphenylhydrazine
    v. Ethybenzene
    vi. Fluoranthene
    vii. Isophorone
    viii. Napthalene
    ix. N-Nitro sodi phenyl amine
    x. Phenol
    xi. Benzo (a) pyrene
    xii. Benzo (ghi) perylene
    xiii. Fluorene
    xiv. Phenanthrene
    xv. Dibenzo (a,h)
    xvi. Anthracene

   xvii. Indeno (1,2,3-c,d) pyrene
   xviii. Pyrene
   xix. Tetrachloroethylene
   xx. Toluene
   xxi. Trichloroethylene
   xxii. Endosulfan sulfate
   xxiii. Bis(2-ethyl hexyl)phthalate
   xxiv. Diethylphthalate
   xxv. 3,4-Benzofluoranthene
   xxvi. Benzo (k) fluoranthene
   xxvii. Chrysene
   xxviii. Acenaphthylene
   xxix. Anthracene
   xxx. Di-n-butyl phthalate
   xxxi. Endrin
   xxxii. Endrin aldehyde
   xxxiii. PCB 1242, 1254, 1221
   xxxiv. PCB 1232, 1248, 1260, 1016
   xxxv. Acenaphthene

18. Stationary casting is the pouring of molten aluminum into molds and allowing the metal to air cool.
19. Wet scrubbers are air pollution control devices used to remove particulates and fumes from air by entraining the pollutants in a water spray.
20. BPT means the best practicable control technology currently available under the U.S. Federal Act Section 304(b)(1).
21. BAT means the best available technology economically achievable under the U.S. Federal Act Section 304(b)(2)(B).
22. BCT means the best conventional pollutant control technology under U.S. Federal Act Section 304(b)(4).
23. The production normalizing mass (kkg) for each core or ancillary operation is the mass (off-kkg or off-lb) processed through that operation.
24. The term off-kilogram (off-pound) shall mean the mass of aluminum or aluminum alloy removed from a forming or ancillary operation at the end of a process cycle for transfer to a different machine or process.

APPENDIX A
Full Scale Treatment of Aluminum Forming Wastewater by Emulsion Breaking and Oil-Water Separation

Removal Data

Sampling: Three 24-Hour or One 72-Hour Composite

	Concentration		
Pollutant/Parameter	**Influent**	**Effluent**	**Percent Removal**
Classical Pollutants (mg/L)			
Suspended solids	760	12	98
COD	80,000	830	99
TOC	39,000	260	99
Phenol	0.21	0.21	0
pH, pH units	NA	4.8	NM
Oil and grease	18,000	42	99
Toxic Pollutants (μg/L)			
Arsenic	BDL	BDL	NM
Cadmium	<200	5	>98
Chromium	<1000	20	>98
Copper	7000	BDL	99[a]
Cyanide	BDL	BDL	NM
Lead	<3000	30	99
Mercury	<70	BDL	NM
Nickel	<1000	40	>96
Zinc	<7000	200	>97
Acenaphthene	5700	6	>99
Benzene	BDL	BDL	NM
Chloroform	16	20	NM
Ethylbenzene	30	BDL	83
Methylene chloride	F400	330	>18
Phenol	90	ND	>99
Bis(2-ethylhexyl) phthalate	1200	44	94
Di-n-butyl phthalate	1300	49	94
Diethyl phthalate	820	65	92
Anthracene	700	ND	>99
Fluorene	330	ND	>99
Phenanthrene	1000	ND	>99
Pyrene	41	ND	>99
Tetrachloroethylene	20	14	30
Toluene	30	BDL	83[a]
4,4-DDE	BDL	BDL	NM
Endrin-aldehyde	14	ND	>99
alpha-BHC	BDL	ND	NM
beta-BHC	ND	BDL	NM
PCB-1242, 1254, 1221	76	BDL	97
PCB-1232, 1248, 1260, 1016	160	BDL	98

Source: U.S. EPA. *Treatability Manual*. Vols. 1–3. U.S. EPA, Washington, DC, 1981.

Blanks indicate data not available.

BDL, below detection limit.

ND, not detected.

NM, not meaningful.

[a] Approximate value.

APPENDIX B

Full Scale Treatment of Aluminum Forming Wastewater by Emulsion Breaking and Ultrafiltration

Removal Data

Sampling: Three 24-Hour or One 72-Hour Composite

	Concentration		
Pollutant/Parameter	**Influent**	**Effluent**	**Percent Removal**
Classical Pollutants (mg/L)			
Oil and grease	13	0.11	99
Suspended solids	2.6	0.019	99
COD	31	2.4	92
TOC	12	1.0	92
Phenol	0.022	0.016	27
pH, pH units	7.9	8.0	NM
Toxic Pollutants (μg/L)			
Arsenic	BDL	BDL	NM
Cadmium	ND	BDL	NM
Chromium	ND	<68	NM
Copper	ND	BDL	NM
Cyanide	BDL	BDL	NM
Lead	ND	BDL	NM
Mercury	ND	1	NM
Nickel	ND	<10	NM
Zinc	ND	BDL	NM
Acenaphthene	ND	3	NM
Benzene	40	ND	99[a]
2,4,6-Trichlorophenol	500	ND	99[a]
Chloroform	17	62	NM
Ethylbenzene	30	36	NM
Methylene chloride	67	320	NM
Naphthalene	ND	66	NM
Phenol	7900	9700	NM
Bis(2-ethylhexyl) phthalate	820	BDL	99[a]
Di-n-butyl phthalate	93	13	86
Diethyl phthalate	110	BDL	95[a]
Tetrachloroethylene	3000	200	93
Toluene	17	BDL	71[a]
4,4-DDE	7	BDL	64[a]
Alpha-endosulfan	BDL	BDL	NM
Endrin aldehyde	BDL	BDL	NM
Alpha-BHC	12	BDL	79[a]
Beta-BHC	5	BDL	50[a]
PCB-1242, 1254, 1221	110	BDL	98[a]
PCB-1232, 1248, 1260, 1016	360	BDL	99[a]

Source: U.S. EPA. *Treatability Manual*. Vols. 1–3. U.S. EPA, Washington, DC, 1981.

Blanks indicate data not available.

ND, not detected.

NM, not meaningful.

BDL, below detection limit.

[a] Approximate value.

APPENDIX C

Full Scale Treatment of Aluminum Forming Wastewater by Chemical Precipitation and Clarification

Removal Data

Sampling: Three 24-Hour or One 72-Hour Composite

	Concentration		
Pollutant/Parameter	**Influent**	**Effluent**	**Percent Removal**
Classical Pollutants (mg/L)			
Oil and grease	86	15	99
Suspended soilds	450	710	NM
COD	260	280	NM
TOC	75	74	1
Phenol	0.003	0.002	33
pH, pH units	2.8	3.7	NM
Toxic Pollutants (μg/L)			
Chromium	900,000	790,000	12
Copper	2,200,000	2,200,000	0
Cyanide	BDL	BDL	NM
Lead	3200	1000	69
Mercury	<1	<1	NM
Nickel	2600	2400	8
Zinc	2,000,000	1,800,000	10
Fluoranthene	10	ND	>99
Methylene chloride	260	15	93
2,4-Dinitrophenol	37	ND	>99
N-nitrosodiphenylamine	67	ND	>99
Chrysene	10	ND	>99
Anthracene/phenanthrene	<26	BDL	NM
Pyrene	16	ND	>99

Source: U.S. EPA. *Treatability Manual*. Vols. 1–3. U.S. EPA, Washington, DC, 1981.

Blanks indicate data not available.

BDL, below detection limit.

ND, not detected.

NM, not meaningful.

APPENDIX D

Full Scale Treatment of Aluminum Forming Wastewater by Chromium Reduction, Chemical Precipitation, and Sedimentation Clarification

Removal Data

Sampling: Three 24-Hour or One 72-Hour Composite

	Concentration		
Pollutant/Parameter	**Influent**	**Effluent**	**Percent Removal**
Classical Pollutants (mg/L)			
Oil and grease	5	< 95	NM
Suspended solids	<2	<5	NM
COD	20	30	NM
TOC	13	9.7	2.3
Phenol	0.003	0.009	NM
pH, pH units	2.6	9.8	NM
Toxic Pollutants (µg/L)			
Cadmium	2.8	BDL	64[a]
Chromium	100,000	90	>99
Copper	40	BDL	89[a]
Lead	30	BDL	67[a]
Mercury	3.4	<5	NM
Zinc	110	BDL	77[a]
Methylene chloride	30	60	NM
Bis(2-ethylhexyl) phthalate	ND	BDL	NM

Source: U.S. EPA. *Treatability Manual*. Vols. 1–3. U.S. EPA, Washington, DC, 1981.

Blanks indicate data not available.

BDL, below detection limit.

ND, not detected.

NM, not meaningful.

[a] Approximate value.

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6 Treatment of Nickel-Chromium Plating Wastes

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CONTENTS

6.1 INTRODUCTION

Applicable local, state, and federal environmental laws require that the waste generated by the nickel-chromium plating process be pretreated to provide a discharge acceptable to the public wastewater treatment system.

The specific purpose of this chapter is to describe the chemical and physical pretreatment methods required for nickel-chromium plating wastewater, to describe the upgrades needed by a municipal wastewater treatment system to manage this waste, and to relate the methods and upgrades to the operation of the total treatment system. Special emphasis is placed on presentation of the following:

1. The chemistry of nickel-chromium plating and waste generation
2. The type of pollutants and their sources
3. Waste minimization
4. Recovery and recycling
5. Conventional reduction–precipitation treatment systems
6. Modified reduction–flotation treatment systems
7. Innovative flotation–filtration treatment systems

6.2 THE NICKEL-CHROMIUM PLATING PROCESS

The nickel-chromium plating process includes the steps in which a ferrous base material is electroplated with nickel and chromium. The electroplating operations for plating the two metals are basically oxidation–reduction reactions. Typically, the part to be plated is the cathode, and the plating metal is the anode.

6.2.1 Nickel Plating

To plate nickel on iron parts, the iron parts form the cathodes, and the anode is a nickel bar. On the application of an electric current, the nickel bar anode oxidizes, dissolving in the electrolyte:

$$\mathrm{Ni} \longrightarrow \mathrm{Ni}^{2+} + 2\mathrm{e}^- \tag{6.1}$$

The resulting nickel ions are reduced at the cathode (the iron part) to form a nickel plate:

$$\mathrm{Ni}^{2+} + 2\mathrm{e}^- \longrightarrow \mathrm{Ni} \tag{6.2}$$

Nickel plating can also be accomplished by an electroless plating technique involving deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited. A special feature of electroless plating is that no external electrical energy is required. The following are the basic ingredients in electroless plating solutions:

1. A source of metal, usually a salt
2. A reducer to reduce the metal to its base state
3. A chelating agent to hold the metal in solution so the metal will not plate out indiscriminately
4. Various buffers and other chemicals designed to maintain stability and increase bath life

Nickel electroless plating on a less noble metal is common.[1–7] For example, the source of nickel can be nickel sulfate. The reducer can be an organic substance, such as formaldehyde. A chelating agent (tartrate or equivalent) is generally required. The nickel salt is ionized in water:

$$\mathrm{NiSO_4} \longrightarrow \mathrm{Ni}^{2+} + \mathrm{SO_4^{2-}} \tag{6.3}$$

There is then a redox reaction with the nickel and the formaldehyde:

$$Ni^{2+} + 2H_2CO + 4OH^- \longrightarrow Ni + 2HCO_2^- + 2H_2O + H_2 \tag{6.4}$$

The base metal nickel now begins to plate out on an appropriate surface, such as a less noble metal.

6.2.2 CHROMIUM PLATING

In chromium plating, the chromium is supplied to the plating baths as chromic acid. For example, plating baths can be prepared by adding hexavalent chromium in the form of either sodium dichromate ($Na_2Cr_2O_7 \bullet H_2O$) or chromium trioxide (CrO_3). When sodium dichromate is used it dissociates to produce the divalent dichromate ion ($Cr_2O_7^{2-}$). When chromium trioxide is used, it immediately dissolves in water to form chromic acid according to the following reaction[8–15]:

$$CrO_3 + H_2O \longrightarrow H_2CrO_4 \tag{6.5}$$

Chromic acid is considered a strong acid, although it never completely ionizes. Its ionization has been described as follows:

$$H_2CrO_4 \longrightarrow H^+ + HCrO_4^- \text{ (acid chromate ion)} \quad K_a = 0.83 \text{ at } 25°C \tag{6.6}$$

$$HCrO_4^- \longrightarrow H + CrO_4^{2-} \text{ (chromate ion)} \quad K_a = 3.2 \times 10^{-7} \text{ at } 25°C \tag{6.7}$$

Moreover, the dichromate ion ($Cr_2O_7^{2-}$) will exist in equilibrium with the acid chromate ion as follows:

$$Cr_2O_7^{2-} + H_2O \longrightarrow 2HCrO_4^- \quad K_a = 0.0302 \text{ at } 25°C \tag{6.8}$$

Theoretically, $HCrO_4^-$ is the predominant species between pH 1.5 and 4.0, $HCrO_4^-$ and CrO_4^{2-} exist in equal amounts at pH 6.5, and CrO_4^{2-} predominates at higher pH values. Chromium plating wastewater is generally somewhat acid, and the acid chromate ion $HCrO^-$ is predominant in this wastewater.

Chromating is one of the chemical conversion coating technologies. Chrome coatings are applied to previously deposited nickel for increased corrosion protection and to improve surface appearance. Chromate conversion coatings are formed by immersing the metal in an aqueous acidified chromate solution consisting substantially of chromic acid or water-soluble salts of chromic acid, together with various catalysts or activators.

6.3 SOURCES OF POLLUTION

A conceptual arrangement of the nickel-chromium plating process can be broken down into three general steps:

1. Surface preparation involving the conditioning of the base material for plating
2. Actual application of the plate by electroplating
3. The posttreatment steps

The major waste sources during normal nickel-chromium plating operations are alkaline cleaners, acid cleaners, plating baths, posttreatment baths, and auxiliary operation units.

The wastestreams generated by the plating process can be subdivided and classified into eight categories[1,5,6,15]:

1. Concentrated acid wastes
2. Concentrated phosphate cleaner wastes
3. Acid rinsewater
4. Alkaline rinsewater
5. Chromium rinsewater
6. Nickel rinsewater
7. Concentrated nickel wastes
8. Concentrated chromium wastes

In the above categories, there are seven major types of aqueous pollutants that must be pretreated and removed[5,15]:

1. Acidity
2. Alkalinity
3. Nickel
4. Chromium
5. Iron
6. Organics (COD, BOD)
7. Suspended solids

The environmental impact of the two most toxic pollutants, nickel and chromium, is briefly presented in the following.[1,16,17] Significant concentrations of these elements pass through conventional treatment plants.

6.3.1 Environmental Impact of Nickel

Nickel is toxic to aquatic organisms at levels typically observed in POTW (publicly owned treatment works) effluents:

1. 50% reproductive impairment of *Daphnia magna* at 0.095 mg/L
2. Morphological abnormalities in developing eggs of *Limnaea palustris* at 0.230 mg/L
3. 50% growth inhibition of aquatic bacteria at 0.020 mg/L

Because surface water is often used as a drinking water source, nickel passed through a POTW becomes a possible drinking water contaminant.

A U.S. Environmental Protection Agency (U.S. EPA) study of 165 sludges showed nickel concentrations ranging from 2 to 3520 mg/kg (dry basis).[18] Nickel toxicity may develop in plants from application of municipal wastewater biosolids on acid soils. Nickel reduces yields for a variety of crops including oats, mustard, turnips, and cabbage.

6.3.2 Environmental Impact of Chromium

Chromium can exist as either trivalent or hexavalent compounds in raw wastewater streams. The chromium that passes through the POTW is discharged to ambient surface water. Chromium is toxic to aquatic organisms at levels observed in POTW effluents[15]:

1. Trivalent chromium significantly impaired the reproduction of *Daphnia magna* at levels of 0.3 to 0.5 mg/L.
2. Hexavalent chromium retards growth of chinook salmon at 0.0002 mg/L. Hexavalent chromium is also corrosive and a potent human skin sensitizer.

Besides providing an environment for aquatic organisms, surface water is often used as a source of drinking water. The National Primary Drinking Water Standards are based on total chromium, the limit being 0.1 mg/L.[19]

A U.S. EPA study of 180 municipal wastewater sludges showed that municipal wastewater sludge contains 10 to 99,000 mg/kg (dry basis) of chromium. Most crops absorb relatively little chromium even when it is present in high levels in soils, but chromium in sludge has been shown to reduce crop yields in concentrations as low as 200 mg/kg.[18]

6.4 WASTE MINIMIZATION

All metal finishing facilities have one thing in common—the generation of metal-containing hazardous waste from the production processes. Reducing the volume of waste generated can save money and at the same time decreases future liabilities. Typical wastes generated are as follows:

1. Industrial wastewater and treatment residues
2. Spent plating baths
3. Spent process baths
4. Spent cleaners
5. Waste solvents and oil

This section identifies areas for reducing waste generation. It also suggests techniques available to metal finishers for waste reduction and is intended to help metal finishing shop owners decide whether waste reduction is a possibility.

Both state (Health and Safety Code) and federal (40 CFR, Part 262, Subpart D) regulations require that generators of hazardous waste file a biennial generator's report. Among other things, this report must include a description of the efforts undertaken and achievements accomplished during the reporting period to reduce the volume and toxicity of waste generated. The Uniform Hazardous Waste Manifest requires that large generators certify that they have a program in place to reduce the volume and toxicity of waste generated that is determined to be economically practicable. Small-quantity generators must certify that they have made a good faith effort to minimize waste generation and have selected the best affordable waste management method available.

As waste reduction methods reduce the amount of waste generated, and also the amount subject to regulation, these practices can help a shop comply with the requirements while also saving money. The shop's owner or manager must be committed to waste reduction and pass that commitment on to the employees, establish training for employees in waste reduction, hazardous material handling and emergency response, and establish incentive programs to encourage employees to design and use new waste reduction ideas. The following is a list of some common waste reduction methods for metal finishing electroplating shops.[20,21]

6.4.1 ASSESSMENT OF HAZARDOUS WASTE

Waste assessments are used to list the sources, types, and amounts of hazardous waste generated to make it easier to pinpoint where wastes can be reduced.

Source reduction is usually the least expensive approach to minimizing waste. Many of these techniques involve housekeeping changes or minor inplant process modifications.

6.4.2 IMPROVED PROCEDURES AND SEGREGATION OF WASTES

These may be summarized as follows:

1. Good housekeeping is the easiest and often the cheapest way to reduce waste. Keep work areas clean.

2. Improve inventory procedures to reduce the amount of off-specification materials generated.
3. Reduce quantities of raw materials to levels where materials will be used up just as new materials are arriving.
4. Designate protected raw material and hazardous waste storage areas with spill containment. Keep the areas clean and organized and give one person the responsibility for maintaining the areas.
5. Label containers as required and cover them to prevent contact with rainfall and avoid spills.
6. Use a "first-in, first-out" policy for raw materials to keep them from becoming too old to be used. Give one person responsibility for maintaining and distributing raw materials.
7. Use bench-scale testing for samples rather than process baths.
8. Designate one person to accept chemical samples and return unused samples to suppliers.
9. Limit bath mixing to trained personnel.
10. Segregate wastestreams for recycling and treatment, and keep nonhazardous material from becoming contaminated.
11. Prevent and contain spills and leaks by installing drip trays and splash guards around processing equipment.
12. Conduct periodic inspections of tanks, tank liners, and other equipment to avoid failures. Repair malfunctions when they are discovered. Use inspection logs to follow up on repairs.
13. Inspect plating racks for loose insulation that would cause increased dragout.
14. Use dry cleanup where possible to reduce the volume of wastewater.

6.4.3 MATERIAL SUBSTITUTION

In summary:

1. Use process chemistries that are treatable or recyclable on site.
2. Use deionized water instead of tap water in process baths or rinsing operations to reduce chemical reactions with impurities in the tap water, which would increase sludge production.
3. Use nonchelated process chemistries rather than chelated chemistries to reduce sludge volume.
4. Replace cyanide process baths with noncyanide process baths to simplify the treatment required.
5. Use alkaline cleaners instead of solvents for degreasing operations; they can be treated on site and usually discharged to the sewer with permit authorization.

6.4.4 EXTENDING PROCESS BATH LIFE

This may be achieved with the following procedures:

1. Treatment of process baths can extend their useful life.
2. Bath replenishment extends the useful life of the bath.
3. Monitoring (using pH meters or conductivity meters) the process baths can determine the need for bath replenishment.

6.4.5 DRAGOUT REDUCTION

Dragout reduction is achieved using the following steps:

1. Minimize bath concentrations to the lower end of their operating range.
2. Maximize bath operating temperatures to lower the solution's viscosity.
3. Use wetting agents (which reduce the surface tension of the solution) in process baths to decrease the amount of dragout.
4. Withdraw workpieces from tanks slowly to allow maximum drainage back into process tank.

5. Use air knives or spray rinses above process tanks to rinse excess solution off a workpiece and into the process bath.
6. Install drainage boards between process tanks and rinse tanks to direct dragout back into process tank.
7. Use dedicated dragout tanks after process baths to capture dragout.
8. Install rails above process tanks to hang workpiece racks for drainage prior to rinsing.
9. Use spray rinses as the initial rinse after the process tank and before the dip tank.
10. Use air agitation or workpiece agitation to improve rinse efficiency.
11. Install multiple rinse tanks (including counterflow rinse tanks) after process baths to improve rinse efficiency and reduce water consumption.

6.4.6 Reactive Rinses

The following steps should be applied:

1. Reuse the acid rinse effluent as influent for the alkaline rinse tank, thus allowing the fresh water feed to the alkaline rinse tank to be turned off (reactive rinsing). This can also be applied to process tank rinses.
2. Treat rinsewater effluent to recover process bath chemicals. This allows the reuse of the effluent for rinsing or neutralization prior to discharge.
3. Reuse the spent reagents from the process baths in the wastewater treatment process.
4. Recycle spent solvents on site or off site.
5. Use treatment technologies to recycle rinsewaters in a closed loop or open loop system.
6. Some recycling and most treatment processes require a permit. Be sure to contact the local Department of Health Services regional office to determine if there is a need for a permit to treat or recycle the wastes.
7. Pretreat process water to reduce the natural contaminants that contribute to the sludge volume.
8. Use treatment chemicals that reduce sludge generation (e.g., caustic soda instead of lime).
9. Use sludge dewatering equipment to reduce sludge volume.
10. Use treatment technologies (such as ion exchange, evaporation, and electrolytic metal recovery) that do not use standard precipitation/clarification methods that generate heavy metal sludges.

6.5 MATERIAL RECOVERY AND RECYCLING

Unlike the 1970s and 1980s when waste management costs were relatively inexpensive, today's metal finishers are facing increasingly higher disposal costs. This change is due in part to a decrease in the volume of available landfill space, which has resulted in escalating landfill fees and more stringent federal and state environmental regulations that mandate treatment prior to landfilling.

Metal finishers are seeing their profits shrink as waste management costs increase. To control waste disposal costs, metal finishers must focus on developing and implementing a facility-wide waste reduction program. In other words, as discussed in Section 6.4, metal finishers must consciously seek out ways to decrease the volume of waste that they generate.

One approach to waste reduction is to recover process materials for reuse. Materials used in metal finishing processes can be effectively recovered using available technologies such as dragout, evaporation, reverse osmosis, ion exchange, electrodialysis, and electrolytic recovery.[22–26]

6.5.1 Dragout Recovery

Dragout recovery is a simple technology used by metal finishers to recover plating chemicals. It involves using drain boards, drip tanks, fog-spray tanks, or dragout tanks separately, or in combination, to capture plating chemicals dragged out of plating tanks from parts being plated.

Drain boards are widely used throughout the metal industry to capture plating solutions. Boards are suspended between process tanks and are constructed of plastic, plain or teflon-coated steel. Solutions drip on the boards and drain back into their respective processing tanks.[22,27]

In contrast, a drip tank recovers process chemicals by collecting dragout into a separate tank, from which it can be returned to the process as needed.

In a fog-spray tank, plating chemicals clinging to parts are recovered by washing them with a fine water-mist. The solution that collects in the fog-spray tank is returned to the process tank as needed. The added water helps to offset evaporative losses from the process tanks.

Dragout tanks are essentially rinse tanks. Dragout chemicals are captured in a water solution, which is returned to the process tank as needed.

The presence of airborne particles and other contaminants in recovered plating chemicals may necessitate treatment of the collected solution to remove the contaminants prior to solution reuse.

There are advantages and disadvantages to dragout recovery. Depending upon the solution, up to 60% of the materials carried out of a plating tank can be recovered for reuse; thus dragout can affect metal deposition and surface finish quality. Impurities can concentrate in the solutions causing a deteriorating effect on the plating process when returned to the plating bath.

6.5.2 EVAPORATIVE RECOVERY

A widely used metal salt recovery technique is evaporation. With evaporation, plating chemicals are concentrated by evaporating water from the solution. Evaporators may use heat or natural evaporation to remove water.[22,28] Additionally, evaporators may operate at atmospheric pressure or under vacuum.

Atmospheric evaporators are more commonly used. They are open systems that use process heat and warm air to evaporate water. These evaporators are relatively inexpensive, require low maintenance and are self-operating. Under the right conditions, they can evaporate water from virtually any plating bath or rinse. A packed-bed evaporator is an example of an atmospheric evaporator.

Vacuum evaporators are also used to recover plating chemicals. They are closed systems that use steam heat to evaporate water under a vacuum. This results in lower boiling temperature, with a reduction in thermal degradation of the solution. Like atmospheric evaporators, they require low maintenance and are self-operating. A climbing file evaporator is an example of a vacuum evaporator.

A typical evaporative recovery system consists of an evaporator, a feed pump, and a heat exchanger. Plating solution or rinsewater containing dilute plating chemicals is circulated through the evaporator. The water evaporates and concentrates the plating chemicals for reuse. In open evaporator systems, the water evaporates and mixes with air and is released to the atmosphere. It may be necessary to vent the contaminated airstream to a ventilation/scrubber treatment system prior to release. In enclosed evaporators the water is condensed from the air and can be reused in rinses, which further increases savings. Water reuse is preferred whenever possible.

As with all process equipment, the design size of an evaporator system is dependent upon volumetric flow, specifically the rinsewater flow rate required and the volume of process solution dragout. When operated properly, a commercial evaporator can attain a 99% material recovery rate.

There are drawbacks to using an evaporator to recover plating chemicals. For instance, impurities are concentrated along with recovered plating chemicals. These impurities can alter desired deposited metal characteristics, including surface finish quality. Vacuum evaporation can be used to avoid degradation of plating solutions containing additives that are sensitive to heat.

The evaporative recovery is a very energy-intensive process. Approximately 538 chu (970 Btu) are required to evaporate 1 lb of water at standard atmospheric pressure. Additional energy is required to raise the temperature of the solution to its boiling point.

6.5.3 REVERSE OSMOSIS

Reverse osmosis (RO) recovers plating chemicals from plating rinsewater by removing water molecules with a semipermeable membrane. The membrane allows water molecules to pass through, but blocks metallic salts and additives.[29]

Like evaporators, RO works on most plating baths and rinse tanks. Most RO systems consist of a housing that contains a membrane and feed pump. There are four basic membrane designs: plate-and-frame, spiral-wound, tubular, and hollow-fiber. The most common types of membrane materials are cellulose acetate, polyether/amide, and polysulfones.[29]

Diluted or concentrated rinsewaters are circulated through the membrane at pressures greater than aqueous osmotic pressure. This action results in the separation of water from the plating chemicals. The recovered chemicals can be returned to the plating bath for reuse, and the permeate, which is similar to the condensate from an evaporator, can be used as make-up water. RO units work best on dilute solutions.[30]

The design and capacity of an RO unit is dependent upon the type of chemicals in the plating solution and the dragout solution rate. Certain chemicals require specific membranes. For instance, polyamide membranes work best on zinc chloride and nickel baths, and polyether/amide membranes are suggested for chromic acid and acid copper solutions. The flow rate across the membrane is very important. It should be set at a rate to obtain maximum product recovery. RO systems have a 95% recovery rate with some materials and with optimum membrane selection.[22]

There are advantages to using RO. Energy usage is much lower than for other recovery systems and plating chemicals can be recovered from temperature-sensitive solutions. However, RO also has limitations. The membrane is susceptible to fouling, which is often caused by the precipitation of suspended and dissolved solids that plug the membrane's pores. Also, as with evaporators, RO can concentrate impurities along with plating chemicals, which degrade plating quality.

6.5.4 ION EXCHANGE

Ion exchange is a molecular exchange process where metal ions in solution are removed by a chemical substitution reaction with an ion-exchange resin.[31] Ion exchange can be used with most plating baths. Metal cations exchange sites with sodium or hydrogen ions and anions (such as chromate) with hydroxyl ions. The exchange resin can generally be regenerated with an acid or alkaline solution and reused. When a cation exchange resin is regenerated, it produces a metal salt. For example, copper is removed from an ion exchange resin by passing sulfuric acid over the resin, producing copper sulfate. This salt can be added directly into the plating bath.[23,32]

The required size of an ion-exchange unit is dependent upon the composition and volume of plating dragout. Each ion-exchange resin has a maximum capacity for recovery of specific ions. The ion-exchange unit's size (volume of resin) is determined by the amount of metal to be removed from the recovered solutions.

Ion exchange has its drawbacks. Most commercially available resins are nonselective and, therefore, similarly charged ions can be exchanged by a given resin whether desired in the process or not. This means that certain contaminants cannot be removed by ion exchange and are returned to the plating tank with the metal salt.[22] The metal salt solution produced after regeneration is often a dilute solution that can only be put back into the process bath if evaporation is used to make room in the process tank. In addition, ion exchange is not a continuous process and system sizing must take into account resin regeneration time.

6.5.5 ELECTRODIALYSIS

Electrodialysis units recover plating chemicals differently from the recovery units discussed thus far. In electrodialysis, electromotive forces selectively drive metal ions through an ion-selective membrane (in RO, pressure is the driving force; in ion exchange, the driving force is chemical attraction). The membranes are thin sheets of plastic material with either anionic or cationic characteristics.[33]

Electrodialysis units are constructed using a plate-and-frame technique similar to filter presses. Alternating sheets of anionic and cationic membranes are placed between two electrodes. The plating or rinse solution to be recovered (electrolyte) circulates past the system's electrodes. Hydrogen and oxygen evolve. Positive ions travel to the negative terminal and negative ions travel to the positive terminal. The electrolyte also provides overall electrical conductivity to the cell. In some units, the current is periodically reversed to reduce membrane fouling.

Electrodialysis is compatible with most plating baths, and the design size of a unit is dependent upon the rinsewater flow rate and concentration.[22]

Electrodialysis has advantages and disadvantages. For instance, the process requires very little energy and can recover highly concentrated solutions. On the other hand, similarly to other membrane processes, electrodialysis membranes are susceptible to fouling and must be regularly replaced.

6.5.6 Electrolytic Recovery

Electrolytic recovery (ER) is the oldest metal recovery technique. Metal ions are plated-out of solution electrochemically by reduction at the cathode.[34] There are essentially two types of cathodes used for this purpose: a conventional metal cathode and a high surface area cathode (HSAC). Both cathodes can effectively plate-out metals, such as gold, zinc, cadmium, copper, and nickel.[22]

Electrolytic recovery systems work best on concentrated solutions. For optimal plating efficiency, recovery tanks should be agitated ensuring that good mass transfer occurs at the electrodes. Another important factor to consider is the anode/cathode ratio. The cathode area (plating surface area) and mass transfer rate to the cathode greatly influence the efficiency of metal deposition.

Electrolytic recovery can be used with most plating baths. The amount of metal to be plated per square meter of cathode determines the electrolytic recovery unit's design capacity. Therefore, the volume and concentration of plating dragout greatly influences system design and size.[22,35]

There are advantages to the electrolytic recovery process. For instance, ER units can operate continuously, and the product is in a metallic form that is very suitable for reuse or resale. Electrolytic units are also mechanically reliable and self-operating. Very importantly, contaminants are not recovered and returned to the plating bath. Thus, electrolytically recovered metals are as pure as "virgin" plating raw material.

The major disadvantage to electrolytic recovery is high energy cost. Energy costs will vary, of course, with cathode efficiencies and local utility rates.[22]

6.5.7 Deionized Water

Using deionized water to prepare plating bath solutions is an effective way of preventing waste generation. Some groundwater and surface waters contain high concentrations of calcium, magnesium, chloride, and other soluble contaminants that may build up in process baths.[22] By using deionized water, buildup of these contaminants can be more easily controlled. Technologies such as RO and ion exchange can also be used to effectively remove soluble contaminants from incoming water.[36]

6.6 CHEMICAL TREATMENT

Treatment for the removal of chromium and nickel from electroplating wastewater involves neutralization, hexavalent chromium reduction, pH adjustment, hydroxide precipitation, and final solid–liquid separation.[15,37–48]

6.6.1 Neutralization

Excess acidity and alkalinity may be eliminated by simple neutralization by either a base or an acid. This is a simple stoichiometric chemical reaction of the following type[5,15,49]:

$$\text{Strong base} + \text{strong acid} \longrightarrow \text{salt} + \text{water} \qquad (6.9)$$

Examples of this include the following:

1. Alkali

$$\underset{\text{Base}}{2\ \mathrm{NaOH}} + \underset{\text{Acid}}{\mathrm{H_2SO_4}} \longrightarrow \underset{\text{Salt}}{\mathrm{Na_2SO_4}} + \underset{\text{Water}}{2\ \mathrm{HOH}} \tag{6.10}$$

2. Acid

$$\underset{\text{Acid}}{\mathrm{HNO_3}} + \underset{\text{Base}}{\mathrm{NaOH}} \longrightarrow \underset{\text{Salt}}{\mathrm{NaNO_3}} + \underset{\text{Water}}{\mathrm{HOH}} \tag{6.11}$$

A slight excess of base may be titrated in the previous reactions to shift the pH to a slight basic condition. This is important for the precipitation of certain metal salts (such as nickel, iron, and trivalent chromium) as hydroxides.

6.6.2 HEXAVALENT CHROMIUM REDUCTION

Chemical treatment of chromium wastewater is usually conducted in two steps. In the first step hexavalent chromium is reduced to trivalent chromium by the use of a chemical reducing agent. The trivalent chromium is precipitated during the second stage of treatment.[15]

Sulfur dioxide (SO_2), sodium bisulfite ($NaHSO_3$), and sodium metabisulfite ($Na_2S_2O_5$) are commonly used as reducing agents.[15,50] All these compounds react to produce sulfurous acid when added to water, according to the following reactions:

$$\mathrm{SO_2 + H_2O \longrightarrow H_2SO_3} \tag{6.12}$$

$$\mathrm{Na_2S_2O_5 + H_2O \longrightarrow 2\ NaHSO_3} \tag{6.13}$$

$$\mathrm{NaHSO_3 + H_2O \longrightarrow H_2SO_3 + NaOH} \tag{6.14}$$

It is the sulfurous acid produced from these reactions that is responsible for the reduction of hexavalent chromium. The reaction is shown in the following equation:

$$\mathrm{2\ H_2CrO_4 + 3\ H_2SO_3 \longrightarrow Cr_2(SO_4)_3 + 5\ H_2O} \tag{6.15}$$

The typical amber color of the hexavalent chromium solution will turn to a pale green once the chromium has been reduced to the trivalent state. Although this color change is a good indicator, redox control is usually employed.

The theoretical amount of sulfurous acid required to reduce a given amount of chromium can be calculated from the above equation. The actual amount of sulfurous acid required to treat a wastewater will be greater than this because other compounds and ions present in the wastewater may consume some of the acid. Primary among these is dissolved oxygen, which oxidizes sulfurous acid to sulfuric acid according to the following reaction:

$$\mathrm{H_2SO_3 + 0.5\ O_2 \longrightarrow H_2SO_4} \tag{6.16}$$

Each part of dissolved oxygen initially present in the wastewater produces 6.1 parts of sulfuric acid.

Undissociated sulfurous acid is responsible for the reduction of hexavalent chromium. Consequently, the reduction reaction is strongly pH-dependent because of the effect of pH on acid dissociation:

$$\mathrm{H_2SO_3 \longrightarrow H^+ + HSO_3^-} \tag{6.17}$$

$$K_a = 1.72 \times 10^{-2} \text{ at } 25°\text{C}$$

$$HSO_3^- \longrightarrow H^+ + SO_3^{2-} \tag{6.18}$$
$$K_a = 1.0 \times 10^{-7} \text{ at } 25°C$$

The dissociation as a function of pH and the effect of pH on reaction rate is shown in Figure 6.1 and Figure 6.2, respectively.[15] Obviously, the reaction proceeds much faster at low pH values, where the concentration of undissociated sulfurous acid is highest. As a result, chromium reduction processes are generally conducted at pH values of 2 to 3 to maximize reaction rates and minimize the volume of reaction vessels. Sulfuric acid is generally added to reduce the pH of the wastewater to the desired level and to maintain it at that level throughout treatment. If the pH is not maintained at the desired level but is allowed to increase during treatment, the reaction may not go to completion in the retention time available, and unreduced hexavalent chromium may exist in the effluent. The amount of acid required to depress the pH to the level selected for chrome reduction will depend on the alkalinity of the wastewater being treated. This acid requirement can be determined by titrating a sample of wastewater with sulfuric acid to the desired pH in the absence of a reducing agent.

In addition to the sulfuric acid required for pH adjustment, some amount of acid is consumed by the reduction reaction (Equation 8.15). If sulfur dioxide is used as the reducing agent, it will provide all the acid consumed by this reaction, and additional acid will not be required. However, if sodium bisulfite or sodium metabisulfite is used, additional acid must be supplied to satisfy the acid demand. This acid requirement is stoichiometric and can be calculated from Equations 6.19 to 6.22.

At pH 3.0 to 4.0:

$$3\ NaHSO_3 + 1.5\ H_2SO_4 + 2\ H_2CrO_4 \longrightarrow Cr_2(SO_4)_3 + 1.5\ Na_2SO_4 + 5\ H_2O \tag{6.19}$$

$$1.5\ Na_2S_2O_5 + 1.5\ H_2SO_4 + 2\ H_2CrO_4 \longrightarrow Cr_2(SO_4)_3 + 1.5\ Na_2SO_4 + 3.5\ H_2O \tag{6.20}$$

At pH 2.0:

$$3\ NaHSO_3 + 2\ H_2SO_4 + 2\ H_2CrO_4 \longrightarrow Cr_2(SO_4)_3 + Na_2SO_4 + NaHSO_4 + 51\ H_2O \tag{6.21}$$

$$1.5\ Na_2S_2O_5 + 2\ H_2SO_4 + 2\ H_2CrO_4 \longrightarrow Cr_2(SO_4)_3 + Na_2SO_4 + NaHSO_4 + 3.5\ H_2O \tag{6.22}$$

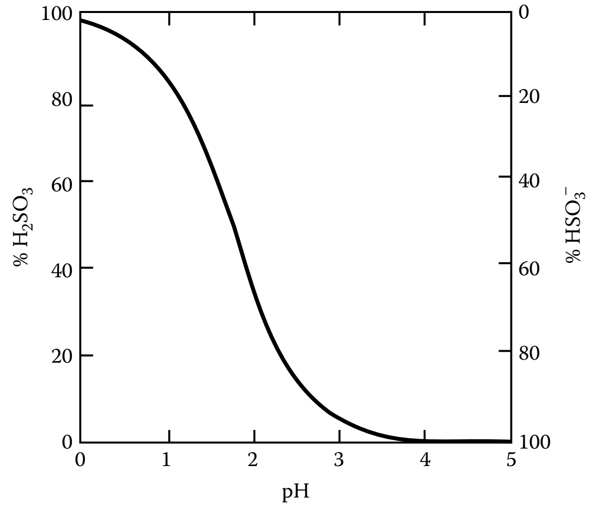


FIGURE 6.1 Relationship between H_2SO_3 and HSO_3^- at various pH values. (Taken from Krofta, M. and Wang, L.K., *Design of Innovative Flotation–Filtration Wastewater Treatment Systems for a Nickel-Chromium Plating Plant*, U.S. Department of Commerce, National Technical Information Service, Springfield, VA, Technical Report PB-88-200522/AS, January 1984.)

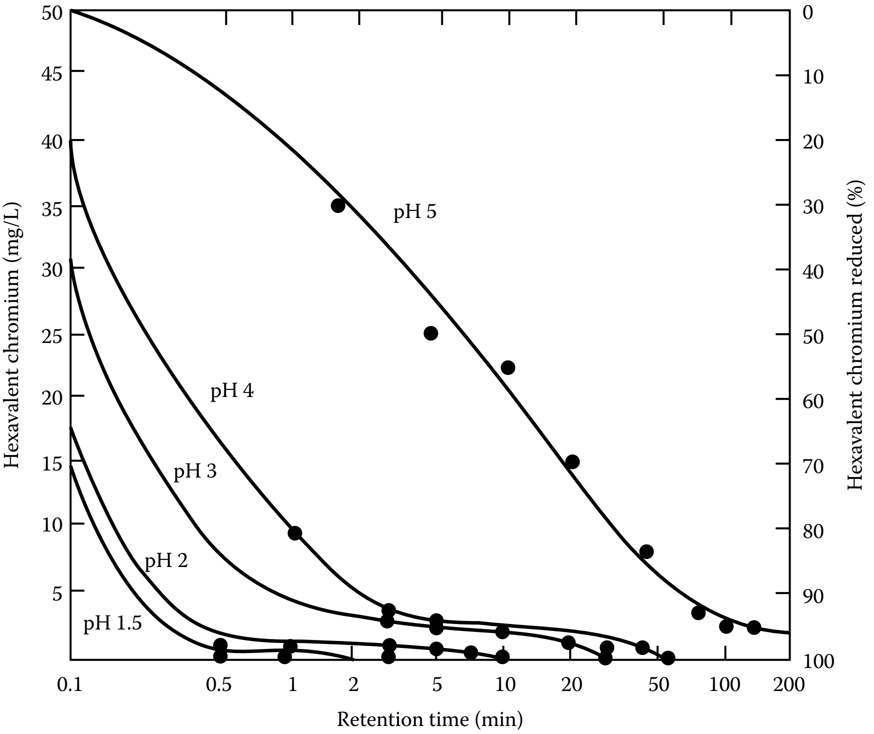


FIGURE 6.2 Rate of reduction of hexavalent chromium in the presence of excess SO_2 at various pH levels. (Taken from Krofta, M. and Wang, L.K., *Design of Innovative Flotation–Filtration Wastewater Treatment Systems for a Nickel-Chromium Plating Plant*, U.S. Department of Commerce, National Technical Information Service, Springfield, VA, Technical Report PB-88-200522/AS, January 1984.)

Similar equations can be developed for pH values between 2 and 3 as a function of the SO_4^{2-} and HSO_4^- distribution.

6.6.3 pH ADJUSTMENT AND HYDROXIDE PRECIPITATION

Wastewater pH is adjusted by addition of an acid or an alkali, depending on the purpose of the adjustment. The most common purposes of wastewater pH adjustment are the following:

1. Chemical precipitation of dissolved heavy metals, as illustrated by Figure 6.3
2. Pretreatment of metal-bearing wastewater before sulfide precipitation so that the formation of hazardous gaseous hydrogen sulfide does not occur
3. Neutralization of wastewater before discharge to either a stream or a sanitary sewer[37–48]

To accomplish hydroxide precipitation, an alkaline substance such as lime or sodium hydroxide is added to the wastewater to increase the pH to the optimum range of minimum solubility at which the metal precipitates as a hydroxide[51]:

$$M(II)^{2+} + Ca(OH)_2 \longrightarrow M(II)(OH)_2 + Ca^{2+} \tag{6.23}$$

$$2\ M(III)^{3+} + 3\ Ca(OH)_2 \longrightarrow 2\ M(III)(OH)_3 + 3\ Ca^{2+} \tag{6.24}$$

where M(II) = divalent metal and M(III) = trivalent metal.

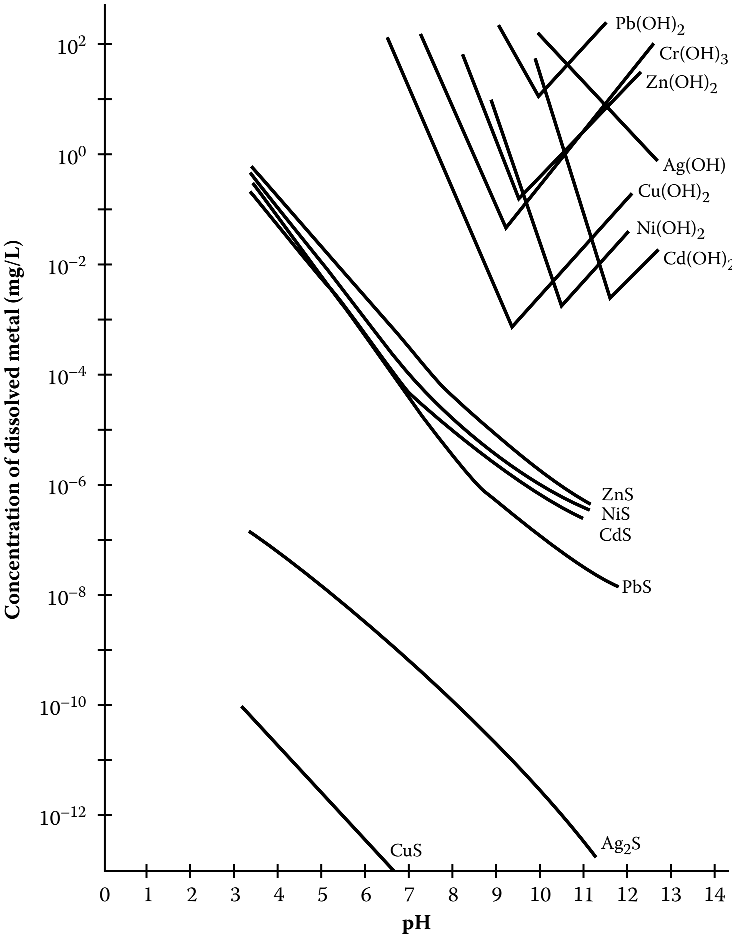


FIGURE 6.3 Solubility of metal hydroxides and sulfides. (Taken from Krofta, M. and Wang, L.K., *Design of Innovative Flotation–Filtration Wastewater Treatment Systems for a Nickel-Chromium Plating Plant*, U.S. Department of Commerce, National Technical Information Service, Springfield, VA, Technical Report PB-88-200522/AS, January 1984.)

The precipitated metal hydroxide can then be removed from the wastewater by clarification or other solid–water separation techniques.[52]

As a practical example, following the reduction of hexavalent chromium, sodium hydroxide, lime, or sodium hydroxide can be added to the wastewater to neutralize the pH and precipitate the trivalent chromium, nickel, iron, divalent, and other heavy metals. If lime is used, lime will react with heavy metals and with any residual sodium sulfate, sulfurous acid, or sodium bisulfite. The following reactions apply:

$$NiC1_2 + Ca(OH)_2 \longrightarrow Ni(OH)_2 + CaC1_2 \quad (6.25)$$

$$NiSO_4 + Ca(OH)_2 \longrightarrow Ni(OH)_2 + CaSO_4 \quad (6.26)$$

$$2\ Fe_2(SO_4)_3 + 6\ Ca(OH)_2 \longrightarrow 4\ Fe(OH)_3 + 6\ CaSO_4 \quad (6.27)$$

$$Cr_2(SO_4)_3 + 3\ Ca(OH)_2 \longrightarrow 2\ Cr(OH)_3 + 3\ CaSO_4 \quad (6.28)$$

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\ H_2O \quad (6.29)$$

$$2\ NaHSO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + Na_2SO_4 + 2\ H_2O \quad (6.30)$$

$$H_2SO_3 + Ca(OH)_2 \longrightarrow CaSO_3 + 2\ H_2O \quad (6.31)$$

$$2\ NaHSO_3 + Ca(OH)_2 \longrightarrow CaSO_3 + Na_2SO_3 + 2\ H_2O \quad (6.32)$$

Chromium hydroxide is an amphoteric compound and exhibits minimum solubility in the pH range of 7.5 to 10.0. Effluents from chromium reduction processes should be neutralized to the range of zero solubility (pH 8.5 to 9.0) to minimize the amount of soluble chromium remaining in solution.

It should be noted that if sodium hydroxide is used instead of lime, the chemical cost will be higher, less sludge will be produced, and effluent sulfate concentration will be higher.[15]

6.6.4 REDUCTION AND FLOTATION COMBINATION

Alternatively, hexavalent chromium can be reduced, precipitated, and floated by ferrous sulfide. By applying ferrous sulfide as a flotation aid to a plating waste with an initial hexavalent chromium concentration of 130 mg/L and total chromium concentration of 155 mg/L, an effluent quality of less than 0.05 mg/L of either chromium species can be achieved if a flotation–filtration wastewater treatment system is used.[15]

Ferrous sulfide acts as a reducing agent at pH 8 to 9 for reduction of hexavalent chromium and then precipitates the trivalent chromium as a hydroxide in one step without pH adjustment.[51,62] So, the hexavalent chromium in the nickel-chromium plating wastewater does not have to be isolated and pretreated by reduction to the trivalent form. The new process is applicable for removal of all heavy metals. All heavy metals other than chromium are removed as insoluble metal sulfides, M(II)S.

$$\mathrm{FeS + M(II)^{2+} \longrightarrow M(II)S + Fe^{2+}} \tag{6.33}$$

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O} \tag{6.34}$$

$$\mathrm{Cr^{3+} + 3\,OH^- \longrightarrow Cr(OH)_3} \tag{6.35}$$

$$\mathrm{Fe^{3+} + 3\,OH^- \longrightarrow Fe(OH)_3} \tag{6.36}$$

M(II)S, $\mathrm{Cr(OH)_3}$, and $\mathrm{Fe(OH)_3}$ are all insoluble precipitates, which can be floated by dissolved air flotation (DAF).

This new method can eliminate the potential hazard of excess sulfide in the effluent and the formation of gaseous hydrogen sulfide. In operation, the FeS is added to wastewater to supply sufficient sulfide ions to precipitate metal sulfides that have lower solubilities than FeS. Typical reactions include the following[51,62]:

$$\mathrm{FeS + Ni^{2+} \longrightarrow NiS + Fe^{2+}} \tag{6.37}$$

$$\mathrm{FeS + Zn^{2+} \longrightarrow ZnS + Fe^{2+}} \tag{6.38}$$

$$\mathrm{FeS + Pb^{2+} \longrightarrow PbS + Fe^{2+}} \tag{6.39}$$

$$\mathrm{FeS + Cd^{2+} \longrightarrow CdS + Fe^{2+}} \tag{6.40}$$

$$\mathrm{FeS + Cu^{2+} \longrightarrow CuS + Fe^{2+}} \tag{6.41}$$

$$\mathrm{FeS + 2Ag^+ \longrightarrow Ag_2S + Fe^{2+}} \tag{6.42}$$

Ferrous sulfide can also react with metal hydroxide to form insoluble metal sulfide:

$$\mathrm{FeS + M(II)(OH)_2 \longrightarrow Fe(OH)_2 + M(II)S} \tag{6.43}$$

Ferrous sulfide itself is also a relatively insoluble compound. Thus, the sulfide ion concentration is limited by its solubility, which amounts to only about 0.02 g/L, and the inherent problems associated with conventional sulfide precipitation are significantly minimized.

The newly developed flotation–filtration process involving the use of ferrous sulfide as a flotation aid offers a distinct advantage in the treatment of nickel-chromium plating wastewater that contains hexavalent chromium, nickel, iron, and other metals.

6.7 CONVENTIONAL REDUCTION–PRECIPITATION SYSTEM

A conventional system for treatment of nickel-chromium plating wastewater involves the use of the following unit processes[37–48]:

1. Neutralization
2. Chromium reduction
3. pH adjustment and hydroxide precipitation
4. Clarification (either sedimentation or DAF)
5. Sludge treatment (filter press and final disposal)

Figure 6.4 shows an example of an existing plating facility and its conventional reduction–precipitation wastewater treatment system in New Britain, TN.[15]

Initially the nickel-chromium plating process is designed to minimize the liquid loading to the waste treatment system. Counterflow rinsing, spray rinsing, and stagnant rinse recovery methods are employed in order to minimize the amount of wastes to be treated and allow as much treatment or retention time in the waste treatment system as is possible.

In the application of the previous chemical methods, a certain amount of steady-state continuity has been built into the system. To accomplish this, initial concentrated alkaline and acid rinse wastewaters are retained after dumping in the waste holding tank [T-91] (Figure 6.4) and acid chromium plating wastewater is stored in the waste holding tank [T-51]. Extremely concentrated chromium plating wastewater from rinse step No. 1 is sent to an evaporation tank [T-40] for

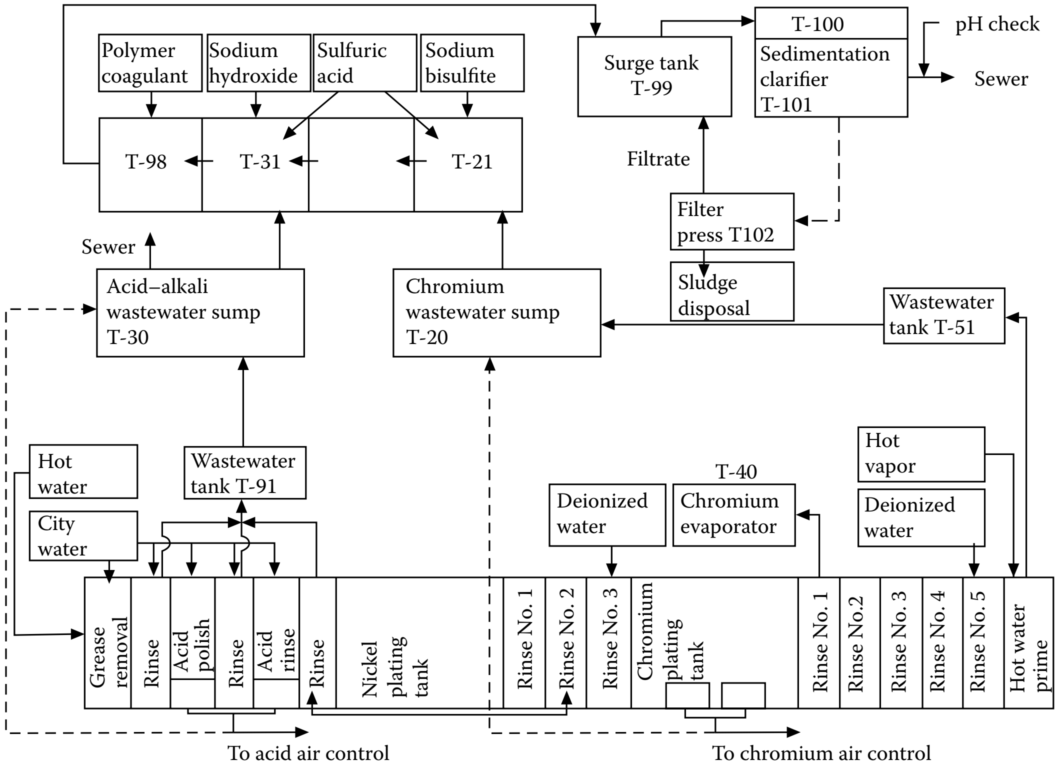


FIGURE 6.4 Conventional reduction–precipitation wastewater treatment system.

chromium recovery. In the case of the wastewater tank [T-51], the waste is slowly bled into the chromium wastewater sump [T-20] to minimize overloading of the total system. The alkaline and acid wastes in [T-.91] are neutralized and slowly bled directly to an acid–alkali wastewater sump [T-30]. It should be noted that the concentrated alkaline wastes are the result of alkaline cleaner replenishment and do not contain heavy metals.

Hexavalent chromium wastes resulting from rinsewater and the concentrated acid bleed accumulate in the chromium waste sump [T-20]. The chromium wastes are then pumped into the chromium treatment module [T-21] for reduction to the trivalent form. This pump is activated only if the oxidation–reduction potential (ORP) and pH are at the proper levels and if the level in the chromium wastewater sump [T-20] is sufficiently high.

Liquid flowing into the chromium treatment module [T-21] is monitored by a pH instrument that controls a feed pump to add the required amount of sulfuric acid from a storage tank. The sulfuric acid is needed to lower the pH to 2.0 to 2.5 for the desired reduction reaction to occur. An ORP instrument controls the injection rate of sodium metabisulfite solution from a metering pump to reduce hexavalent chromium (Cr^{6+}) to the trivalent state (Cr^{3+}).

The acid and alkali wastes are pumped from the acid–alkali wastewater sump [T-30] into the acid–alkali treatment module [T-31]. Metering pumps controlled by pH instruments feed either acid or caustic to the module as required to maintain an acceptable alkalinity for the formation of metal hydroxides prior to discharge to the precipitator consisting of a mixing tank [T-98], a surge tank [T-99], and a sedimentation clarifier [T-101]. The pH is adjusted to a value of 8.5 for optimum metal hydroxide formation and removal.

An ultrasonic transducer is installed on the pH probe mount in the acid–alkali treatment module [T-3l]. This prevents fouling of the electrodes and provides a more closely controlled pH in the effluent discharged to the precipitator.

The first step in the precipitator is the addition of polyelectrolyte solution in the flash mix tank [T-98], surge tank [T-99], and then into the slow mix unit [T-100] containing a variable speed mixing paddle. The purpose of this unit is to coagulate and flocculate[53] the metal hydroxide precipitates.

From the slow mix unit [T-100], the waste flows into the lamellar portion of the sedimentation clarifier [T-101].[54,55] The lamella in the clarifier concentrates the metal hydroxide precipitates. Clarified effluent can be discharged to the sewer.

Concentrated metal hydroxide sludge is pumped from the clarifier to a polypropylene plate filter press [T-102]. The plate filter press[56] is of sufficient capacity without any buildup in the lamellar portion of the unit. This also prevents any overflow of precipitate to the sewer system. The metal hydroxides form a dense sludge cake suitable for disposal in an approved landfill. The liquid effluent from the plate filter is returned to the surge tank [T-99].

A sampling station is provided on the rear exterior wall of the facility for flow measurement and monitoring of the effluent stream.

6.8 MODIFIED REDUCTION–FLOTATION WASTEWATER TREATMENT SYSTEM

A modified reduction–flotation system (Figure 6.5) is very similar to the existing conventional reduction–precipitation system (Figure 6.4), except that a DAF clarifier [T-101F] is used for clarification[15,57] instead of using a conventional sedimentation clarifier (Tank T-101, Figure 6.4).

The flotation system consists of four major components: air supply, pressurizing pump, air dissolving tube, and flotation chamber.[57,58] According to Henry's Law, the solubility of gas (such as air) in aqueous solution increases with increasing pressure. The influent feedstream can be saturated at several times atmospheric pressure, 1.8 to 6 kg/cm^2 (25 to 85 psig), by a pressurizing pump. The pressurized feedstream is held at this high pressure for about 0.5 min in an air dissolving tube (i.e., a pressure vessel) designed to provide sufficient time for dissolution of air into the stream to be

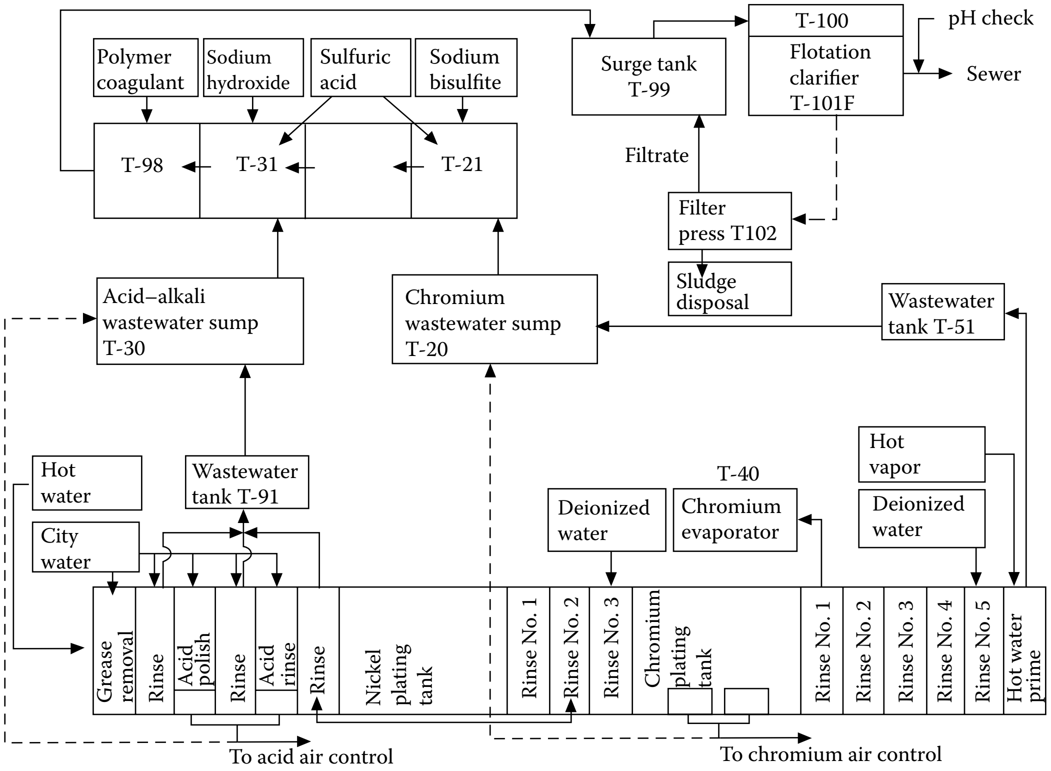


FIGURE 6.5 Modified reduction–precipitation wastewater treatment system.

treated. From the air dissolving tube, the stream is released back to atmospheric pressure in the flotation chamber.[15,57]

Most of the pressure drop occurs after a pressure reducing valve and in the transfer line between the air dissolving tube and the flotation chamber so that the turbulent effects of the depressurization can be minimized. The sudden reduction in pressure in the flotation chamber results in the release of microscopic air bubbles (average diameter 50 μm or smaller) which nucleate on suspended or colloidal particles in the process water in the flotation chamber. This results in agglomeration that, due to the entrained air, gives a net combined specific gravity less than that of water, causing the flotation phenomenon. The vertical rising rate of air bubbles ranges between 15 and 60 cm/min (0.5 to 2.0 ft/min). The floated material rises to the surface of the flotation chamber to form a floated layer. Specially designed flight scrapers or other skimming devices continuously remove the floated material. The surface sludge layer can in certain cases reach a thickness of many inches and can be relatively stable for a short period. The layer thickens with time, but undue delays in removal will cause a release of particulates back to the liquid. Clarified subnatant water (effluent) is drawn off from the flotation chamber and either recovered for reuse or discharged.

The retention time in the flotation chamber is usually about 3 to 5 min, depending on the characteristics of the process water and the performance of the flotation unit. The process effectiveness depends upon the attachment of air bubbles to the particles to be removed from the process water.[57] The attraction between the air bubbles and particles is primarily a result of the particle surface charges and bubble size distribution. The more uniform the distribution of water and microbubbles, the shallower the flotation unit can be.

A high-rate DAF unit with only 3 min of retention time can treat water and wastewater at an overflow rate of 2.4 L/s/m^2 (3.5 gal/min/ft^2) for a single unit and up to 7.2 L/s/m^2 (10.5 gal/min/ft^2)

for triple stacked units. The comparison between a flotation clarifier and a settler shows the following[59,60]:

1. The DAF unit floor space requirement is only 15% of the settler.
2. The DAF unit volume requirement is only 5% of the settler.
3. In DAF, higher biosolids densities are obtained than in sedimentation. Even in shallow flotation clarifiers a satisfactory biosolids density is attainable.
4. The degrees of clarification of both clarifiers are the same with the same flocculating chemical addition.
5. The operational cost of the DAF clarifier is slightly higher than that for the settler, but this is offset by the considerably lower cost of the installation's financing.
6. DAF clarifiers are mainly prefabricated in stainless steel for erection cost reduction, corrosion control, better construction flexibility, and possible future upgrades, contrary to *in situ* constructed heavy concrete sedimentation tanks.

It should be noted that the chemical reactions of the conventional reduction–precipitation system (Figure 6.4) and the modified reduction–flotation system are identical.

Comparatively, the modified reduction–flotation system will have lower annual total cost (amortized capital cost plus O&M cost) and will require less space, because the flotation unit is very shallow in depth and thus can be elevated. It is expected, however, that the treatment efficiency of the modified system will be higher due to the fact that the DAF clarifier can separate not only the suspended solids but also organics such as oil and grease, detergent, and so on.[57,58,61] Conventional sedimentation clarifiers can separate only insoluble suspended solids.

6.9 INNOVATIVE FLOTATION–FILTRATION WASTEWATER TREATMENT SYSTEMS

6.9.1 Flotation–Filtration System Using Conventional Chemicals

There are two innovative flotation–filtration wastewater treatment systems that are technically feasible for the treatment of the nickel-chromium plating wastewater.

The first system, shown in Figure 6.6, is identical to the conventional reduction–precipitation in chemistry (i.e., neutralization, chromium reduction, pH adjustment, metal hydroxide precipitation, and so on). However, a flotation–filtration clarifier (Tank T101SF, as shown in Figure 6.6) is used. The unit consists of rapid mixing, flocculation, high-rate DAF, and sand filtration.[15,57]

The treatment efficiency of this system (Figure 6.6) is much higher than that of the conventional reduction–precipitation wastewater treatment system (Figure 6.4).[15]

6.9.2 Flotation–Filtration System Using Innovative Chemicals

Another innovative flotation–filtration wastewater treatment system adopts the innovative use of the chemical ferrous sulfide (FeS), which reduces the hexavalent chromium and allows separation of chromium hydroxide, nickel hydroxide, and ferric hydroxide in one single step at pH 8.5. Figure 6.7 illustrates the entire system. Again, a DAF–filtration clarifier plays the most important role in this wastewater treatment system.

It is seen from Figure 6.7 that this system is much simpler, more cost-effective, and easier to operate in comparison with all other process systems discussed earlier. The treatment efficiency of the new flotation–filtration system is expected to be higher than that of the conventional reduction–precipitation system. The new flotation–filtration system also requires much less land space.[15]

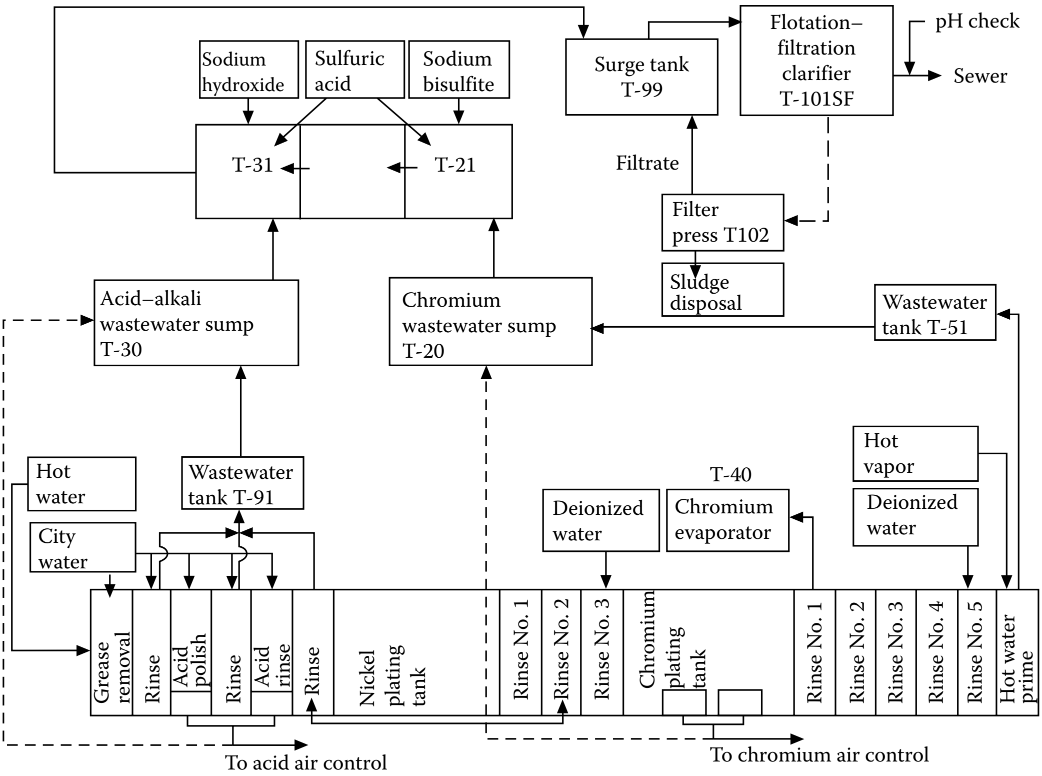


FIGURE 6.6 Innovative flotation–filtration wastewater treatment system using conventional chemicals.

6.9.3 FLOTATION–FILTRATION SYSTEMS

6.9.3.1 Combined Flotation–Filtration Unit

A combined flotation–filtration unit, shown in Figure 6.8, is an advanced water clarification system, using a combination of chemical flocculation, DAF, and rapid sand filtration in one unit. The average processing time from start to finish is less than 15 min.[15,57,58]

Its unique compact and efficient design is made possible by the use of the principle of zero velocity eliminating internal water turbulence (see below). The flocculated water thus stands still in the flotation tank for optimum clarification. The unit is complete with automatic backwash filter in which dirty backwash water is recycled back to the unit inlet for reprocessing. The average waste flow from the process is less than 1.0% of the incoming raw water.

The flotation unit maximum loading is 2.1 L/s/m^2 (3.1 gal/min/ft^2). The maximum filtration rate is 1.7 L/s/m^2 (2.5 gal/min/ft^2). Each filter compartment is backwashed at or more than 10.2 L/s/m^2 (15 gal/min/ft^2) during the backwash operation. The single-medium backwash filter consists of 28 mm (11 in.) high-grade silica sand. The effective size and uniformity coefficient for the sand are 0.35 mm and 1.55, respectively.

The following paragraphs briefly describe how the flotation–filtration unit shown in Figure 6.8, works.[15,57,58]

The influent raw water or wastewater enters the unit at the center near the bottom [1] and flows through a hydraulic rotary joint [2] and an inlet distributor [3] into the rapid mixing section of the slowly moving carriage. The entire moving carriage consists of a rapid mixer [3], flocculator [4], backwash pumps [5 & 6] and sludge discharge scoop [7]. To flocculate colloids and suspended solids, chemicals [8] are added at the inlet [1].

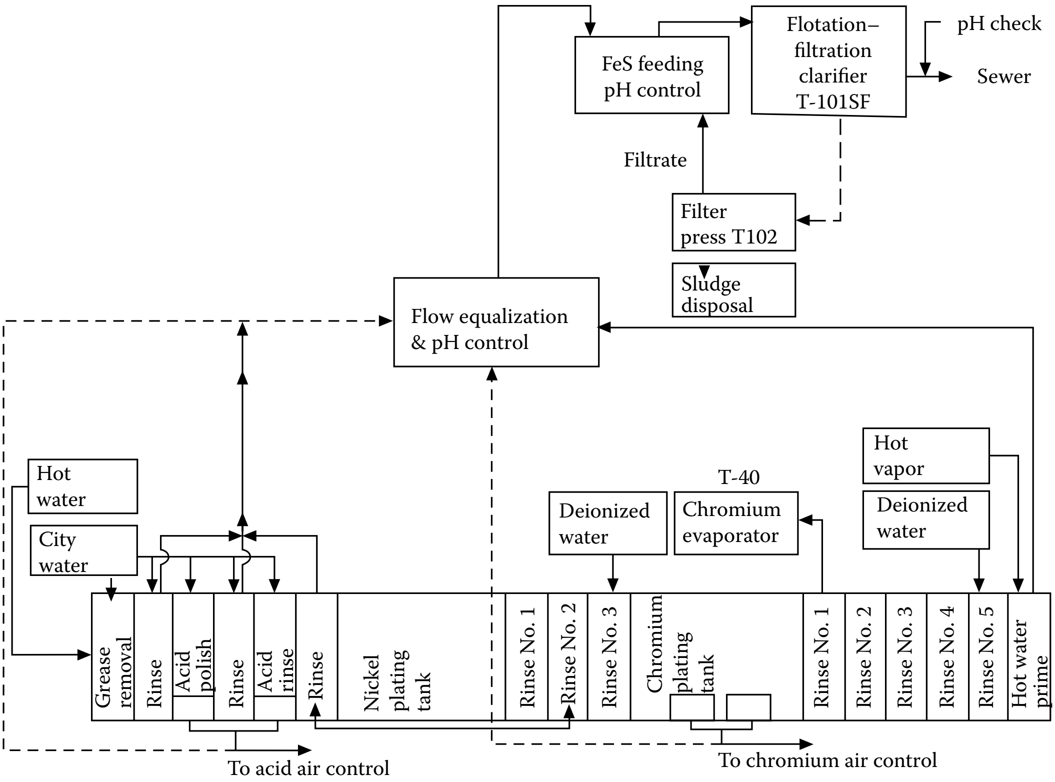


FIGURE 6.7 Innovative flotation–precipitation wastewater treatment system using an innovative chemical.

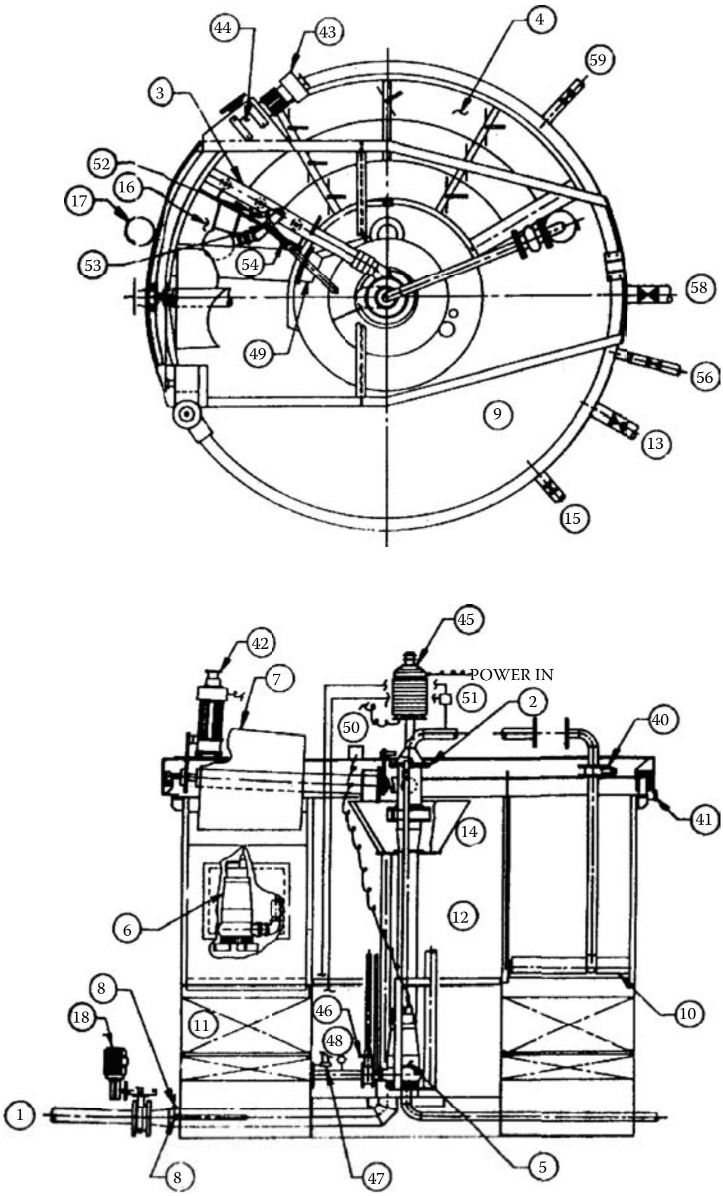
From the rapid mixing section [3] water enters the hydraulic flocculator [4], gradually building up the flocs by gentle mixing. The flocculated water moves from the flocculator into the flotation tank [9], clockwise, with the same velocity as the entire carriage including flocculator simultaneously moves counterclockwise. The outgoing flocculator effluent velocity is compensated by the opposite velocity of the moving carriage, resulting in a zero horizontal velocity of the flotation tank influent. The flocculated water thus stands still in the flotation tank for optimum clarification.

At the outlet of the flocculator [10], a small percentage of chemically pretreated raw water with microscopic air bubbles is added to the flotation tank [9] in order to float the insoluble flocs and suspended matter to the water surface. The floating sludge accumulated on the water surface is scooped off by a sludge discharge scoop [7] and discharged into the center sludge collector [14] where there is a sludge outlet [15] to an appropriate sludge treatment facility.

The small microscopic air bubbles are the product of raw water pressurized to 4 to 6 kg/cm^2 (55 to 85 psi) in the air dissolving tube (ADT) [32]. Water enters the ADT tangentially [33] at one end and is discharged at the opposite end. During its short passage, the water cycles inside the tube and passes repeatedly by an insert fed by compressed air. Very thorough mixing under pressure dissolves the air into the water.

The bottom of the unit is composed of multiple sections of sand filter [11] and clearwell [12]. The clarified flotation effluent passes through the sand filter downward and enters the clearwell through the circular hole underneath each sand filter section; the filter effluent then enters the center portion of the clearwell where there is an outlet for the effluent.[13]

For backwashing of the sandbeds, two pumps [5 & 6] are placed on the carriage. One pump [5] is at the center of the clearwell for pumping washing water during the backwash cycle through the individual clearwell compartments. The turbid backwash water is collected in a traveling hood [16],



1. Raw water inlet
2. Hydraulic rotary joint
3. Rapid mixing section
4. Flocculator
5. Backwash washing pump
6. Backwash recycle pump
7. Sludge discharge scoop
8. Chemical lines
9. Flotation tank
10. Pressure release manifold
11. Sand filter (silica sand 11 in. depth)
12. Clear well
13. Clear well effluent outlet (gate valve)
14. Center sludge collector
15. Floated sludge outlet (gate valve)
16. Backwash hood area
17. Level control
18. Inlet motorized butterfly valve
19. Clear well electrodes
20. Control panel
21. Raw water inlet manual valve
22. Inlet flow meter
23. Inlet flow meter
24. Chemical pump discharge gate valve
25. Chemical pump
26. Pressure pump suction gate valve
27. Pressure pump discharge gate valve
28. Pressure pump
29. Pressure gate valve
30. Pressure gage 0–100 psi
31. Pressure gate valve
32. Safety valve set to 100 psi
33. Air dissolving tube
34. Air dissolving tube inlet orifice
35. Air compressor
36. Air filter
37. Air regulator
38. Air rotometer
39. Gate valve
40. Gate valve
41. Pressure reducing butterfly valve
42. Limit switch
43. Scoop drive motor
44. Carriage drive motor
45. Carriage drive wheel
46. Electrical rotary contact
47. Butterfly valve
48. Backwash cylinder
49. Pressure gage (0–100 psi)
50. Backwash shoe
51. Delay timer solenoid valve
52. Gate valve
53. Pressure gage (0–100 psi)
54. Gate valve
55. Clear well site tube
56. Clear well drain (gate valve)
57. Bleed off vent
58. Pressurized inlet (gate valve)
59. Pressurized suction pipe (gate valve)

FIGURE 6.8 Top and side views of the flotation–filtration unit. (Taken from Krofta, M. and Wang, L.K., Flotation Engineering, Technical Manual Lenox/1-06-2000/368, Lenox Institute of Water Technology, Lenox, MA, 2000.)

where the second backwash pump [6] collects the water and discharges it into the rapid mix inlet section [3] for reprocessing.

The flotation–filtration unit can be either manually operated or completely automated with a level control [17] that operates the inlet flow valve [18]. Filter backwashing can also be automated by a timer or head loss control [19].

6.9.3.2 Separate Flotation and Filtration Units

It is important to note that all flotation clarifiers[63,64] may be used for treatment of nickel-chromium plating wastes regardless of their shapes (rectangular or circular) or manufacturers. A filtration unit is an optional step for final polishing. The treatment efficiency of separate flotation and filtration units[65] will be similar to that of a combined flotation–filtration unit (Figure 6.8).

The authors of this chapter are introducing a modern technology involving the use of flotation and filtration for treating nickel-chromium plating wastes. The authors are not endorsing any manufacturer's products.

6.10 SUMMARY

Waste reduction methods reduce the amount of waste generated and also the amount subject to environmental regulations. Hence, these practices can help an electroplating shop comply with requirements and save money. The shop's owner or manager must be committed to waste reduction and pass that commitment on to the employees.

Technologies exist for capturing and reclaiming metal finishing waste, including rinsewaters. It is important to treat each recovery system with as much care as the plating baths. Regular maintenance and the use of trained operators will help ensure that the recovery system performs at its optimum design capacity. The recovery and reuse of the chemical solutions will add dollars into the metal finisher's pockets.

All four wastewater treatment systems introduced in this chapter are technically feasible for treating nickel-chromium plating wastewater in order to meet the maximum permissible concentrations shown in Table 6.1 for industrial wastewater discharge into a municipal sewerage system[15] or Table 6.2 for discharge to surface waters.[21]

TABLE 6.1
Maximum Permissible Concentrations of Industrial Wastewater Discharge into Municipal Systems

Parameter	Maximum Permissible Concentration (mg/L)
Arsenic	0.1
Boron	10.0
Barium	0.5
Cadmium	0.2
Copper	0.1
Cyanide	0.5
Lead	1.0
Mercury	0.5
Nickel	0.5
Silver	0.03
Chromium (total)	0.5

Continued

TABLE 6.1 (continued)

Parameter	Maximum Permissible Concentration (mg/L)
Vanadium	0.5
Zinc	0.5
Chloroform	1.0
BOD	1000
TSS	1000
COD	1500
Oil and grease (nonmineral)	300
Oil and grease (mineral)	100
Chlorinated hydrocarbons	0.02
Phenolic compounds	1.0
pH	5.5–9.5
Temperature	55.5°C

Source: Krofta, M. and Wang, L.K., *Design of Innovative Flotation–Filtration Wastewater Treatment Systems for a Nickel-Chromium Plating Plant*, U.S. Department of Commerce, National Technical Information Service, Springfield, VA, Technical Report PB-88-200522/AS, January 1984.

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids.

TABLE 6.2
Maximum Permissible Concentrations of Electroplating Wastewater Discharge to Surface Waters

Parameter	Maximum Permissible Value (mg/L)
pH	7–10
TSS	25
Oil and grease	10
Arsenic	0.1
Cadmium	0.1
Chromium (hexavalent)	0.1
Chromium (total)	0.5
Copper	0.5
Lead	0.2
Mercury	0.01
Nickel	0.5
Silver	0.5
Zinc	2
Total metals	10
Cyanides (free)	0.2
Fluorides	20
Trichloroethane	0.05
Trichloroethylene	0.05
Phosphorus	5

Source: See Table 6.1.

TSS, total suspended solids.

TABLE 6.3
Characteristics of Typical Wastewater Discharge of Conventional Reduction–Precipitation System[a]

Characteristic	Concentration (mg/L)	Amount of Pollutant Discharged (kg/d)
Chromium, Cr^{6+}	<0.006	<0.0003
Chromium, total	0.79	0.04
Iron	0.15	0.008
Nickel	0.21	0.011
TSS	<0.10	<0.51
Settleable solids	<0.1 mL/L	
pH	7.6–8.2	

TSS, total suspended solids.

[a] See Figure 6.4.

Table 6.3 shows the characteristics of a typical effluent discharge from a conventional reduction–precipitation system. The effluent quality meets industrial pretreatment requirements.

The modified reduction–flotation wastewater treatment system (Figure 6.5) will be very attractive if all or most of an existing wastewater treatment facilities are to be reused. The high-rate DAF clarifier is a very low-cost clarification unit.

The treatment efficiencies of the two innovative flotation–filtration wastewater treatment systems (Figures 6.6 and 6.7) are expected to be higher than those of the conventional reduction–precipitation system.

The innovative flotation–filtration wastewater treatment system (Figure 6.6) using conventional chemicals has the highest flexibility and best performance. When desirable, the innovative chemical FeS or equivalent can also be used.

Another innovative flotation–filtration wastewater treatment system using FeS (Figures 6.7 and 6.8) is highly recommended if a totally new system is to be designed and installed for treatment of nickel-chromium plating wastewater. This system is extremely compact, easy to operate, and cost-effective. Treatment efficiency is also excellent.

All flotation clarifiers[63] may be used for the treatment of nickel-chromium plating wastes regardless of their shapes (rectangular or circular) or manufacturers. A filtration unit is an optional step for final polishing. The treatment efficiency of separate flotation and filtration units[64] will be similar to that of a combined flotation–filtration unit (Figure 6.8).

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7 Waste Treatment and Management in the Coil Coating Industry

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7.1 GENERAL DESCRIPTION OF COIL COATING INDUSTRY AND OPERATIONS

The U.S. coil coating industry consists of about 80 plants processing approximately 1.5 billion square meters of painted coil each year. Facilities vary in size and corporate structure, ranging from independent shops to captive operations. Independent shops obtain untreated coil, conversion coating chemicals, and paints, and produce a wide variety of coated coil. Typically, the annual production at these coil coating plants is low compared to that from the captive coating operations. The captive coil coating operation is usually an integral part of a large corporation engaged in many other kinds of metal production and finishing.

The coil coating sequence, regardless of basis material or conversion coating process used, consists of three operational steps:

1. Cleaning
2. Conversion coating
3. Painting

There are three types of cleaning operations used in coil coating, and they can be used alone or in combination. These cleaning operations are as follows:

1. Mild alkaline cleaning
2. Strong alkaline cleaning
3. Acid cleaning

There are four basic types of conversion coating operations, and the use of one precludes the use of the others on the same coil:

1. Chromating
2. Phosphating
3. Use of complex oxides
4. No-rinse conversion coating

Some of these conversion coating operations are designed for use on specific basis materials. The painting operation is performed by roll coating and is independent of the basis material and conversion coating. Some specialized coatings are supplied without conversion-coating the basis material. For example, Zincrometal is a specialized coating consisting of two coats of special paints that do not require conversion coating. In this process, coils are cleaned and dried, and then receive two coats of the special paints.

The selection of basis material, conversion coating, and paint formulation is an art based upon experience. The variables that are typically involved in the selection are appearance, color, gloss, corrosion resistance, abrasion resistance, process line capability, availability of raw materials, customer preference, and cost. Some basis materials inherently work better with certain conversion coatings, and some conversion coatings work better with certain paint formulations. On the whole, however, the choice of which combination to use on a basis material is limited only by plant and customer preferences.[1–4]

The following subsections describe the coil coating processes in more detail.

7.2 CLEANING OPERATION OF COIL COATING

Coil coating requires that the basis material be clean. A thoroughly clean coil ensures efficient conversion coating and a resulting uniform surface for painting. The soils, oils, and oxide coatings found on a typical coil originate from rolling mill operations and storage conditions prior to coil coating. Such substances can stop the conversion coating reaction, cause a coating void on part of the basis material, and result in the production of a nonuniform coating. Cleaning operations must chemically and physically remove these interfering substances without degrading the surface of the basis material. Excessive cleaning can roughen a basically smooth surface to a point where a paint film will not provide optimum protective properties.

7.2.1 MILD ALKALINE CLEANING

Aluminum and galvanized steel are prone to develop an oxide coating that acts as a barrier to chemical conversion coatings. However, these oxide films are easier to remove than rust and, therefore, require a less vigorous cleaning process. A mild alkaline cleaner is usually applied with power spray equipment to remove the oxide coating and other interfering substances. The cleaning solutions normally used consist of combinations of sodium carbonates, phosphates, silicates, and hydroxides. These compounds give the solution its alkaline character and emulsify the removed soils. Soap and detergents may be added to the solution to lower the surface and interfacial tension.

7.2.2 Strong Alkaline Cleaning

A good cleaning solution also rinses easily. Solutions may be made stronger with the addition of more sodium hydroxide.

A spray rinse follows either the mild alkaline cleaning step or strong alkaline cleaning step. Spray rinsing is conducive to the fast line speeds that make coil coating an economical coating procedure. The spray rinse physically removes alkaline cleaning residues and soil by both the physical impingement of the water and the diluting action of the water. The rinsewater is usually maintained at approximately 66°C (150°F) to keep the coil warm for the subsequent conversion coating reactions and to help the rinsing action. The rinsing action prevents contamination of the conversion coating bath with cleaning residues that are dragged out on the strip and that could be subsequently deposited in the conversion coating solutions. The rinsing step also keeps the surface of the metal wet and active, which permits faster conversion coating film formation.

7.2.3 Acid Cleaning

Steel, unless adequately protected with a film of oil subsequent to rolling mill operations, has a tendency to form surface rust rather quickly. This rust on the surface of the metal prevents proper conversion coating. A traditional method of removing rust is an acid applied by power spray equipment. The spraying action cleans both by physical impingement and the etching action of the acid. The power spray action is followed by a brush scrub, which further removes soil loosened by the acid. The brush scrub is followed by a strong alkaline spray wash, which removes all traces of the acid and neutralizes the surface.[1–5]

7.2.4 Special Cleaning

The no-rinse conversion coating and the Zincrometal processes require a coil that is clean, warm, and dry. For these processes a squeegee roll and forced air drying are used to assure a clean, dry coil following alkaline cleaning and rinsing.

7.3 CONVERSION COATING PROCESS OF COIL COATING

The basic objective of the conversion coating process is to provide a corrosion-resistant film that is integrally bonded chemically and physically to the base metal and that provides a smooth and chemically inert surface for subsequent application of a variety of paint films. The conversion coating processes effectively render the surface of the basis material electrically neutral and immune to galvanic corrosion. Conversion coating on basis material coils does not involve the use of applied electric current to coat the basis material. The coating mechanisms are chemical reactions that occur between solution and basis material.[1–4]

Four types of conversion coatings are normally used in coil coating:

1. Chromate conversion coatings
2. Phosphate conversion coatings
3. Complex oxides conversion coatings
4. No-rinse conversion coatings

Chromate conversion coatings, phosphate conversion coatings, and complex oxide conversion coatings are applied in basically the same manner. No-rinse conversion coatings are roll applied and use quite different chemical solutions than phosphating, chromating, or complex oxides solutions. However, the dried film is used as basis for paint application similar to phosphating, chromating, and complex oxide conversion coating films.

7.3.1 CHROMATE CONVERSION COATINGS

Chromate conversion coatings can be applied to both aluminum and galvanized surfaces but are generally applied only to aluminum surfaces. These coatings produce an amorphous layer of chromium chromate complexes and aluminum ions. The coatings offer unusually good corrosion-inhibiting properties but are not as abrasion resistant as phosphate coatings. Scratched or abraded films retain a great deal of protective value because the hexavalent chromium content of the film is slowly leached by moisture, providing a self-healing effect. Under limited applications, these coatings can serve as the finished surface without being painted. If further finishing is required, it is necessary to select an organic finishing system that has good adhesive properties. Chromate conversion coatings are extremely smooth, electrically neutral, and quite resistant to chemical attack.

Chromate conversion coatings for aluminum are carried out in acidic solutions. These solutions usually contain one chromium salt, such as sodium chromate or chromic acid and a strong oxidizing agent such as hydrofluoric acid or nitric acid. The final film usually contains both products and reactants and water of hydration. Chromate films are formed by the chemical reaction of hexavalent chromium with a metal surface in the presence of "accelerators" such as cyanides, acetates, formates, sulfates, chlorides, fluorides, nitrates, phosphates, and sulfamates.

Chromate conversion coating requires that the basis material be alkaline-cleaned and spray-rinsed with warm water. The cleaning and rinsing assures a clean, warm, wet surface on which the conversion coating process takes place. Once the film is formed, it is rinsed with water followed by a chromic acid sealing rinse. This latter rinse seals the free pore area of the coating by forming a chromium chromate gel. Also, the sealing rinse more thoroughly removes precipitated deposits that may have been formed by hard water in previous operations. The coil is then subjected to a forced air drying step to assure a uniformly dry surface for the following painting operation.

7.3.2 PHOSPHATE CONVERSION COATINGS

Phosphate conversion coatings provide a highly crystalline, electrically neutral bond between a base metal and paint film. The most widespread use of phosphate coatings is to prolong the useful life of paint finishes. Phosphate coatings are primarily used on steel and galvanized surfaces but can also be applied to aluminum. Basically, there are three types of phosphate coatings:

1. Iron phosphate coating
2. Zinc phosphate coating
3. Manganese phosphate coating

Manganese phosphate coatings are not used in coil coating operations because they are relatively slow in forming and, as such, are not amenable to the high production speeds of coil coaters.

The remaining two phosphate coatings are applied by spraying or immersing the coil, with the major difference between them being the weight and thickness of the dried coating. Iron phosphate coatings are the thinnest and lightest and generally the cheapest. Iron phosphate solutions are applied chiefly as a base for paint films. Spray application of iron phosphating solutions is most commonly used. The coating weights range from 0.22 to 0.86 g/m^2.

Zinc phosphate coatings are quite versatile and can be used as a base for paint or oil, as an aid to cold forming, to increase wear resistance, and to provide rust-proofing. Zinc phosphate coatings can be applied by spray or immersion, with applied coating weights ranging from 1.08 to 10.8 g/m^2 for spray coating and from 1.61 to 43.1 g/m^2 for immersion coating.

Phosphate coatings are formed in the metal surface, incorporating metal ions dissolved from the surface. This creates a coating that is integrally bonded to the base metal. In this respect, phosphate coatings differ from electrodeposited coatings, which are superimposed on the metal. Most metal phosphates are insoluble in water but soluble in mineral acids. Phosphating solutions consist of metal phosphates dissolved in carefully balanced solutions of phosphoric acid. As long as the acid concentration of the bath remains above a critical point, the metal ions remain in solution. Accelerators speed up film formation and prevent the polarization effect of hydrogen on the surface of the metal. The accelerators commonly used include nitrites, nitrates, chlorates, and peroxides. Cobalt and nickel nitrite accelerators are the most widely used and develop a coarse crystalline structure. The peroxides are relatively unstable and difficult to control, whereas chlorate accelerators generate a fine sludge that may cause dusty or powdery deposits.

After phosphating, the coil is passed through a recirculating hot water spray rinse. The rinsing action removes excess acid and unreacted products, thereby stopping the conversion coating reaction. Insufficient rinsing could cause blistering under the subsequent paint film from the galvanic action of the residual acid and metal salts.

The basis material is then passed through an acid sealing rinse comprising up to 0.1% by volume of phosphoric acid, chromic acid, and various metallic conditioning agents, notably zinc. This solution seals the free pore area of the coating by forming a chromium chromate gel. Also, this acidic sealing rinse more thoroughly removes precipitated deposits formed by hard water in the previous rinses. Modified chromic acid rinses have been used extensively in the industry. These rinses are prepared by reducing chromic acid with an organic reductant to form a mixture of trivalent chromium and hexavalent chromium in the form of a complex chromium chromate.

7.3.3 COMPLEX OXIDE CONVERSION COATING

Complex oxide conversion coatings can be applied to aluminum and galvanized surfaces but are generally applied to only galvanized surfaces. The nature of the film and the chemical and physical actions of its formation are a function and a reinforcement of the naturally occurring protective oxide coating that is found on galvanized surfaces. The physical properties of the complex oxide conversion coating film are comparable to those of chromate conversion coating films and phosphate conversion coating films.

Complex oxide film is formed in a basic solution, whereas the films described earlier are formed in an acidic solution. Complex oxide conversion coating reactions do not contain either hexavalent or trivalent chromium ions. However, the sealing rinse contains much greater quantities of hexavalent and trivalent chromium ions than do the sealing rinses associated with phosphate conversion coatings and chromate conversion coatings.

7.3.4 NO-RINSE CONVERSION COATINGS

Recent developments in chromate conversion coating solutions have resulted in a solution that can be applied to cold rolled steel, galvanized steel, or aluminum without the need for any rinsing after the coating has formed on the basis material. The basis material must first be alkaline cleaned, thoroughly rinsed, and forced-air dried prior to conversion coating. The conversion coating solution is applied with a roll mechanism used in roll coating paint. Once the solution is roll coated onto the basis material, the coil is forced-air dried at approximately 66°C. The no-rinse solutions are formulated in such a way that once a film is formed and dried, there are no residual or detrimental products left on the coating that could interfere with normal coil coating paint formulations.

Although no-rinse conversion coatings currently represent a small proportion of the conversion coating techniques that are used, they offer several advantages, including fewer process steps in a physically smaller process line, higher line speeds, application of a very uniform thickness by roll coating rather than spray or dip coating, and reduction of waste treatment requirements because of the reduced use of chromium compounds. Disadvantages include roll coating mechanism wear possibly reducing quality, the closer coordination of the entire line that is needed, difficulty in adaptation, and the hazardous organic acids content of the no-rinse conversion coating chemicals.

7.4 PAINTING OPERATION OF COIL COATING

Roll coating of paint is the final process in a coil coating line. Roll coating is an economical method to paint large areas of metal with a variety of finishes and to produce a uniform and high-quality coating. The reverse roll procedure for coils is used by the coil coating industry, and allows both sides of the coil to be painted simultaneously.

The paint formulations used in the coil coating industry have high pigmentation levels (providing hiding power), adhesion, and flexibility. Most coatings of this type are thermosetting and are based on vinyl, acrylic, and epoxy functional aromatic polyethers, and some reactive monomer or other resin with reactive functions, such as melamine formaldehyde resins. Also, a variety of copolymers of butadiene with styrene or maleic anhydride are used in coating formulations. These coatings are cured by oxidation mechanisms during baking, similar to those that harden drying oils.

After paint application, all coils are cured in an oven. Curing temperatures depend upon basis material, conversion coating, paint formulation, and line speed. Typical temperatures range from ~93°C to a maximum of ~454°C. Upon leaving the oven, the coils are quenched with water to induce rapid cooling prior to rewinding.

The quench is necessary for all basis materials, conversion coatings, and paint formulations. A coil that is rewound when too warm will develop internal and external stresses, causing a possible degradation of the appearance of the paint film and of the forming properties of the coil. The volume of water used in the quench often has the largest flow rate of all of the coil-coating processes. However, the water is often circulated to a cooling tower for heat dissipation and reuse.

The finished coils are used in a variety of industries. The building products industry utilizes prefinished coils to fabricate exterior siding, window and door frames, storm windows, storm gutters, and various other trim and accessory building products. The food and beverage industries utilize various types of coils and finishes to safely and economically package and ship a wide variety of food and beverage products. Until recently, the automotive and appliance industries have made limited use of prefinished coils. These industries have relied on postassembly finishing of their products. Recently, the automotive industry has begun using a cold rolled steel coil coated on one side with a finish called Zincrometal. This coating is applied to the under surfaces of exterior automobile sheet metal to protect them from corrosion. The appliance industry uses prefinished coils in constructing certain models of refrigerator exteriors to provide a finished product that minimizes the costly and labor-intensive painting operation after forming.

Coil coating operations are located throughout the country, usually in well established industrial centers. Compared to some other industries, coil coating operations are not physically large. Coil coating operations use large quantities of water and are often a significant contributor to municipal waste treatment systems or surface waters. In addition, the curing ovens from coil coating operations are a source of air pollution in the form of reactive hydrocarbons.

7.5 SUBCATEGORIES OF THE COIL COATING INDUSTRY

7.5.1 General Description of Subcategorization

The primary purpose of subcategorization is to establish groupings within the coil coating industry such that each group has a uniform set of effluent limitations. Although subcategorization is based on wastewater characteristics, a review of the other subcategorization factors reveals that the basis material used and the processes performed on these basis materials are the principal factors affecting the wastewater characteristics of plants in the coil coating industry. The coil coating industry is therefore divided into the following three subcategories:

1. Coil coating on steel
2. Coil coating on zinc-coated steel (galvanized)
3. Coil coating on aluminum or aluminized steel

Of all coil coating plants in the U.S., about 36% of the plants pretreat their industrial effluents and directly discharge their pretreated effluents to the receiving waters, and the remaining 54% of the plants pretreat and discharge their effluents to the municipal wastewater treatment plants for further treatment. The following subsections describe the above subcategories.[1–3]

7.5.2 COIL COATING ON STEEL SUBCATEGORY

In the U.S., 59 facilities in the coil coating industry were surveyed for process type and pollutant levels. Of these, 38 plants are in the coil coating on steel subcategory. Ten facilities coat steel alone and the remaining 28 coat a combination of steel coils and coils from the other subcategories. The production rate is approximately 85,000 m^2/h. Operations used at these facilities include acid cleaning, strong alkaline cleaning, phosphating, no-rinse conversion coating, roll coating, and Zincrometal coating. Water usage rates for the general operations at steel coating facilities are listed in Table 7.1.

7.5.3 COIL COATING ON ZINC COATED STEEL (GALVANIZED STEEL) SUBCATEGORY

Within the 59 plants surveyed, 17 coil coat on galvanized steel with a production of ~60×10^3 m^2/h. Only two facilities produce coated galvanized steel alone. Operations used at the galvanized coating facilities include mild alkaline cleaning, phosphating, chromating, complex oxide treatment, no-rinse conversion coating, roll coating, and Zincrometal coating. Table 7.1 also presents water usage data for the general operations at galvanized coating facilities.[1,2]

TABLE 7.1
Summary of Water Usage Rates for the Coil Coating Industry by Subcategory

Operation	Number of Plants Sampled	Water Use (L/m^2) Range	Mean
Steel			
Cleaning	11	0.04–7.3	1.9
Conversion coating	8	0.04–0.76	0.43
Quenching	4	2.0–5.7	4.0
All operations	13	0.37–13	4.5
Galvanized			
Cleaning	10	0.17–8.8	1.9
Conversion coating	10	0.03–0.98	0.49
Quenching	5	0.44–5.1	2.7
All operations	12	0.65–8.4	3.6
Aluminum			
Cleaning	12	0.21–2.0	0.97
Conversion coating	12	0.18–1.8	0.56
Quenching	9	1.2–3.5	2.3
All operations	15	0.26–5.8	2.5

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

7.5.4 Coil Coating on Aluminum Subcategory

Thirty-nine of the facilities in the U.S. coil coat on aluminum with a production rate of 90×10^3 m^2/h. Nineteen facilities coat only aluminum coils. The aluminum coating facilities use mild alkaline cleaning, phosphating, chromating, complex oxide treatment, no-rinse conversion coating, and roll coating. Water usage rates for the general processes in this subcategory are listed in Table 7.1.

Water is used in virtually all coil coating operations. It provides the mechanism for removing undesirable compounds from the basis material, is the medium for the chemical reactions that occur on the basis material, and cools the basis material following baking. Water is the medium that permits the high degree of automation associated with coil coating and the high quality of the finished product. The nature of coil coating operations, the large amount of basis material processed, and the quantity and type of chemicals used produces a large volume of wastewater that requires treatment before discharge.

Wastewater generation occurs for each basis material (steel, galvanized and aluminum) and for each functional operation (cleaning, conversion coating, and painting). The wastewater generated by the three functional operations may be handled in one of the following ways:

1. It may flow directly to a municipal wastewater treatment system or surface water.
2. It may flow directly to an onsite waste treatment system and then to a municipal wastewater treatment system or surface water.
3. It may be reused directly or following intermediate treatment.
4. It may undergo a combination of the above processes.

Coil coating operations that produce wastewater are characterized by the pollutant constituents associated with respective basis materials. The constituents in the raw wastewaters include ions of the basis material, oil and grease found on the basis material, components of the cleaning and conversion coating solutions, and the paints and solvents used in roll coating the basis materials. The following tables present wastewater characterization data for each subcategory. The data presented are the results of verification analysis of the industry. Prior to verification sampling, a screening program was conducted to identify the presence or absence of the 129 priority pollutants. Those pollutants detected in screening at a concentration greater than 10 μg/L were further studied in the verification analysis. The minimum detection limit in the verification analysis for pesticides was 5 μg/L and for all other toxic pollutants, 10 μg/L. Any value below its detection limit is presented in the following tables as below detection limit (BDL).

Tables 7.2 through 7.5 present raw wastewater characterization data for each general process in each subcategory and for the wastewater in each subcategory when combined into a single representative stream as a whole. Table 7.6 presents raw wastewater flow data for each subcategory.

7.6 WASTEWATER CHARACTERIZATION OF THE COIL COATING INDUSTRY

7.6.1 Effluent Characteristics of Coil Coating on Steel Operation

Wastewaters from the coil coating on steel subcategory generally have higher levels of phosphorus than that from the other subcategories because of the use of concentrated phosphate alkaline cleaners. Oil and grease in this subcategory are also found in larger concentrations than the other basis materials' wastewater because of the increased raw material protection needed to inhibit rust. This can often cause an increase in the number of hydrocarbons found in the wastewater. Suspended solids may be at higher levels because of the adhering dirt in the oil.[1–3]

7.6.2 Effluent Characteristics of Coil Coating on Zinc Coated Steel (Galvanized Steel) Operation

Coil coating on galvanized steel generally produces significant suspended solids concentrations in wastewater. Another pollutant problem is the high concentration of dissolved zinc and iron in the

TABLE 7.2
Toxic and Classical Pollutants in Raw Wastewater of the Steel Subcategory, Verification Data

Pollutant	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples
	Cleaning Operations				Conversion Operations			
Toxic Organic Pollutants (μg/L)								
1,1-Trichloroethane	6	5	ND–BDL	BDL	8	3	ND–40	BDL
1,1-Dichloroethane	5	0	—	—	7	1	ND–77	11
1,1-Dichloroethylene	2	0	—	—	2	0	—	—
1,2-trans-Dichloroethylene	2	0	—	—	2	0	—	—
2,4-Dimethylpheno1	3	0	—	—	3	0	—	—
Fluoranthene	9	1	ND–68	BDL	7	1	ND–BDL	BDL
Isophorone	9	1	ND–18	BDL	7	0	—	—
Naphthalene	9	2	ND–20	BDL	7	4	ND–BDL	BDL
Phenol	3	0	—	—	3	0	—	—
Bis(2-ethylhexyl)phthalate	9	7	ND–150	34	7	5	ND–110	20
Butyl benzyl phthalate	9	1	ND–360	40	7	0	—	—
Di-n-butyl phthalate	9	5	ND–30	BDL	7	3	ND–14	BDL
Di-n-octyl phthalate	9	3	ND–BDL	BDL	7	1	ND–760	110
Diethyl phthalate	9	6	ND–210	46	7	6	ND–180	100
Dimethyl phthalate	9	0	—	—	7	0	—	—
1,2-Benzanthracene	9	2	ND–30	BDL	7	0	—	—
Benzo(a)pyrene	9	0	—	—	7	0	—	—
3,4-Benzo fluoranthene	9	0	—	—	7	0	—	—
Benzo(k)fluoranthene	9	0	—	—	7	0	—	—
Chrysene	9	2	ND–30	BDL	7	0	—	—
Acenaphthylene	9	1	ND–BDL	BDL	7	1	ND–BDL	BDL
Anthracene	9	7	ND–280	51	7	3	ND–BDL	BDL
1,1,2-Benzoperylene	9	0	—	—	7	0	—	—

Fluorene	9	1	ND–BDL	ND	7	2	ND–BDL	BDL
Phenanthrene	9	7	ND–280	51	7	3	ND–BDL	BDL
1,2,5,6-Dibenzanthracene	9	0	—	—	7	0	—	—
Ideno(1,2,3-cd)pyrene	9	0	—	—	7	0	—	—
Pyrene	9	0	—	—	7	0	—	—
Toluene	3	0	—	—	3	0	—	—
Trichloroethylene	6	4	ND–22	BDL	8	3	ND–89	13
Toxic Metals and Inorganics (μg/L)								
Cadmium	9	2	ND–BDL	BDL	8	3	ND–73	10
Chromium, total	9	8	ND–620	210	8	8	280–920,000	320,000
Chromium, hexavalent	9	0	—	—	8	7	ND–410,000	110,000
Copper	9	9	21–180	70	8	6	ND–160	41
Cyanide, total	8	5	ND–120	28	7	1	ND–92	12
Cyanide, amn. to chlorine	8	3	ND–99	17	7	1	ND–12	BDL
Lead	9	4	ND–1100	240	8	3	ND–3600	530
Nickel	9	5	ND–210	38	8	4	ND–19,000	4,000
Zinc	9	9	220–42,000	10,000	8	8	530–140,000	54,000
Classical Pollutants (mg/L)								
Aluminum	9	7	ND–0.85	0.35	8	5	ND–11	1.9
Fluorides	9	9	0.18–3.4	1.3	8	8	1.1–74	31
Iron	9	9	0.93–80	25	8	8	3.3–77	19
Manganese	9	9	0.26–1.7	0.8	8	8	0.11–1.5	0.61
Oi1 and grease	9	9	9.8–1600	520	7	6	ND–18	6.5
Phenols, total	9	5	ND–0.27	0.18	7	4	ND–0.23	0.038
Phosphorus	7	7	11–78	46	6	6	9.7–70	41
TDS	4	4	1100–17,000	9300	3	3	3300–3500	3400
TSS	9	9	52–440	220	8	8	27–250	130

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit; ND, not detected.

[a] BDL was calculated in the mean concentration as equal to zero.

TABLE 7.3
Toxic and Classical Pollutants in Raw Wastewater of the Galvanized Subcategory, Verification Data

Pollutant	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples
	Cleaning Operations				Conversion Operations			
Toxic Organic Pollutants (μg/L)								
1,1,1-Trichloroethane	10	4	ND–BDL	BDL	10	4	ND–140	21
1,1-Dichloroethane	1	0	—	—	1	0	—	—
1,1-Dichloroethylene	10	0	—	—	10	1	ND–BDL	BDL
1,2-*trans*-dichloroethylene	10	0	—	—	10	2	ND–15	BDL
2,4-Dimethyl phenol	2	0	—	—	2	0	—	—
Fluoranthene	10	3	ND–BDL	BDL	10	1	ND–23	BDL
Isophorone	10	1	ND–47	BDL	10	1	ND–520	52
Naphthalene	10	2	ND–38	BDL	10	5	ND–15	BDL
Phenol	4	0	—	—	4	0	—	—
Bis(2-ethylhexyl) phthalate	10	9	ND–340	110	10	9	ND–1200	220
Butyl benzyl phthalate	10	1	ND–130	13	10	3	ND–BDL	BDL
Di-n-butyl phthalate	10	7	ND–170	30	10	3	ND–20	BDL
Di-n-octyl phthalate	10	1	ND–BDL	BDL	10	0	—	—
Diethyl phthalate	10	8	ND–420	110	10	9	ND–300	77
Dimethyl phthalate	10	0	—	—	10	0	—	—
1,2-Benzanthracene	10	4	ND–27	13	10	1	ND–BDL	BDL
Benzo(a)pyrene	10	0	—	—	10	0	—	—
3,4-Benzo fluoranthene	10	0	—	—	10	0	—	—
Benzo(k)fluoranthene	10	0	—	—	10	0	—	—
Chrysene	10	4	ND–27	BDL	10	1	ND–BDL	BDL
Acenaphthylene	10	0	—	—	10	1	ND–BDL	BDL
Anthracene	10	3	ND–250	27	10	3	ND–290	29
1,1,2-Benzoperylene	10	0	—	—	10	0	—	—

Fluorene	10	4	ND–85	13	10	1	ND–BDL	BDL
Phenanthrene	10	3	ND–47	BDL	10	3	ND–290	29
1,2,5,6-Dibenzanthracene	10	0	—	—	10	0	—	—
Ideno(1,2,3-cd)pyrene	10	0	—	—	10	0	—	—
Pyrene	10	3	ND–BDL	BDL	10	1	ND–11	BDL
Toluene	4	0	—	—	4	0	—	—
Trichloroethylene	10	2	ND–BDL	BDL	10	2	ND–110	14
Toxic Metals and Inorganics (μg/L)								
Cadmium	10	8	ND–120	36	10	5	ND–110	21
Chromium, total	10	9	ND–610	280	10	10	3400–780,000	290,000
Chromium, hexavalent	9	1	ND–260	29	10	10	50–310,000	140,000
Copper	10	9	ND–57	27	10	8	ND–140	25
Cyanide, total	10	4	ND–43	BDL	10	5	ND–470	150
Cyanide, amn. to chlorine	10	3	ND–21	BDL	10	4	ND–330	48
Lead	10	9	ND–2600	1,400	10	10	BDL–1300	560
Nickel	10	1	ND–150	15	10	6	ND–31,000	4600
Zinc	10	10	690–120,000	63,000	10	10	33,000–710,000	220,000
Classical Pollutants (mg/L)								
Aluminum	10	9	ND–4.9	2.2	10	9	ND–11	3.2
Fluorides	10	10	0.16–16	2.5	10	10	1.5–71	16
Iron	10	10	0.19–17	4.8	10	10	0.84–21	6.6
Manganese	10	9	ND–0.73	0.17	10	10	0.035–1.3	0.25
Oil and grease	10	10	10–970	270	10	10	1.3–110	19
Phenols, total	9	7	ND–0.079	0.029	10	7	ND–0.067	0.015
Phosphorus	9	9	9.4–56	33	7	7	3.8–66	33
TDS	1	1	2001	—	1	1	2,500	—
TSS	10	10	19–630	250	10	10	68–450	250

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit; ND, not detected.

[a] BDL was calculated in the mean concentration as equal to zero.

TABLE 7.4
Toxic and Classical Pollutants in Raw Wastewater of the Aluminum Subcategory, Verification Data

Pollutant	Number of Samples	Number of Detections	Range of Smaples	Mean[a] of Samples	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples
	Cleaning Operations				Conversion Operations			
Toxic Organics (μg/L)								
Fluoranthene	12	0			12	0		
Isophorone	12	0			12	0		
Naphthalene	9	3	ND–BDL	BDL	12	3	ND–BDL	BDL
Phenol	2	0			2	0		
Bis(2-ethylhexyl)phthalate	12	10	ND–450	no	12	9	ND–300	37
Butyl benzyl phthalate	12	0			12			
Di-n-butyl phthalate	12	2	ND–12	BDL	12	2	ND–BDL	BDL
Di-n-octyl phthalate	12	0			12	1	ND–BDL	BDL
Diethyl phthalate	12	7	ND–450	99	12	9	ND–200	57
Dimethyl phthalate	12	2	ND–BDL	BDL	12	I	ND–110	BDL
1,2-Benzanthracene	12	0			12	0		
Benzo(a)pyrene	12	3	ND–BDL	BDL	12	2	ND–BDL	BDL
3,4-Benzo fluoranthene	12	0			12	0		
Benzo(k)fluoranthene	12	0			12	0		
Chrysene	12	0			12	0		
Acenaphthylene	12	0			12	0		
Anthracene	12	2	ND–BDL	BDL	12	4	ND–BDL	BDL
1,1,2-Benzoperylene	12	0			12	0		
Fluorene	12	1	ND–BDL	BDL	12	0		
Phenanthrene	12	2	ND–BDL	BDL	12	4	ND–BDL	BDL

1,2,5,6-Dibenz anthracene	12	0			12	0		
Ideno(1,2,3-cd)pyrene	12	0			12	0		
Pyrene	12	0			12	0		
Toluene	2	0			2	0		
Toxic Metals and Inorganics (µg/L)								
Cadmium	12	3	ND-21	BDL	12	3	ND–19	BDL
Chromium, total	12	9	ND–6000	980	12	12	15,000–960,000	270,000
Chromium, hexavalent	11	1	ND–6600	600	12	12	11,000–330,000	120,000
Copper	12	9	ND–210	63	12	10	ND–980	160
Cyanide, total	12	9	ND–260	30	12	9	ND–7500	2400
Cyanide, amn. to chlorine	12	8	ND–240	25	9	6	ND–7000	1400
Lead	12	5	ND–220	58	12	2	ND–400	48
Nickel	12	0			12	4	ND–260	40
Zinc	12	10	ND–14,000	1300	12	12	16–43,000	8800
Classical pollutants, (mg/L)								
Aluminum	12	12	8.6–940	400	12	12	11–410	160
Fluorides	12	9	ND–9.5	1.5	12	12	17–510	210
Iron	12	12	0.077–0.69	0.34	12	12	0.8–87	21
Manganese	12	9	ND–15	3.8	12	12	0.049–12	1.4
Oil and grease	12	9	ND–2800	400	12	9	ND–60	7.1
Phenols, total	12	11	ND–0.16	0.043	12	8	ND–0.14	0.02
phosphorus	9	6	ND–100	42	2	2	13–16	14
TSS	12	12	6.0–970	180	12	12	4.2–1200	160

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit; ND, not detected.

[a] BDL was calculated as equal to zero in the mean concentration.

TABLE 7.5
Toxic and Classical Pollutants in Quenching Raw Wastewater of All Subcategories, Verification Data

Pollutant	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples
Toxic Organic Pollutants (µg/L)				
1, 1, 1-Trichloroethane	9	4	ND–3100	400
1, 1-Dichloroethane	3	0	—	—
1, 1-Dichloroethylene	6	1	ND–36	BDL
1, 2-*trans*-Dichloroethylene	6	1	ND–43	BDL
2, 4-Dimethylphenol	3	0	—	—
Fluoranthene	18	1	ND–BDL	BDL
Isophorone	18	0	—	—
Naphthalene	18	3	ND–BDL	BDL
Phenol	7	0	—	—
Bis(2-ethylhexyl)phthalate	18	14	ND–880	72
Butyl benzyl phthalate	18	2	ND–15	BDL
Di-n-butyl phthalate	18	6	ND–20	BDL
Di-n-octyl phthalate	18	1	ND–BDL	BDL
Diethyl phthalate	18	15	ND–330	64
Dimethyl phthalate	18	2	ND–BDL	BDL
1,2-Benzanthracene	18	0	—	—
Benzo(a)pyrene	18	1	ND–BDL	BDL
3,4-Benzo fluoranthene	18	1	ND–BDL	BDL
Benzo(k)fluoranthene	18	1	ND–BDL	BDL
Chrysene	18	0	—	—
Acenaphthylene	18	0	—	—
Anthracene	18	2	ND–BDL	BDL
1,1,2-Benzoperylene	18	1	ND–BDL	BDL
Fluorene	18	0	—	—
Phenanthrene	18	2	ND–BDL	BDL
1,2,5,6-Dibenzanthracene	18	0	—	—
Ideno(1,2,3-cd)pyrene	18	0	—	—
Pyrene	18	0	—	—
Toluene	7	0	—	—
Trichloroethylene	9	5	ND–3100	410
Toxic Metals and Inorganics (µg/L)				
Cadmium	20	3	ND–270	15
Chromium, total	20	15	ND–440	43
Chromium, hexavalent	20	0	—	—
Copper	20	7	ND–17	BDL
Cyanide, total	20	17	ND–200	33
Cyanide, amn. to chlor.	20	11	ND–80	14
Lead	20	2	ND–64	BDL
Nickel	20	1	ND–190	BDL
Zinc	20	20	14–5000	610

Continued

TABLE 7.5 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Samples	Mean[a] of Samples
Classical Pollutants (mg/L)				
Aluminum	20	8	ND–1.4	0.38
Fluorides	20	20	0.15–11	1.6
Iron	20	20	0.018–1.6	0.37
Manganese	20	15	ND–0.78	0.14
Oi1 and grease	20	15	ND–26	5.3
Phenols, total	20	15	ND–0.04	0.012
Phosphorus	18	11	ND–15	1.2
TDS	3	3	99–1100	440
TSS	20	18	ND–24	6.2

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit; ND, not detected.

[a] BDL was calculated as equal to zero in the mean concentration.

wastewater as a result of the dissolved metals from the cleaning operation. Significant concentrations of hexavalent chromium are generally expected in all three subcategory wastewaters.

7.6.3 EFFLUENT CHARACTERISTICS OF COIL COATING ON ALUMINUM OPERATION

Wastewaters from the coil coating on aluminum subcategory contain higher levels of cyanide and fluorides than the other subcategories as a result of chromating solutions containing cyanide ions

TABLE 7.6
Wastewater Flows (m^3/day) for the Coil Coating Industry

Operation	Number of Samples	Flow Range	Flow Mean
Steel			
Cleaning	9	7.7–650	170
Conversion coating	8	1.4–75	38
Galvanized			
Cleaning	10	15–330	110
Conversion coating	10	1.8–75	36
Aluminum			
Cleaning	12	11–160	83
Conversion coating	12	15–60	39
Total industry			
Quenching	20	36–1100	320

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

and hydrofluoric acid. Aluminum wastewater is also more acidic and contains more dissolved aluminum. This is due to the acidic nature of the chromating solutions that dissolve more aluminum than the phosphating solutions.

Painting wastewater generally consists of quench water. Wastewater from this operation is generally less toxic than wastewater from the other general operations; normally, only the following pollutants are expected to exceed 10 µg/L: oil and grease, fluorides, TSS, iron, zinc, bis(2-ethylhexyl) phthalate, and diethyl phthalate.

7.7 PLANT-SPECIFIC EFFLUENT CHARACTERIZATION DATA

A limited amount of plant-specific data for the coil coating industry is available. Data available in the reference documents on the effluent streams for the plants discussed in the following subsections are summarized in Table 7.7. These data are verification data. All three subcategories are represented by the facilities.[1]

TABLE 7.7
Plant-Specific Effluent Concentrations, Verification Data

Pollutant	Steel Subcategory Plant A	Galvanized Subcategory Plant B	Aluminum Subcategory Plant C
Toxic Organic Pollutants (µg/L)			
1,1,1-Trichloroethane	BDL	BDL	—
1,1-Dichloroethane	ND	—	—
1,1-Dichloroethylene	—	ND	—
1,2-*trans*-Dichloroethylene	—	ND	—
2,4-Dimethylphenol	ND	—	—
Fluoranthene	BDL	BDL	ND
Isophorone	ND	BDL	ND
Naphthalene	BDL	BDL	BDL
Phenol	—	—	—
Bis(2-ethylhexyl)phthalate	BDL	42	15
Butyl benzyl phthalate	—	ND	ND
Di-n-butyl phthalate	BDL	BDL	ND
Di-n-octyl phthalate	ND	ND	ND
Diethyl phthalate	BDL	330	140
Dimethyl phthalate	BDL	ND	BDL
1,2-Benzanthracene	BDL	BDL	ND
Benzo(a)pyrene	—	ND	ND
3,4-Benzo fluoranthene	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND
Chrysene	BDL	BDL	ND
Acenaphthylene	ND	ND	ND
Anthracene	12	BDL	ND
1,1,2-Benzoperylene	—	ND	ND
Fluorene	BDL	BDL	ND
Phenanthrene	12	BDL	ND
1,2,5,6-Dibenzanthracene	—	ND	ND
Ideno(1,2,3-cd)pyrene	—	ND	ND
Pyrene	BDL	BDL	ND
Toluene	—	—	—
Trichloroethylene	BDL	ND	—

Continued

TABLE 7.7 (continued)

Pollutant	Steel Subcategory Plant A	Galvanized Subcategory Plant B	Aluminum Subcategory Plant C
Toxic Metals and Inorganics (μg/L)			
Cadmium	ND	ND	BDL
Chromium, total	1700	1300	BDL
Chromium, hexavalent	600	ND	ND
Copper	120	BDL	ND
Cyanide, total	BDL	ND	14
Cyanide, amn. to chlor.	ND	ND	ND
Lead	11	ND	ND
Nickel	10	15	ND
Zinc	290	2900	390
Classical Pollutants (mg/L)			
Aluminum	37	3900	5900
Fluorides	—	—	2300
Iron	700	250	130
Manganese	90	BDL	BDL
Oil and grease	3000	10,000	5900
Phenols, total	BDL	33	24
Phosphorus	4600	1700	BDL
TSS	460,000	27,000	8600

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit; ND, not detected.

7.7.1 PLANT A: COATING COLD ROLLED STEEL AND GALVANIZED STEEL

This site coats cold rolled steel and galvanized steel. The data presented are the analyses of the effluent from the cold rolled steel operations. Approximately 11 million m^2 of steel material are cleaned, coated and painted annually in the U.S. The plant uses water at a rate of 1.2 L/m^2 of product and produces 1630 m^2/h of coated steel coil.

7.7.2 PLANT B: COATING BOTH COLD ROLLED STEEL AND GALVANIZED STEEL

This facility coats both cold rolled steel and galvanized steel. The data presented are the analyses of the effluent from the galvanized steel operations. Approximately 22 million m^2 of galvanized steel are cleaned and coated and 45 million m^2 painted annually in the U.S. Water is used at a rate of 0.63 L/m^2 of product and the production rate of painted galvanized steel is 2700 m^2/h.

7.7.3 PLANT C: COATING ALUMINUM AND OTHER METALS

No production information is available for this facility. The data presented are the analyses of the effluent from the aluminum operations. Treatment consists of lagooning and sedimentation.

Tables 7.8 and 7.9 present the major pollutants and combined wastewater characteristics, respectively, of coil coating wastewater streams.

TABLE 7.8
Major Pollutants in Coil Coating Wastewater That Must Be Monitored and Removed

Industrial Category	40 CFR Reference	SIC Codes (Partial List)	Subparts	Promulgation Date	New Source Date	Regulated Parameters for Pretreatment
Coil Coating	465	3411	A—Steel basis material	12/01/82	1/12/81	Cr, Cn, Zn, TTO, oil and grease, Mn, F, P, Cu
Processes by which long thin strips of metal (coils) are cleaned and painted with an organic paint, includes canmaking		3412	B—Galvanized basis material			
		3479	C—Aluminum basis material			
		3497	D—Canmaking	11/17/83	2/10/83	

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

7.8 COIL COATING EFFLUENT TREATMENT TECHNOLOGIES

This section describes the treatment technologies currently in use to recover or remove wastewater pollutants normally found at coil coating facilities. The treatment processes can be divided into six categories: recovery techniques, oil removal, dissolved inorganics removal, cyanide destruction, trace organics removal, and solids removal.[5–14] Adoption of specific treatment processes will depend on the following:

1. The wastewater characteristics of a specific wastewater stream to be treated
2. The effluent discharge limitations imposed by the Federal and local governments

TABLE 7.9
Heavy Metal Concentration Ranges of Combined Coil Coating Wastewater

Pollutant	Minimum Concentration (mg/L)	Maximum Concentration (mg/L)
Cadmium	<0.1	3.83
Chromium	<0.1	116
Copper	<0.1	108
Lead	<0.1	29.2
Nickel	<0.1	27.5
Zinc	<0.1	337
Iron	<0.1	263
Manganese	<0.1	5.98
TSS	4.6	4390

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

7.8.1 ION EXCHANGE

Recovery of process chemicals in coil coating plants is applicable to chromating baths and sealing rinses. Recovery techniques currently in use include ion exchange and electrochemical chromium regeneration.[8,9]

Other possible recovery processes that are not currently in use include evaporation and insoluble starch xanthate. Ion exchange columns are used at four facilities within the coil coating industry. The wastewater stream is filtered to remove solids and then flows through a column of ion exchange resin, which retains copper, iron, and trivalent chromium. The stream then passes through an anion exchanger, which retains hexavalent chromium. Several columns may be necessary to achieve the desired levels. By regenerating the exchange resin, the life expectancy of the column is extended. In some regeneration procedures, hexavalent chromium is removed by conversion to sodium dichromate with sodium hydroxide. The sodium dichromate is then passed through a cation exchanger, which converts it to chromic acid for reuse. The cation exchanger can be regenerated with sulfuric acid.[9] Figure 7.1 illustrates how an ion exchange process can be applied to coil coating effluent treatment and Table 7.10 introduces some anticipated ion exchange capabilities for removal of heavy metals from coil coating wastewater streams.

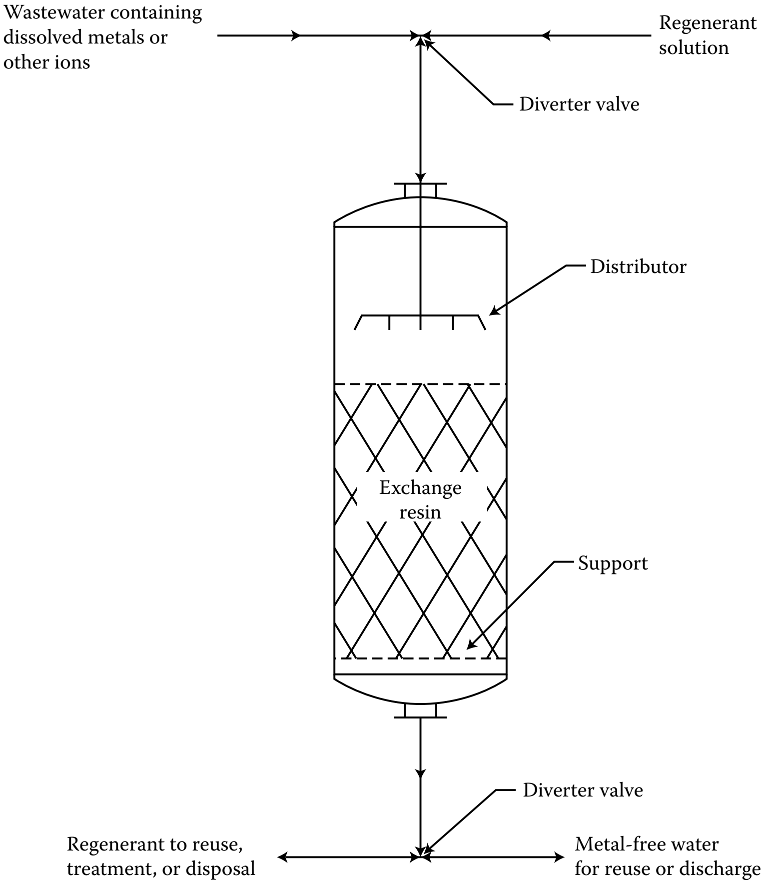

FIGURE 7.1 Ion exchange process. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

TABLE 7.10
Removal of Heavy Metals and Sulfate from Coil Coating Wastewater by Ion Exchange Process

	Plant A		Plant B	
Parameter (mg/L)	**Prior to Purification**	**After Purification**	**Prior to Purification**	**After Purification**
Aluminum	5.6	0.20	—	—
Cadmium	5.7	0.00	—	—
Chromium^{3+}	3.1	0.01	—	—
Chromium^{6+}	7.1	0.01	—	—
Copper	4.5	0.09	43.0	0.10
Cyanide	9.8	0.04	3.40	0.09
Gold	—	—	2.30	0.10
Iron	7.4	0.01	—	—
Lead	—	—	1.70	0.01
Manganese	4.4	0.00	—	—
Nickel	6.2	0.00	1.60	0.01
Silver	1.5	0.00	9.10	0.01
SO_4	—	—	210.00	2.00
Tin	1.7	0.00	1.10	0.10
Zinc	14.8	0.40	—	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

7.8.2 ELECTROCHEMICAL CHROMIUM REGENERATION

Electrochemical chromium regeneration oxidizes trivalent chromium to hexavalent chromium by electrooxidation. This system can be used with the wastewater or the dragout sludge from a settling basin. One coil coating operation presently uses this technique for chromic acid regeneration. This system offers relatively low energy consumption, operation at normal bath temperatures, elimination of metallic sludges, and regeneration of chromic acid.[8–10]

7.8.3 OIL SKIMMING

Oils occurring in wastewaters from the coil coating industry generally come from cutting fluids, lubricants, and preservative coatings used in metal fabrication operations. Oil skimming is the only current method used in this industry to remove oil. Oil flotation, as shown in Figure 7.2, has been suggested for this industry to achieve low oil concentrations or to remove emulsified oils, but is not in current practice.[8,9] Table 7.11 presents the treatment results of the emulsion breaking process.

Oil skimming as a pretreatment method is effective in removing naturally floating waste material. It can also improve the performance of subsequent downstream treatments. Many coil coating plants employ this treatment process.

7.8.4 CHROMIUM REDUCTION AND CHEMICAL PRECIPITATION

The dissolved inorganic pollutants for the coil coating category are hexavalent chromium, chromium (total), copper, lead, nickel, zinc, cadmium, iron, and phosphorus. Removal of these inorganics is often

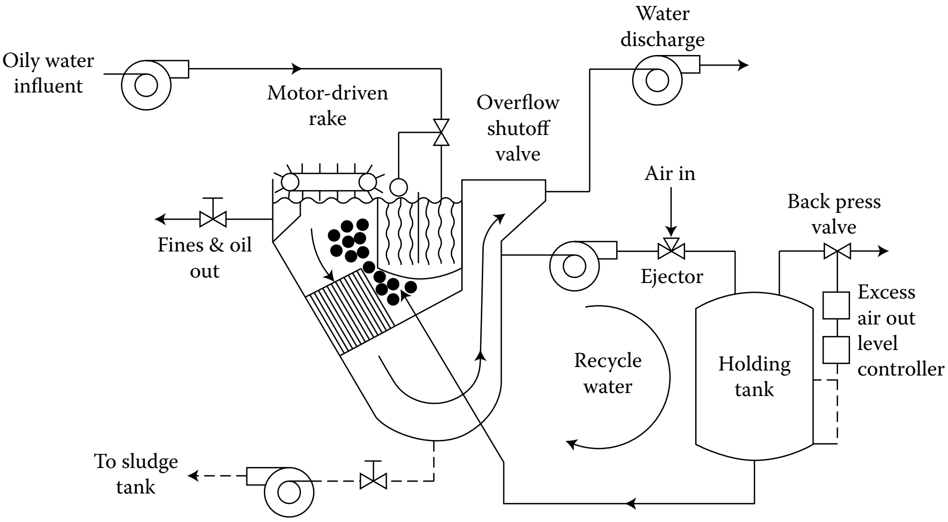

FIGURE 7.2 Dissolved air flotation process. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

a major step toward detoxifying wastewater. Chromium reduction, which can be carried out chemically or electrochemically, is frequently a preliminary step, as shown in Figure 7.3. The next major step in the classic treatment system is chemical precipitation, which is often accomplished by the addition of lime, sodium sulfide, sodium hydroxide, sodium carbonate, or ammonia. These additives result in the precipitation of metal hydroxides. The chemical reactions of the chromium reduction and chemical precipitation system for coil coating wastewater can be found in the literature.[8,9]

7.8.5 CYANIDE DESTRUCTION

Cyanide destruction in coil coating facilities is necessary to reduce the cyanide concentration in wastewater from the plating and cleaning baths. Cyanide is generally destroyed by oxidation. Alkaline chlorination is the standard technique used in the coil coating industry, but oxidation by ozone, hydrogen peroxide, or by electrochemical means has been suggested. These alternative techniques, however, have not been demonstrated at this time. The reader is referred to the literature[9] for details of the cyanide destruction and removal system.

7.8.6 OIL–WATER SEPARATION, BIOLOGICAL TREATMENT, POWDERED ACTIVATED CARBON ADSORPTION, AND CLARIFICATION

Plant sampling data show that organic compounds tend to be removed in standard biological wastewater treatment process equipment. Oil separation not only removes oil but also removes organics that are more soluble in the oil than in water. Combined powdered activated carbon (PAC) adsorption and clarification also removes organic solids by adsorption on inorganic solids. PAC adsorption to remove organics has been demonstrated in the electroplating industry, but is not commonly used in the coil coating industry. Wang, Hung, and Shammas[9] have introduced detailed processes for PAC and oil–water separation. Table 7.12 indicates that many toxic organic substances are removed simultaneously when oil is removed during coil coating wastewater treatment.

Clarification by either sedimentation or dissolved air flotation is the most common solid–water separation technique used for the removal of precipitates. In this process application, clarification

TABLE 7.11
Removal of Total Suspended Solids and Oil and Grease from Coil Coating Wastewater by Emulsion Breaking and Clarification Process

	Concentration (mg/L)		
Parameter	**Influent**	**Effluent**	**Reference**
Oil and grease	6060	98	Sampling data[a]
TSS	2612	46	
Oil and grease	13,000	277	Sampling data[b]
	18,400	—	
	21,300	189	
TSS	540	121	
	680	59	
	1060	140	
Oil and grease	2300	52	Sampling data[c]
	12,500	27	
	13,800	18	
TSS	1650	187	
	2200	153	
	3470	63	
Oil and grease	7200	80	Sampling data[d]

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

[a] Oil and grease and total suspended solids were taken as grab samples before and after batch emulsion breaking treatment, which used alumn and polymer on emulsified rolling oil wastewater.

[b] Oil and grease (grab) and total suspended solids (grab) samples were taken on three consecutive days from emulsified rolling oil wastewater. A commercial demulsifier was used in this batch treatment.

[c] Oil and grease (grab) and total suspended solids (composite) samples were taken on three consecutive days from emulsified rolling oil wastewater. A commercial demulsifier (polymer) was used in this batch treatment.

[d] This result is from a full-scale batch chemical treatment system for emulsified oils from a steel rolling mill.

(sedimentation or dissolved air flotation) is preceded by chemical precipitation, which converts dissolved pollutants to a solid form, and by coagulation, which enhances separation by coagulating suspended precipitates into larger flocs. The major advantage of clarification is the simplicity of the process. Clarification is used in 55 coil coating plants in various forms, including ponds, lagoons, slant tube clarifiers, flotation clarifiers, and Lamella clarifiers.

7.8.7 GRANULAR BED FILTRATION AND GRANULAR ACTIVATED CARBON FILTRATION

Granular bed filters are used in ten coil coating plants to remove residual solids from the clarifier effluent, and are considered to be tertiary or advanced wastewater treatment. Chemicals may be added upstream to enhance the solids removal. Pressure filtration is also used in this industry to reduce the solids concentration in clarifier effluent and to remove excess water from the clarifier sludge. Figure 7.4 shows a granular bed filter and Table 7.13 presents the heavy metal removal data of a lime clarification and filtration system.

Granular activated carbon (GAC) and peat adsorption are two tertiary wastewater filtration processes using GAC and peat, respectively, as the media for removing not only insoluble suspended solids, but also dissolved organic solids.[8] Tables 7.14 and 7.15 report the adsorption efficiencies for

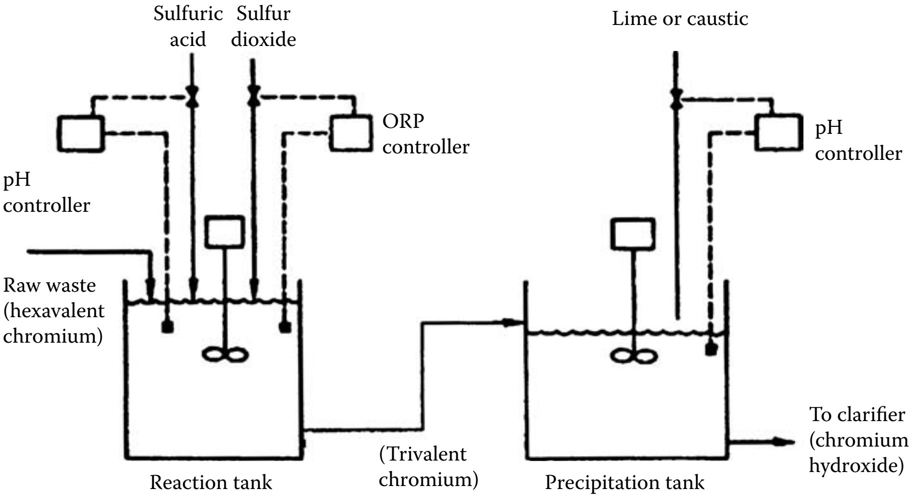

FIGURE 7.3 Chromium reduction and precipitation system. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

TABLE 7.12
Removal of Total Toxic Organics and Oil and Grease from Coil Coating Wastewater by Oil–Water Separation

Pollutant	Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
001	Acenaphthene	5.7	ND
038	Ethylbenzene	0.089	0.01
055	Naphthalene	0.75	0.23
062	N-nitrosodiphenylamine	1.5	0.091
065	Phenol	0.18	0.04
066	Bis(2-ethylhexyl)phthalate	1.25	0.01
068	Di-n-butyl phthalate	1.27	0.019
078/081	Anthracene/phenanthrene	2.0	0.1
080	Fluorene	0.76	0.035
084	Pyrene	0.075	0.01
085	Tetrachloroethylene	4.2	0.1
086	Toluene	0.16	0.02
087	Trichloroethylene	4.8	0.01
097	Endosulfan sulfate	0.012	ND
098	Endrin	0.066	0.005
107	PCB 1254[a]	1.1	0.005
110	PCB 1248[b]	1.8	0.005

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

[a] PCB 1242, PCB 1254, PCB 1221, PCB 1232 reported together.

[b] PCB 1248, PCB 1260, PCB 1016 reported together.

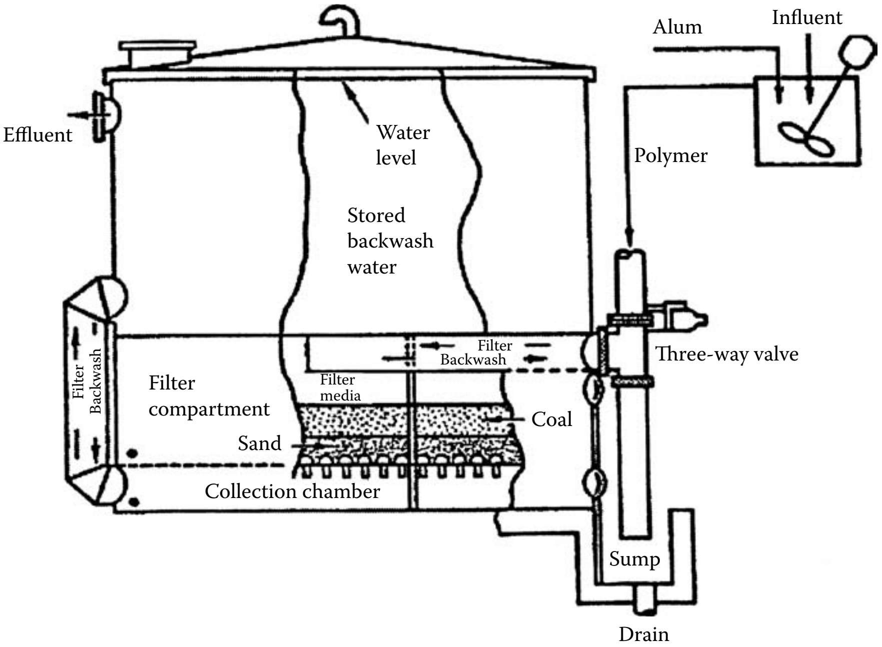

FIGURE 7.4 Granular bed filtration. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

removing mercury by GAC and heavy metals by peat, respectively. Figure 7.5 is a schematic of the granular activated carbon filtration process.

7.8.8 MEMBRANE PROCESSES

Membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), electrodialysis reversal (EDR), and so on.[9–10,13] MF, UF, NF, and RO are also called membrane filtration processes, of which only UF has been widely used by the coil coating industry for wastewater treatment. Membrane filtration is a physical unit process used to segregate dissolved or suspended solids from a liquid stream on the basis of molecular size. Figures 7.6 and 7.7 illustrate how a UF process works. The ultrafilter membrane forms a molecular screen that separates molecular particles based on their differences in size, shape, and chemical structure. A hydrostatic pressure, ranging from 34 to 690 kPa (5 to 100 psi), is applied to the upstream side of a membrane unit, which acts as a filter passing small particles while blocking (rejecting) larger emulsified and suspended matter. The pores of UF membranes are much smaller than the retained particles, thereby preventing the particles from clogging the membrane. In contrast to ordinary filtration, the concentrated retained particles are continuously washed off the membrane filter rather than being held by the filter. Tables 7.16 and 7.17 show some treatability data of UF in treating the coil coating wastewater streams.

7.8.9 OTHER WATER–SOLIDS SEPARATION TECHNOLOGIES

Other sludge dewatering technologies used include vacuum filtration, centrifugation, and sludge bed drying. No pollutant removability data are currently available for this industry.

TABLE 7.13
Removal of Heavy Metals from Coil Coating Wastewater by Lime Precipitation, Clarification, and Filtration

Parameters	No. of Plants	Range (mg/L)	Mean ± s.d.	Mean + 2 s.d.
For 1979–Treated Wastewater				
Chromium	47	0.015–0.13	0.045 ± 0.029	0.10
Copper	12	0.01–0.03	0.019 ± 0.006	0.03
Nickel	47	0.08–0.64	0.22 ± 0.13	0.48
Zinc	47	0.08–0.53	0.17 ± 0.09	0.35
Iron				
For 1978–Treated Wastewater				
Chromium	47	0.01–0.07	0.06 ± 0.10	0.26
Copper	28	0.005–0.055	0.016 ± 0.010	0.04
Nickel	47	0.10–0.92	0.20 ± 0.14	0.48
Zinc	47	0.08–2.35	0.23 ± 0.34	0.91
Iron	21	0.26–1.1	0.49 ± 0.18	0.85
Raw Waste				
Chromium	5	32.0–72.0		
Copper	5	0.08–0.45		
Nickel	5	1.65–20.0		
Zinc	5	33.2–32.0		
Iron	5	10.0–95.0		

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

s.d., standard deviation.

TABLE 7.14
Removal of Mercury from Coil Coating Wastewater by Granular Activated Carbon Filtration

	Mercury Levels (mg/L)	
Plant	In	Out
A	28.0	0.9
B	0.36	0.015
C	0.008	0.0005

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

TABLE 7.15
Removal of Heavy Metals from Coil Coating Wastewater by Peat Adsorption

Pollutant (mg/L)	In	Out
Chromium^{6+}	35,000	0.04
Copper	250	0.24
Cyanide	36.0	0.7
Lead	20.0	0.025
Mercury	1.0	0.02
Nickel	2.5	0.07
Silver	1.0	0.05
Antimony	2.5	0.9
Zinc	1.5	0.25

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

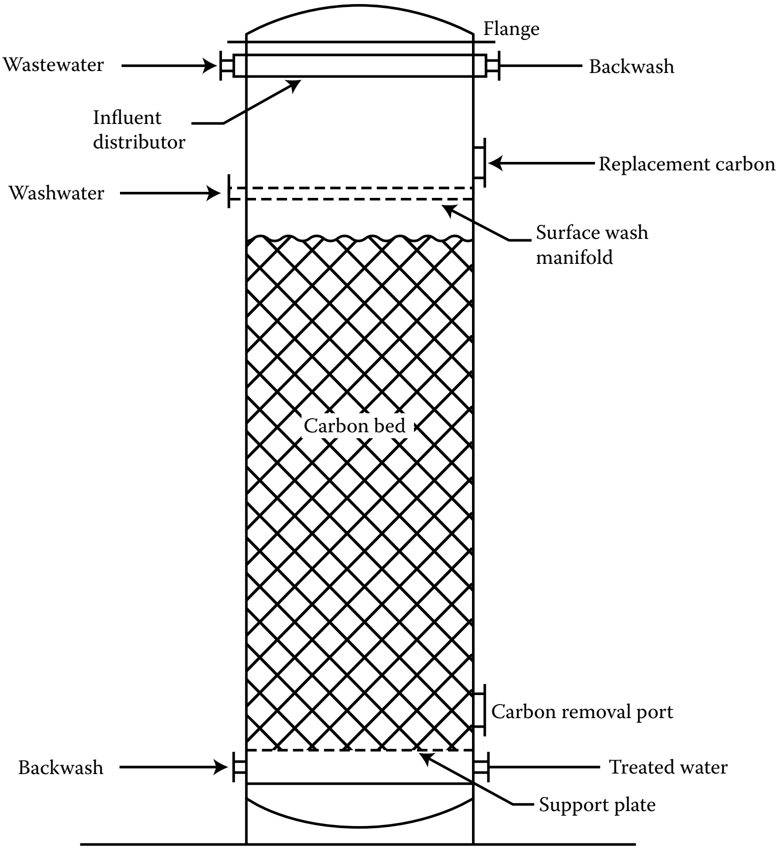

FIGURE 7.5 Schematic of granular activated carbon filtration process. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

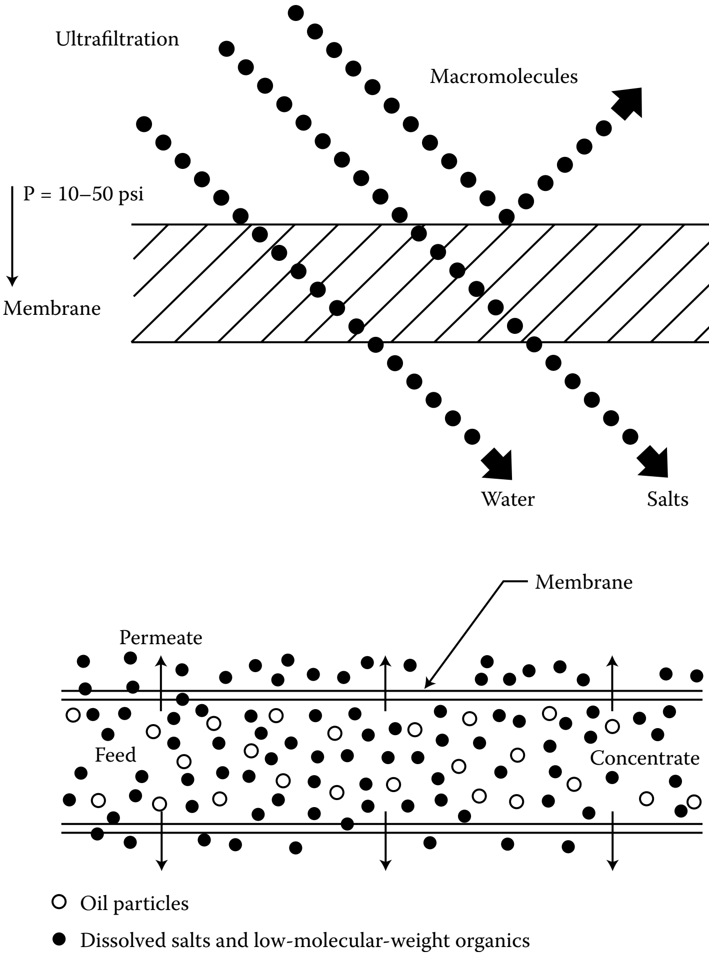

FIGURE 7.6 Membrane ultrafiltration. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

7.8.10 FULL-SCALE WASTEWATER TREATMENT CASE HISTORY: STEEL SUBCATEGORY

Hamilton Standard of the U.S. EPA has reported several coil coating plants' wastewater treatment case histories.[8,9] A full-scale wastewater treatment plant system has performed well for treatment of the wastewater generated from coil coating steel subcategory operations. The process principles and operational data of the full-scale treatment of a steel subcategory wastewater are summarized herein for the convenience of readers:

1. The process flow scheme consists of chromium reduction, lime precipitation, and clarification.
2. The sources of theories and principles for chromium reduction using an acid, chemical precipitation using a base, and clarification are detailed in Refs. 8 to 10.
3. The flow rate of the wastewater treatment facility is 174,000 m^3/d.
4. The acid used for chromium reduction is sulfuric acid.
5. The base used for neutralization and chemical precipitation is lime (note: sodium hydroxide can also be used for neutralization and chemical precipitation).

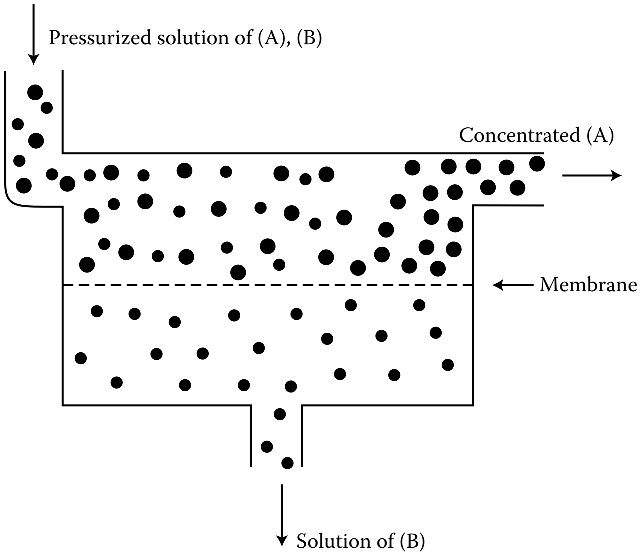

FIGURE 7.7 Schematic of membrane ultrafiltration process. [From U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.]

TABLE 7.16
Removal of COD, TSS, TS, and Oil and Grease from Coil Coating Wastewater by Ultrafiltration

Parameter	Feed (mg/L)	Permeate (mg/L)
Oil (freon extractable)	1230	4
COD	8920	148
TSS	1380	13
Total solids	2900	296

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

TABLE 7.17
Removal of Heavy Metals from Coil Coating Wastewater by Membrane Filtration

Specific Metal, mg/L	Manufacturers' Guarantee	Plant 19066		Plant 31022		Predicted Performance
		In	Out	In	Out	
Aluminum	0.5	—	—	—	—	—
Chromium^{6+}	0.02	0.46	0.01	5.25	<0.005	—
Chromium (total)	0.03	4.13	0.018	98.4	0.057	0.05
Copper	0.1	18.8	0.043	8.00	0.222	0.20

Continued

TABLE 7.17 (continued)

Specific Metal, mg/L	Manufacturers' Guarantee	Plant 19066		Plant 31022		Predicted Performance
Iron	0.1	288	0.3	21.1	0.263	0.30
Lead	0.05	0.652	0.01	0.288	0.01	0.05
Cyanide	0.02	<0.005	<0.005	<0.005	<0.005	0.02
Nickel	0.1	9.56	0.017	194	0.352	0.40
Zinc	0.1	2.09	0.046	5.00	0.051	0.10
TSS	—	632	0.1	13.0	8.0	1.0

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

6. The type of clarification used comprises eight sedimentation tanks (note: dissolved air flotation can also be used for clarification).
7. The sedimentation hydraulic detention time is 3.9 h.
8. The sedimentation hydraulic loading rate is 733 L/h/m^2.
9. The operation mode is continuous, 24 h/d.
10. The pollutant removal data are as follows:

	Initial Concentration	Reduction (%)
TSS	34 mg/L	82
Iron	2 mg/L	50
Tin	0.02 mg/L	55
Oil and grease	20 mg/L	10
Cobalt	0.5 mg/L	60
Cadmium	8 μg/L	99
Lead	200 μg/L	>99
1,1,1-Trichloroethane	2400 μg/L	88
Trichloroethylene	2700 μg/L	93
1,1-Dichloroethylene	530 μg/L	87
1,2-*trans*-Dichloroethylene	16 μg/L	38
Ethylbenzene	2 μg/L	>99
Isophorone	170 μg/L	35
Tetrachloroethylene	4 μg/L	50
Toluene	29 μg/L	83

7.8.11 FULL-SCALE WASTEWATER TREATMENT CASE HISTORY: GALVANIZED SUBCATEGORY

A full-scale wastewater treatment plant system has performed well for treatment of the wastewater generated from coil coating galvanized subcategory operations. The process principles and operational data of the full-scale treatment of a galvanized subcategory wastewater are summarized as follows:

1. The process flow diagram consists of chromium reduction, chemical precipitation, and clarification.
2. The sources of theories and principles for chromium reduction using an acid, chemical precipitation using a base, and clarification can be found in Refs. 8 to 10.

3. The flow rate of the wastewater treatment facility is 174,000 m^3/d.
4. The acid used for chromium reduction is sulfuric acid.
5. The base used for neutralization and chemical precipitation is lime (note: sodium hydroxide can also be used for neutralization and chemical precipitation).
6. The type of clarification used comprises eight sedimentation tanks (note: dissolved air flotation can also be used for clarification).
7. The sedimentation hydraulic detention time is 3.9 h.
8. The sedimentation hydraulic loading rate is 733 L/h/m^2.
9. The operation mode is continuous, 24 h/d.
10. The pollutant removal data are as follows:

	Initial Concentration	Reduction (%)
TSS	170 mg/L	88
Iron	44 mg/L	96
Aluminum	1.8 mg/L	62
Oil and grease	54 mg/L	61
Manganese	0.38 mg/L	76
Copper	14 μg/L	>99
Chromium	1300 μg/L	92
Lead	260 μg/L	>99
Zinc	2000 μg/L	95
1,1,1-Trichloroethane	3100 μg/L	19
Trichloroethylene	3800 μg/L	21
1,2-*trans*-Dichloroethylene	34 μg/L	44

7.8.12 FULL-SCALE WASTEWATER TREATMENT CASE HISTORY: ALUMINUM SUBCATEGORY

A full-scale wastewater treatment plant system has performed well for treatment of the wastewater generated from coil coating aluminum subcategory operations. The process principles and operational data of the full-scale treatment of the aluminum subcategory wastewater are summarized as follows:

1. The process flow diagram consists of chromium reduction, chemical precipitation, and clarification.
2. The sources of theories and principles for chromium reduction using an acid, chemical precipitation using a base, and clarification are detailed in Refs. 8 to 10.
3. The flow rate of the wastewater treatment facility is 3930 L/d.
4. The acid used for chromium reduction is sulfuric acid.
5. The base used for neutralization and chemical precipitation is sodium hydroxide (note: lime can also be used for neutralization and chemical precipitation).
6. The type of clarification used consists of tube plate settlers (note: dissolved air flotation can also be used for clarification).
7. The operation mode is continuous, 24 h/d.
8. The pollutant removal data are as follows:

	Initial Concentration	Reduction (%)
TSS	530 mg/L	93
Iron	7.3 mg/L	99
Phosphorus	46 mg/L	97
Oil and grease	1400 mg/L	98

Continued

	Initial Concentration	Reduction (%)
Phenol, total	0.07 mg/L	71
Aluminum	530 mg/L	99
Manganese	1.1 mg/L	99
Cadmium	5.5 μg/L	>99
Chromium	330,000 μg/L	99
Copper	220 μg/L	95
Nickel	95 μg/L	>99
Zinc	19,000 μg/L	>99
Lead	115 μg/L	>99
Bis(2-ethyhexyl)phthalate	140 μg/L	96
Diethyl phthalate	240 μg/L	99
Hexavalent chromium	140,000 μg/L	>99

7.9 WASTEWATER TREATMENT LEVELS VERSUS COSTS

The investment cost, operating and maintenance costs, and energy costs for the application of control technologies to the wastewater of the coil coating industry have been analyzed. These costs were developed to reflect the practical application of technologies in this industry. A detailed presentation of the cost methodology and cost data is available in the literature.[1–19]

Application of the wastewater treatment technologies can fall into one of the following legal categories:

1. The best practicable control technology (BPT) currently available under the U.S. Federal Act Section 304(b)(1)
2. The best available technology (BAT) economically achievable under the U.S. Federal Act Section 304(b)(2)(B)
3. The best conventional pollutant control technology (BCT), under U.S. Federal Act Section 304(b)(4)

The available industry-specific cost information is characterized as follows. Unit operation/unit process configurations have been analyzed for the cost of application to the wastewater of this industry. Recommended unit process configurations for BPT and BAT levels of treatment and their costs are summarized briefly in the following sections.

7.9.1 BPT Level Treatment

7.9.1.1 Suggested BPT

The BPT treatment train for the steel, galvanized, and aluminum subcategories of wastewater consists of chemical oxidation of cyanide and chemical reduction of chromium for cyanide- and chromium-bearing wastestreams; oil skimming, chemical precipitation with lime, and sedimentation of combined wastestreams; and a vacuum filter to dewater sludge. For the purpose of cost estimates, cyanide oxidation was assumed to be a required treatment process only for the aluminum subcategory, because of the presence of cyanide in the chromating bath applied to aluminum. Chromium reduction was included in the system costs for all subcategories to treat chromium wastes from the chromic acid sealer and conversion coating rinses, where appropriate.

7.9.1.2 System Component of the Suggested BPT

Cyanide oxidation consists of a reaction with sodium hypochlorite under alkaline conditions in either a batch or continuous system. A complete system includes reactors, sensors, controls, mixers, and chemical feed equipment. Chromium reduction consists of reaction with sulfur dioxide under acid conditions for continuous systems and reaction with sodium bisulfite under acid conditions for batch systems. A complete system consists of reaction tanks, mixers and controls, and chemical feed equipment. Oil is separated from process wastewater by gravity in a baffled rectangular concrete tank and removed by a skimming device. Chemical precipitation and sedimentation may be by either a continuous or batch treatment system. A continuous system includes chemical storage and feeding equipment, a mix tank for reagent feed addition, a flocculator, and settling tank with associated equipment. A batch treatment system consists of dual tanks and chemical storage and feeding equipment.

7.9.1.3 Unit Cost of the Suggested BPT

Total annual unit costs consisting of annual cost of capital, depreciation, operation and maintenance cost, and energy cost for medium, low, and high flow rates are summarized in Table 7.18.

7.9.2 BAT Level of Treatment

7.9.2.1 Suggested BAT

The BAT level of treatment consists of all components of BPT except segregation and recirculation of quench wastewater. The combined wastewater after sedimentation is treated in multimedia filters and then discharged.

7.9.2.2 System Components of the Suggested BAT

Quench waste recirculation requires installation of a cooling tower to lower the temperature of the quench wastewater stream. The multimedia filter system for the final polishing of effluent includes a backwash mechanism, pumps, control media, and the filter structure.

7.9.2.3 Unit Cost of the Suggested BAT

Total annual unit costs for the complete BAT system, which includes components described in the BPT system for the three different flow rates, are summarized in Table 7.19.

7.10 MULTIMEDIA WASTE MANAGEMENT IN THE COIL COATING INDUSTRY

7.10.1 Air Pollution Control

In the U.S., the Clean Air Act regulates the emission of volatile organic compounds (VOCs) (40 CFR Part 60) and hazardous air pollutants (HAPs) (40 CFR Part 61 and 40 CFR Part 63).

TABLE 7.18
Total Annual Unit Cost for BPT Level of Treatment in 2008 U.S. Dollars

Coil Coating Subcategory	Flow[a] (L/min)	Cost ($/m^3)	Flow[a] (L/min)	Cost ($/m^3)	Flow[a] (L/min)	Cost ($/m^3)
Steel	4	21	342	0.94	657	0.47
Galvanized	26	5.6	131	1.4	526	0.70
Aluminum	13	12	158	1.9	394	1.2

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

[a] For flows less than 342 L/min treatment is by batch system.

TABLE 7.19
Total Annual Unit Cost for BAT Level of Treatment in 2008 U.S. Dollars

Coil Coating Subcategory	Flow (L/min)	Cost ($/m^3)	Flow (L/min)	Cost ($/m^3)	Flow (L/min)	Cost ($/m^3)
Steel	2	NA	137	2.6	263	1.6
Galvanized	23	28	46	7.0	184	2.3
Aluminum	5	47	55	7.0	138	3.7

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Coil Coating Point Source Category* (Canmaking Subcategory), Final report 440/1-83/071, Washington, DC, November 1983; U.S. EPA, *Coil Coating Forming Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

Note: All costs are for batch treatment systems.

Depending on the solvent content of the coating material used with roll and coil methods, solvents can evaporate and produce sufficient VOC and HAP emissions to subject an operator to major source requirements and Title V permitting requirements.[15] The Act also provides specific standards of performance to control emissions from coil coating operations (40 CFR Part 60 TT). Controlling VOC emissions from roll and coil coating areas can be accomplished in several ways. First, a coating material with a lower VOC content can be used. Second, air pollution control equipment can be attached to the ventilation system to capture VOCs prior to their release into the atmosphere. Roll and coil coating systems apply coating materials, which may include solvents classified as volatile organic compounds and/or hazardous air pollutants. The solvents evaporate and may accumulate above limits allowed by Clean Air Act Title V permits. Ventilation and exhaust systems must operate properly to ensure the vapors are removed from the coating area. Air pollution control equipment should be attached to exhaust systems to recover or destroy volatile organic compounds instead of releasing them to the air. All air pollution control technologies are discussed in two recent books published by Wang, Pereira, and Hung.[6,7]

7.10.2 WATER POLLUTION CONTROL

As part of the Clean Water Act, Effluent Guidelines and Standards for Coil Coating (40 CFR Part 465) have been established that limit concentrations of heavy metals, toxic organics, and conventional pollutants in wastewater streams in the U.S.[15] The organic solvents often contained in liquid coatings used with roll and coil coating application methods may be classified as toxic organics. These materials can enter the wastewater when cleaning coatings from containers or equipment. Actual limits for effluent constituents are dependent on the size of the operation and the amount of wastewater generated from the facility. If the facility discharges directly to receiving waters, these limits will be established through the facility's National Pollutant Discharge Elimination System (NPDES) permit (40 CFR Part 122). Facilities that are indirect dischargers releasing to a POTW must meet limits in the POTW's discharge agreement. Roll and coil coating systems utilize liquid coating materials and solvent and water rinses, which can contaminate water streams. Contamination may occur when cleaning equipment or from accidental spills or leaks from equipment. Contaminated water streams may contain pollutants or heavy metals in concentrations that exceed the limits established by facility NPDES or POTW discharge agreement permits. In such cases, effluent may not be directly released to water systems or to publicly owned treatment works without pretreatment.

Wastewater streams with concentrations exceeding permit limits will require pretreatment prior to discharge to receiving waters or to publicly owned treatment works. Pretreatment may include separation of liquid wastes to remove big suspended solids, oils, solvents, and so on, as discussed in Section 7.8.

7.10.3 Solid and Hazardous Wastes Management and Disposal

Under the Resource Conservation and Recovery Act (RCRA), organic finishing facilities are required to manage listed and characteristic hazardous wastes (40 CFR Part 261) in the U.S.[15] Liquid coatings used with roll and coil coating application methods may contain constituents listed or characterized as hazardous wastes. Materials contaminated with the coatings, such as roller surface covers, conveyor components, and rags or other materials used for cleaning, may require treatment as hazardous waste depending on their formulation. Hazardous waste management (40 CFR Part 262) includes obtaining permits for the facility in order to generate wastes, meeting accumulation limits for waste storage areas, and manifesting waste containers for offsite disposal.

Roll and coil coating systems utilize liquid coating materials with organic solvents, which must be stored, manifested, and disposed of according to 40 CFR Part 262 if classified as hazardous waste under 40 CFR Part 261.

Responsibilities will vary according to the amount of hazardous waste generated; facilities generating at least 100 kg of hazardous waste per month must comply with the Federal and the State hazardous waste generator requirements. Each state or region is primarily responsible for the regulation of nonhazardous solid wastes (those not governed by the hazardous waste provisions of RCRA). State environmental agencies should be contacted for specific guidance.

7.10.4 Waste Minimization and Cleaner Production Alternatives for Roll and Coil Coating

"Cleaner production" means the conceptual and procedural approach to production that demands that all phases of the life-cycle of a product or of a process should be addressed with the objectives of prevention of pollution and minimization of short- and long-term risks to humans and the environment.

The following pollution prevention and cleaner production alternatives are recommended by the Paints and Coatings Resource Center of U.S. EPA[15]:

1. Liquid coating materials with low organic solvent content should be used to minimize the amount of volatile organic compounds that will be volatized and to reduce the volume of solid and liquid hazardous waste created.
2. The use of roll and coil coating systems leads to pollution prevention over traditional spray application systems due to their higher transfer efficiency (>95%) and lower volatilization of organic solvents.
3. Paint jobs should be scheduled to minimize changing colors in roll and coil coating equipment. Paint with light colors first, then darker ones; the lighter coating does not need to be completely removed from the equipment, but can blend into the darker coating. As most roll and coil lines apply only one color, this is typically not an issue.
4. Roll and coil coating equipment should be cleaned regularly to prevent coating materials from drying on rollers and feed lines. Water should be used in cleaning steps to reduce the amount of organic solvents used and the amount of hazardous waste generated. Initial cleaning should be performed with used solvents, saving fresh solvents for final cleaning stages.
5. Nonhazardous coating solids and water should be segregated from hazardous solvents and thinners, and containers labeled to prevent mixing. Separation of the materials reduces the amount of hazardous waste that is produced. Coating material solids can be dried and treated as a solid waste allowing for disposal in a landfill.
6. Roll and coil coating equipment should be maintained to sustain proper operation. Valves, gages, and rollers should be checked to ensure they are in proper working order.
7. Roll and coil coating areas should be kept clean so that problems with equipment can be found and fixed quickly, and accidents prevented.

8. Employees should be trained on safe handling of materials and wastes and encouraged to continuously improve. Training familiarizes workers with their responsibilities, which reduces spills and accidents.

7.11 COIL COATING INDUSTRY LIQUID EFFLUENT LIMITATIONS, PERFORMANCE STANDARDS, AND PRETREATMENT STANDARDS

Table 7.8 indicates that the major regulated parameters for pretreatment of coil coating industrial wastewater are chromium, cyanide, zinc, total toxic organics (TTO), oil and grease, manganese, fluoride, phosphorus, and copper. The effluent limitations of all coil coating operations represent the following:

1. The degree of effluent reduction attainable by the application of the BPT currently available
2. The degree of effluent reduction attainable by the application of the BAT economically achievable, which can be found from the U.S. Code of Federal Register 40CFR–Chapter I, Part 465, Coil Coating Point Source Category[4]

Also documented in this chapter for reference by the readers are the latest U.S. performance standards and pretreatment standards of four subcategories:

1. Steel basis material
2. Galvanized basis material
3. Aluminum basis material
4. Canmaking

7.11.1 Effluent Limitations, Performance Standards, and Pretreatment Standards of the Steel Basis Material Subcategory

Table 7.20 shows the effluent limitations of the steel basis material subcategory that represents the degree of effluent reduction attainable by the application of the BPT currently available. Table 7.21

TABLE 7.20

The Effluent Limitations of the Steel Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

Pollutant or Pollutant Property	BPT Effluent Limitations [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	1.16	(0.24)	0.47	(0.096)
Cyanide	0.80	(0.17)	0.33	(0.068)
Zinc	3.66	(0.75)	1.54	(0.32)
Iron	3.39	(0.70)	1.74	(0.36)
Oil and grease	55.1	(11.3)	33.1	(6.77)
TSS	113.0	(23.1)	55.1	(11.3)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.21
The Effluent Limitations of the Steel Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

	BPT Effluent Limitations [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
Pollutant or Pollutant Property	**Maximum for Any 1 Day**		**Maximum for Monthly Average**	
Chromium	0.50	(0.10)	0.20	(0.041)
Cyanide	0.34	(0.07)	0.14	(0.029)
Zinc	1.56	(0.32)	0.66	(0.14)
Iron	1.45	(0.30)	0.74	(0.15)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

shows the effluent limitations of the steel basis material subcategory that represents the degree of effluent reduction attainable by the application of the BAT economically achievable. Table 7.22 lists the new source performance standards of the steel basis material subcategory that establish the quantity or quality of pollutants or pollutant properties. Table 7.23 lists the pretreatment standards for existing sources of the steel basis material subcategory effluents. Table 7.24 lists the pretreatment standards for new sources of the steel basis material subcategory effluents.

7.11.2 EFFLUENT LIMITATIONS AND PERFORMANCE STANDARDS OF THE GALVANIZED BASIS MATERIAL SUBCATEGORY

Table 7.25 shows the effluent limitations of the galvanized basis material subcategory that represents the degree of effluent reduction attainable by the application of the BPT currently available. Table 7.26 shows the effluent limitations of the galvanized basis material subcategory that represents the degree of effluent reduction attainable by the application of the BAT economically achievable.

TABLE 7.22
The New Source Performance Standards (NSPS) of the Steel Basis Material Subcategory that Establish the Quantity or Quality of Pollutants or Pollutant Properties

	NSPS [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
Pollutant or Pollutant Property	**Maximum for Any 1 Day**		**Maximum for Monthly Average**	
Chromium	0.12	(0.024)	0.047	(0.01)
Cyanide	0.063	(0.013)	0.025	(0.005)
Zinc	0.33	(0.066)	0.14	(0.027)
Iron	0.39	(0.086)	0.20	(0.041)
Oil and grease	3.16	(0.65)	3.16	(0.65)
TSS	4.74	(0.97)	3.79	(0.78)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.23
The Pretreatment Standards for Existing Sources (PSES) of the Steel Basis Material Subcategory Effluents

Pollutant or Pollutant Property	PSES [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	0.50	(0.10)	0.20	(0.041)
Cyanide	0.34	(0.07)	0.14	(0.029)
Zinc	1.56	(0.32)	0.66	(0.14)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

TABLE 7.24
The Pretreatment Standards for New Sources (PSNS) of the Steel Basis Material Subcategory Effluents

Pollutant or Pollutant Property	PSNS [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	0.12	(0.024)	0.047	(0.01)
Cyanide	0.063	(0.013)	0.025	(0.005)
Zinc	0.33	(0.066)	0.14	(0.027)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

TABLE 7.25
The Effluent Limitations of the Galvanized Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

Pollutant or Pollutant Property	BPT Effluent Limitations [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	1.10	(0.23)	0.45	(0.091)
Copper	4.96	(1.02)	2.61	(0.54)
Cyanide	0.76	(0.16)	0.32	(0.064)
Zinc	3.47	(0.71)	1.46	(0.30)
Iron	3.21	(0.66)	1.65	(0.34)
Oil and grease	52.2	(10.7)	31.3	(6.42)
TSS	107.0	(21.9)	52.2	(10.7)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.26

The Effluent Limitations of the Galvanized Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

	BAT Effluent Limitations [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
Pollutant or Pollutant Property	**Maximum for Any 1 Day**		**Maximum for Monthly Average**	
Chromium	0.37	(0.077)	0.16	(0.031)
Copper	1.71	(0.35)	0.90	(0.19)
Cyanide	0.26	(0.053)	0.11	(0.022)
Zinc	1.20	(0.25)	0.51	(0.11)
Iron	1.10	(0.23)	0.57	(0.12)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

Table 7.27 lists the new source performance standards of the galvanized basis material subcategory that establish the quantity or quality of pollutants or pollutant properties. Table 7.28 lists the pretreatment standards for existing sources of the galvanized basis material subcategory effluents. Table 7.29 lists the pretreatment standards for new sources of the galvanized basis material subcategory effluents.

7.11.3 EFFLUENT LIMITATIONS AND PERFORMANCE STANDARDS OF THE ALUMINUM BASIS MATERIAL SUBCATEGORY

Table 7.30 shows the effluent limitations of the aluminum basis material subcategory that represents the degree of effluent reduction attainable by the application of the BPT currently available. Table 7.31 shows the effluent limitations of the aluminum basis material subcategory that represents

TABLE 7.27

The New Source Performance Standards (NSPS) of the Galvanized Basis Material Subcategory that Establish the Quantity or Quality of Pollutants or Pollutant Properties

Pollutant or Pollutant Property	NSPS [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		**Maximum for Monthly Average**	
Chromium	0.13	(0.027)	0.052	(0.011)
Copper	0.44	(0.090)	0.21	(0.043)
Cyanide	0.07	(0.015)	0.028	(0.006)
Zinc	0.35	(0.08)	0.15	(0.030)
Iron	0.43	(0.09)	0.22	(0.045)
Oil and grease	3.43	(0.71)	3.43	(0.702)
TSS	5.15	(1.06)	4.12	(0.84)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.28
The Pretreatment Standards for Existing Sources (PSES) of the Galvanized Basis Material Subcategory Effluents

Pollutant or Pollutant Property	PSES [mg/m² (lb/10⁶ ft²) of Area Processed] Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	0.37	(0.077)	0.16	(0.031)
Copper	1.71	(0.35)	0.90	(0.19)
Cyanide	0.26	(0.053)	0.11	(0.022)
Zinc	1.20	(0.25)	0.51	(0.11)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

TABLE 7.29
The Pretreatment Standards for New Sources (PSNS) of the Galvanized Basis Material Subcategory Effluents

Pollutant or Pollutant Property	PSNS [mg/m² (lb/10⁶ ft²) of Area Processed] Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	0.13	(0.027)	0.052	(0.011)
Copper	0.44	(0.090)	0.21	(0.043)
Cyanide	0.07	(0.015)	0.028	(0.006)
Zinc	0.35	(0.072)	0.15	(0.030)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

TABLE 7.30
The Effluent Limitations of the Aluminum Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

Pollutant or Pollutant Property	BPT Effluent Limitations [mg/m² (lb/10⁶ ft²) of Area Processed] Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	1.42	(0.29)	0.58	(0.12)
Cyanide	0.98	(0.20)	0.41	(0.083)
Zinc	4.48	(0.92)	1.89	(0.39)
Aluminum	15.3	(3.14)	6.26	(1.28)
Oil and grease	67.3	(13.8)	40.4	(8.27)
TSS	138.0	(28.3)	67.3	(13.8)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.31
The Effluent Limitations of the Aluminum Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

	BAT Effluent Limitations [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
Pollutant or Pollutant Property	**Maximum for Any 1 Day**		**Maximum for Monthly Average**	
Chromium	0.42	(0.085)	0.17	(0.034)
Cyanide	0.29	(0.059)	0.12	(0.024)
Zinc	1.32	(0.27)	0.56	(0.12)
Aluminum	4.49	(0.92)	1.84	(0.38)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

the degree of effluent reduction attainable by the application of the BAT economically achievable. Table 7.32 lists the new source performance standards of the aluminum basis material subcategory that establish the quantity or quality of pollutants or pollutant properties. Table 7.33 lists the pretreatment standards for existing sources of the aluminum basis material subcategory effluents. Table 7.34 lists the pretreatment standards for new sources of the aluminum basis material subcategory effluents.

7.11.4 EFFLUENT LIMITATIONS, PERFORMANCE STANDARDS, AND PRETREATMENT STANDARDS OF CANMAKING SUBCATEGORY

Table 7.35 shows the effluent limitations of the canmaking subcategory that represents the degree of effluent reduction attainable by the application of the best practicable control technology (BPT) currently available. Table 7.36 shows the effluent limitations of the canmaking subcategory

TABLE 7.32
The New Source Performance Standards (NSPS) of the Aluminum Basis Material Subcategory that Establish the Quantity or Quality of Pollutants or Pollutant Properties

Pollutant or Pollutant Property	NSPS [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		**Maximum for Monthly Average**	
Chromium	0.18	(0.037)	0.072	(0.015)
Cyanide	0.095	(0.020)	0.038	(0.008)
Zinc	0.49	(0.10)	0.20	(0.041)
Aluminum	1.44	(0.30)	0.59	(0.121)
Oil and grease	4.75	(0.98)	4.75	(0.98)
TSS	7.13	(1.46)	5.70	(1.17)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.33
The Pretreatment Standards for Existing Sources (PSES) of the Aluminum Basis Material Subcategory Effluents

Pollutant or Pollutant Property	PSES [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	0.42	(0.085)	0.17	(0.034)
Cyanide	0.29	(0.059)	0.12	(0.024)
Zinc	1.32	(0.27)	0.56	(0.12)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

TABLE 7.34
The Pretreatment Standards for New Sources (PSNS) of the Aluminum Basis Material Subcategory Effluents

Pollutant or Pollutant Property	PSNS [mg/m^2 (lb/10^6 ft^2) of Area Processed]			
	Maximum for Any 1 Day		Maximum for Monthly Average	
Chromium	0.18	(0.037)	0.072	(0.015)
Cyanide	0.095	(0.02)	0.038	(0.008)
Zinc	0.49	(0.10)	0.20	(0.041)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

TABLE 7.35
The Effluent Limitations of the Canmaking Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

Pollutant or Pollutant Property	BPT Effluent Limitations [g (lb)/10^6 Cans Manufactured]	
	Maximum for Any 1 Day	Maximum for Monthly Average
Chromium	94.60 (0.209)	38.70 (0.085)
Zinc	313.90 (0.692)	131.15 (0.289)
Aluminum	1382.45 (3.048)	688.00 (1.517)
Fluoride	12,792.50 (28.203)	5676.00 (12.514)
Phosphorus	3590.50 (7.916)	1468.45 (3.237)
Oil and grease	4300.00 (9.480)	2580.00 (5.688)
TSS	8815.00 (19.434)	4192.50 (9.243)
pH	7.0–10.0[a]	7.0–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.36
The Effluent Limitations of the Canmaking Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

	BAT Effluent Limitations [g (lb)/10^6 Cans Manufactured]	
Pollutant or Pollutant Property	**Maximum for Any 1 Day**	**Maximum for Monthly Average**
Chromium	36.92 (0.081)	15.10 (0.033)
Zinc	122.49 (0.270)	51.18 (0.113)
Aluminum	539.48 (1.189)	268.48 (0.592)
Fluoride	4992.05 (11.001)	2214.96 (4.883)
Phosphorus	1401.13 (3.089)	573.04 (1.263)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

that represents the degree of effluent reduction attainable by the application of the best available technology (BAT) economically achievable. Table 7.37 lists the new source performance standards of the canmaking subcategory that establish the quantity or quality of pollutants or pollutant properties. Table 7.38 lists the pretreatment standards for existing sources of the canmaking subcategory effluents. Table 7.39 lists the pretreatment standards for new sources of the canmaking subcategory effluents.

7.12 TECHNICAL TERMINOLOGIES OF COIL COATING OPERATIONS AND POLLUTION CONTROL

1. "Cleaner Production" means the conceptual and procedural approach to production that demands that all phases of the life-cycle of a product or of a process should be addressed with the objectives of prevention of pollution and minimization of short- and long-term risks to humans and the environment.

TABLE 7.37
The New Source Performance Standards (NSPS) of the Canmaking Subcategory that Establish the Quantity or Quality of Pollutants or Pollutant Properties

	NSPS [g (lb)/10^6 Cans Manufactured]	
Pollutant or Pollutant Property	**Maximum for Any 1 Day**	**Maximum for Monthly Average**
Chromium	27.98 (0.062)	11.45 (0.025)
Zinc	92.86 (0.205)	38.80 (0.086)
Aluminum	408.95 (0.902)	203.52 (0.449)
Fluoride	3784.20 (8.343)	1679.04 (3.702)
Phosphorus	1062.12 (2.342)	434.39 (0.958)
Oil and grease	1272.00 (2.804)	763.20 (1.683)
TSS	2607.60 (5.749)	1240.20 (2.734)
pH	7.0–10.0[a]	7.0–10.0[a]

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

[a] Within this range at all times.

TABLE 7.38
The Pretreatment Standards for Existing Sources (PSES) of the Canmaking Subcategory Effluents

	PSES [g (lb)/10^6 Cans Manufactured]	
Pollutant or Pollutant Property	**Maximum for Any 1 Day**	**Maximum for Monthly Average**
Chromium	36.92 (0.081)	15.10 (0.033)
Copper	159.41 (0.351)	83.90 (0.185)
Zinc	122.49 (0.270)	51.18 (0.113)
Fluoride	4992.05 (11.001)	2214.96 (4.883)
Phosphorus	1401.13 (3.089)	573.04 (1.263)
Manganese	57.05 (0.126)	24.33 (0.053)
TTO	26.85 (0.059)	12.59 (0.028)
Oil and grease (for alternative monitoring)	1678.00 (3.699)	1006.80 (2.220)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

2. “Coil” means a strip of basis material rolled into a roll for handling.
3. “Coil coating” means the process of converting basis material strip into coated stock. Usually cleaning, conversion coating, and painting are performed on the basis material. Coil coating processes perform any two or more of the three operations.
4. “Basis material” means the coiled strip that is processed.
5. “Area processed” means the area actually exposed to process solutions. Usually this includes both sides of the metal strip.
6. “Steel basis material” means cold rolled steel, hot rolled steel, and chrome, nickel and tin coated steels that are processed in coil coating.
7. “Galvanized basis material” means zinc coated steel, galvanized brass, and other copper base strip that is processed in coil coating.
8. “Aluminum basis material” means aluminum, aluminum alloys, and aluminum coated steels that are processed in coil coating.

TABLE 7.39
The Pretreatment Standards for New Sources (PSNS) of the Canmaking Subcategory Effluents

	PSNS [g (lb)/10^6 Cans Manufactured]	
Pollutant or Pollutant Property	**Maximum for Any 1 Day**	**Maximum for Monthly Average**
Chromium	27.98 (0.0617)	11.45 (0.025)
Copper	120.84 (0.267)	63.60 (0.140)
Zinc	92.86 (0.205)	38.80 (0.086)
Fluoride	3784.20 (8.345)	1679.04 (3.702)
Phosphorus	1062.12 (2.342)	434.39 (0.958)
Manganese	43.25 (0.095)	18.44 (0.041)
TTO	20.35 (0.045)	9.54 (0.0210)
Oil and grease (for alternative monitoring)	1272.00 (2.804)	763.20 (1.683)

Source: U.S. EPA. *Code of Federal Regulations (CFR). Title 40 Protection of Environment. Part 465. Coil Coating Point Source Category.* Washington, DC, 2008.

9. The term "can" means a container formed from sheet metal and consisting of a body and two ends or a body and a top.
10. The term "canmaking" means the manufacturing process or processes used to manufacture a can from a basic metal.
11. The term "total toxic organics (TTO)" means the sum of the mass of each of the following toxic organic compounds, which are found at a concentration greater than 0.010 mg/L:

    (a) 1,1,1-Trichloroethane
    (b) 1,1-Dichloroethane
    (c) 1,1,2,2-Tetrachloroethane
    (d) Bis(2-chloroethyl)ether
    (e) Chloroform
    (f) 1,1-Dichloroethylene
    (g) Methylene chloride (dichloromethane)
    (h) Pentachlorophenol
    (i) Bis(2-ethylhexyl)phthalate
    (j) Butyl benzyl-phthalate
    (k) Di-n-butyl phthalate
    (l) Phenanthrene
    (m) Tetrachloroethylene
    (n) Toluene

REFERENCES

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8 Waste Treatment in the Porcelain Enameling Industry

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CONTENTS

8.1 INDUSTRY DESCRIPTION

8.1.1 Historical Cultural Development

Enameling is an old and widelyadopted technology.[1–9] The ancient Egyptians applied enamels to pottery and stone objects. The ancient Greeks, Celts, Russians, and Chinese also used enameling processes on metal objects.[9]

Enameling was also used to decorate glass vessels during the Roman period, and there is evidence of this as early as the late Republican and early Imperial periods in the Levantine, Egypt, Britain, and the Black Sea.[1] Enamel powder could be produced in two ways, either through the powdering of colored glass, or the mixing of colorless glass with colorants such as a metallic oxide.[2] Designs were either painted freehand or over the top of outline incisions, and the technique probably originated in metalworking. Once painted, enameled glass vessels needed to be fired at a temperature high enough to melt the applied powder, but low enough that the fabric of the vessel itself was not melted. Production is thought to have come to a peak in the Claudian period and persisted for some 300 years, although archaeological evidence for this technique is limited to some 40 vessels or vessel fragments.[1]

8.1.2 Industrial Technology Development

Porcelain enameling began in the U.S. in the late 1800s. Following the Depression, the manufacture of porcelain enameled refrigerators, stoves, and other household items expanded manyfold.[3–7] The demand for porcelain enamel products and finishes reached a peak in the 1960s and 1970s. The majority of the porcelain enameling plants in the U.S. are located east of the Mississippi River.[3]

The porcelain enameling industry consists of at least 116 plants enameling approximately 150 million square meters (150 km^2) of steel, iron, aluminum, and copper each year (each coat of multiple coats is considered in this total). Porcelain enameling is the application of glass-like coatings to the metals mentioned above. The purpose of the coating is to improve resistance to chemicals, abrasion, and water, and to improve thermal stability, electrical resistance, and appearance. The coating applied to the metal, called a "slip," is composed of one of many combinations of frits (glassy raw materials), clays, coloring oxides, water, and special additives such as suspending agents. These vitreous inorganic coatings are applied to the metal by a variety of methods such as spraying, drying, and flow coating, and are bonded to the metal at temperatures over 500°C (over 1000°F).

Several processes are used in the porcelain enameling industry regardless of the metal being coated. These processes, discussed below, include preparation of the enamel slip, surface preparation of the base material, and enamel application and firing to fuse the coating to the metal.[3–6]

8.2 PORCELAIN ENAMELING PROCESS STEPS

8.2.1 Enamel Slip Preparation

The preparation of the enamel slip includes ball milling the frit and raw materials to the appropriate consistency. Frit is the glassy raw material that makes up the backbone of porcelain enameling. Most frit is manufactured outside the operation but some plants do include captive operations. Other raw materials, such as clay and gums, are mixed into the frit by the ball mill that then releases this mixture to the coating operation.[3–6]

8.2.2 Base Material Surface Preparation

In order for the porcelain enamel to form a good bond with the workpiece, the base metal to be coated must be properly prepared. Depending on the type of metal being finished, one or more preparation processes are performed. Solvent cleaning removes oil, greases, and fingerprints from the metal by exposing it to nonflammable solvents such as trichloroethylene or 1,1,2-trichloro-ethane at their boiling points. This process may also be combined with water to provide a two-phase cleaning system for solvent-soluble and water-soluble contaminants.

Alkaline cleaning removes oils and soils from the workpieces by the detergent nature of the solution. Soaking, spraying, and electrolytic alkaline cleaning are the most common methods used, with the electrolytic process providing the cleanest surface. If aluminum is the metal being coated, a stronger alkaline solution is often used as a mild etch that removes the surface oxides.

Acid treatment is used to remove rust, scale, and oxides from the base and may be carried out in the form of acid cleaning, pickling, or etching. Each option involves a slightly stronger acid solution. Generally, sulfuric acid is used for this treatment, although other acids may be applied.

Nickel deposition is a common step when enameling steel in order to improve the bonding of the enamel to the metal. Nickel is normally deposited after the part has been acid treated and rinsed. Neutralization normally follows acid pickling and nickel deposition to remove the last traces of acid left on the metal. Chromate cleaning and grit blasting may also be used to prepare the base metal prior to the coating process. When used, grit blasting is normally the sole preparation step because it cleans the metal and roughens the surface, providing a good base for bonding.[3–6]

8.2.3 Enamel Application and Firing

Once the workpiece has undergone proper base metal preparation and the enamel slip has been prepared, the next step is the actual application of the porcelain enamel. Included among the application methods are air spraying, electrostatic spraying, dip coating, flow coating, powder coating, and silk screening. After each coating is applied, the part is fired in a furnace to achieve a fusion between the enamel coating and the base metal or substrate.

Air spraying is the most widely used method for enamel application. In this process, the enamel is atomized and propelled by air onto the base metal to form an enamel coating. Overspraying is a common problem with this technique, because the atomized particles may not adhere to the part. Spray booths to collect this oversprayed enamel are necessary. A modification of this technique is the electrostatic spray coating method where the atomized particles are charged at 70,000 to 100,000 V and directed toward the grounded part. This charge increases the adhering efficiency but does not eliminate the need for spray booth collectors. Other advantages such as edging and the coating of both sides at once are also applicable.

Dip coating consists simply of dipping the workpiece in an enamel bath and allowing it to drain. Flow coating floods the piece with enamel and then recycles the unused, recovered enamel. Powder coating is the dusting of a red hot cast iron workpiece with porcelain enamel in the form of a dry powder. The glass powder melts as it strikes the hot surface. Silk screening is used to apply a decorative pattern on a porcelain enameled piece.[3–6]

Porcelain enameling plants are located primarily in the states of Wisconsin, Illinois, Indiana, Michigan, Ohio, Pennsylvania, Kentucky, and Tennessee. Of the facilities, 76% discharge to publicly owned treatment works (POTWs), 22% to streams or rivers, and 2% to both. Approximately 10% of the plants recycle, with an average recycle of 9.6 m^3/h, which represents 46% of the average process water usage rate of 20.8 m^3/h. The total porcelain enamel applied each year by all plants is estimated at 150×10^6 m^2.

Of the 130 porcelain enameling industrial plants studied, 30 plants treat their wastewaters for direct discharge into receiving waters, and 100 plants pretreat their wastewaters for discharge into POTWs.

8.3 SUBCATEGORY DESCRIPTIONS OF THE PORCELAIN ENAMELING INDUSTRY

The porcelain enameling industry consists of four subcategories:

1. Porcelain enameling on steel
2. Porcelain enameling on iron
3. Porcelain enameling on aluminum
4. Porcelain enameling on copper

This subcategorization was chosen on the basis of the base metals used. Other possible subcategories (dependent on wastewater characterization, manufacturing processes, products, water use, and so on) were considered, but all were found to be directly related to the base metal used. In addition to the four subcategories selected, steel and aluminum base metals may be further divided into two segments, sheet and strip, to account for the significant water-saving potential of continuous operations relative to individual sheet processing. However, because only two porcelain enameling facilities treat strip, no separate division is necessary at this time.

In general, only 10% of the porcelain enameling facilities enamel more than one type of base metal. Over 70% of the plants enamel solely on steel, 10% on aluminum, and 8% on iron. Less than 1% of the plants enamel copper, strip steel, or strip aluminum separately.[3–6]

8.3.1 Porcelain Enameling on Steel Subcategory

Steel is by far the most widely used base metal for porcelain enameling, with the average yearly production of a plant being 1.34×10^6 m^2 (14.4×10^6 ft^2). This figure represents the area of enamel applied. For multiple coats, the area for each coat is considered. Among the products that use porcelain enameled steel are the following: cooking and heating equipment such as ranges, home laundry equipment (washers and dryers), refrigerators, freezers, dishwashers, water heaters, process vessels, architectural panels, plumbing fixtures, and various appliance parts.

Several processes are used when enameling on steel. The parts to be coated are first alkaline cleaned and rinsed to remove soils. An acid treatment step and rinse follow in that sulfuric acid, ferric sulfate in conjunction with sulfuric acid, or muriatic acid are used for oxide removal. A nickel deposition step and rinse ensues, followed by a neutralization operation, which removes any remaining traces of acid.

Following surface preparation and drying, the part is ready for enamel application. Steel parts are either sprayed, dipped, or flow coated. The enamel slip can be applied in a single coating operation (referred to as direct-on), or a ground coat and a cover coat may be applied separately. For the direct-on process, corners and edges are usually reinforced (precoated) to ensure coverage. For either case, each coat is fired at a temperature of approximately 820°C (1500°F). The total thickness of sheet steel enamels involving a ground coat and cover coat is in the range of 0.13 to 0.20 mm (5 to 9 mils).

When the direct-on process is utilized, surface preparation requirements are more critical to ensure effective enamel adhesion. The acid etch is often deeper and the nickel deposition is always thicker. Typically, the nickel coating is 0.01 to 0.02 g/m^2 for direct-on coating as compared to 0.002 to 0.007 g/m^2 for two-coat applications. A few porcelain enamelers prefer to omit the nickel deposition step. Although the nickel enhances enamel bonding, product quality requirements may not require nickel deposition. The omission of the nickel step necessitates the utilization of a heavy acid etch to ensure a clean, properly conditioned surface for enamel bonding.[3–6]

8.3.2 PORCELAIN ENAMELING ON CAST IRON SUBCATEGORY

Cast iron is porcelain enameled primarily for plumbing fixtures for the sanitary products industry. It is also used for cookware and for various appliance parts such as grates for gas ranges. The average yearly production of a plant is 1.56×10^6 m^2 (16.8×10^6 ft^2). This figure represents the areas of enamel applied. For multiple coats, the area for each coat is considered.

The porcelain enameling of cast iron is a process in which water is not generally used for metal preparation but is sometimes used for coating application. The casting to be coated is blasted with sand or a combination of grit and sand to produce a smooth, velvety surface. The parts are then brushed off and any rough edges are removed by grinding.

The ground coat is then applied by spraying, dipping, or flow coating. If only one coat is required, a heavy ground coat is applied. If there is to be a ground coat and a top coat, a thin layer of enamel is used for the ground coat. The ground coat is then fired. The firing period is longer than for sheet steel because of the greater mass of the enameled body, and firing temperature is reduced to avoid excessive baking. When the cast is removed from the furnace and still red hot, the top coat is applied by powder coating. The enamel in powder form is dusted on the hot part and fused to the surface. The total thickness of dry process coatings is approximately 0.50 mm (20 mils).

8.3.3 PORCELAIN ENAMELING ON ALUMINUM SUBCATEGORY

Porcelain enameling on aluminum finds use in the cookware and housewares industry. It is also used for panels and signs. The average yearly production for a plant in this subcategory is 0.25×10^6 m^2 (2.7×10^6 ft^2). This figure represents the area of enamel applied. For multiple coats, the area for each coat is considered.[3–6]

Although all aluminum parts can be coated in a similar fashion, the surface preparation can vary from company to company. The choice of surface preparation methodology is based upon the alloy type of the base metal and the cleanliness requirements involved. Pure aluminum requires only a cleaning step. A heat-treatable alloy may require a pickling step in addition to cleaning. Porcelain enameling on a high-magnesium alloy could necessitate a chromate cleaning process. This chromate coating retards the oxidation of the magnesium in this high-strength alloy.

Nearly all aluminum parts are first treated in an alkaline solution. In some cases, this is only a cleaner for removing grease and soils; sometimes it is a mild etchant to remove a layer of metal and its oxides. Frequently, this is all the surface preparation that is necessary. Any further preparation steps are to remove residual oxides (e.g., chemical deoxidizing with nitric acid) or to impart a thin protective layer on the metal (alkaline chromate treatment). The users of such processes were limited in the plants studied.

Aluminum does not require a ground coat. Enamel is generally applied by spraying, with firing accomplished by heating to 450–550°C (850–1040°F) for 2–10 min.

8.3.4 Porcelain Enameling on Copper Subcategory

Porcelain enameling on copper represents a very small part of the porcelain enameling category. It is not practiced by many firms and the ones involved do it on a small scale. Enameled copper is used mostly for ornamental purposes, such as jewelry, decorative ware, and metal sculpture. The average yearly production of a plant in this subcategory is 1.4×10^4 m^2 (1.5×10^4 ft^2).

As it is essential to remove all the oil and grease on the copper before coating, the part is first alkaline cleaned, degreased, or annealed. After cleaning, the part is then typically pickled for oxide removal.

Enamel application involves two processes: a ground coat or backing coat and a cover coat to prevent the copper base from being taken into solution with the enamel and causing discoloration. This ground coat is applied by either spraying or dipping. The cover coat can be applied by powder coating or with silk screening to achieve patterns.

8.3.5 Porcelain Enameling on Continuous Strip Subdivision

In addition to the above subcategories, porcelain enameling on continuous strip is a subdivision within this industry. However, because there are only two plants in the U.S. producing this product, a separate subcategory is not necessary. These plants start with coils of steel, aluminum, or aluminized steel, porcelain enamel them and either recoil them for sale to metal fabricators or shear them into pieces for use as architectural panels or chalkboards. The estimated production was 2.0×10^6 m^2 (22×10^6 ft^2). This figure represents the area of enamel applied. For multiple coats, the area for each coat is considered.

The surface preparation operations for strip are dependent upon whether the basis material is steel or aluminum. The surface preparation steps for steel strip are minimal in comparison to porcelain enameling on steel sheets because precleaned strip steel is used. Steel strip is nickel immersion plated prior to the enameling step. Surface preparation for aluminum involves only cleaning. The enamel for either basis material is applied by means of spray guns that are aimed at the surface of the moving strip. Two coats are normally applied, the strip being fired after each coat.

8.4 WASTEWATER CHARACTERIZATION OF THE PORCELAIN ENAMELING INDUSTRY

This section presents water uses and discharges, and waste constituents emanating from the porcelain enameling category. Published literature, data collection portfolio (DCP) responses, and screening and verification sampling data have been used to obtain the relevant information. The screening analysis of the porcelain enameling category consisted of a sampling program for all 129 priority pollutants. Those pollutants that were detected in the screening program were further studied in the verification analysis. Only those pollutants included in the verification program are presented in the following tables. The minimum detection limit for toxic pollutants is 10 μg/L and any value below 10 μg/L is presented in the following tables as below detection limit (BDL). Table 8.1 presents wastewater flow data on a subcategory and stream basis for the porcelain enameling industry.[3–10]

TABLE 8.1
Wastewater Flows from the Porcelain Enameling (PE) Industry

Stream	Number of Samples	Flow Range (m^3/d)	Flow Median (m^3/d)	Flow Mean (m^3/d)
PE on steel				
Alkaline cleaning	21	1.64–122	30.3	47.2
Acid etch	21	0.556–56.2	19.6	23.7
Nickel flash	12	19.1–31.2	24.8	25.2
Neutralization	8	0.999–19.8	15.1	14.1
Coating	21	0.783–505	4.03	107
Total raw waste	21	11.3–711	175	197
PE on iron				
Coating	7	0.636–7.21	1.23	2.88
PE on aluminum				
Alkaline cleaning	8	19.2–217	169	131
Coating	8	4.84–546	297	285
Total raw waste	8	68.2–223	197	160
PE on copper				
Acid etch	3	6.14–7.27	7.27	6.89
Coating	4	0.008–1.27	0.636	0.638
Total raw waste	4	1.27–7.90	7.02	5.81

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

8.4.1 WASTEWATER FROM THE PORCELAIN ENAMELING ON STEEL SUBCATEGORY

Wastewater from porcelain enameling on steel is generated by base metal surface preparation, enamel application, ball milling, and related operations. The constituents in the wastewater include the base material being coated (iron), as well as the components of the surface treatment solutions and enamels being applied.

Water rinses are used in surface preparation operations such as acid pickling, alkaline cleaning, and nickel deposition to remove any process solution film left from the previous bath. A water rinse may also follow the neutralization step. Another common water use is in the ball milling process, which uses water as the vehicle for the enamel ingredients, as a cooling medium, and for cleaning the equipment. Coating application processes normally use wet spray booths to capture oversprayed enamel particles. Water wash spray booths use a water curtain into which the enamel particles are blown and captured.

The major sources of waste generated by this subcategory are the process solutions used in basis material preparation, the base metal being coated, and the enamel being prepared. Alkaline cleaning solution varies with the type of soil being removed. Wastewaters from this operation contain constituents of the cleaning solution as well as oil and grease. These wastewaters also contain iron but in lesser concentrations than those from the acid pickling process. Alkaline cleaning wastes enter the wastestream in three ways: during the rinse step, from the cleaning bath overflow, and in the batch dump of the spent alkaline bath.

Acid treatment is typically sulfuric acid with lesser amounts of hydrochloric, phosphoric, and nitric acids being used. Acid solutions develop a high metallic content due to the dissolution of the steel itself during the pickling operation. As a result, the baths are frequently dumped, introducing large amounts of iron into the wastestream. Also present in significant concentrations are phosphorus and manganese. The stream has a low pH.

Nickel deposition can place large amounts of nickel and iron into the wastestream by batch dumping and dragout. The neutralization step eases the pH burden and adds little additional loading of any pollutant.

The introduction of enamel into the wastestream results in an increase in the concentration of metals, but these metals (antimony, titanium, zirconium, tin, cobalt, and manganese) are in solid form whereas the metals generated by surface preparation are normally in dissolved form. These solid metals increase the suspended solids concentration of the stream. Other metals that may be found in the enamel preparation and application wastestream in significant amounts include aluminum, copper, iron, lead, nickel, and zinc. Table 8.2 presents pollutant sampling data for the processes used in the porcelain enameling on steel industry.

8.4.2 Wastewater from the Porcelain Enameling on Cast Iron Subcategory

There are two different types of cast iron porcelain enameling:

1. Dry process enameling cast iron, which uses no water and does not produce wastewater
2. Wet process enameling cast iron, which uses water for ball milling and enamel application

These processes are very similar to the ones described for the steel subcategory. Surface preparation involves sand or grit blasting and uses water only in an air scrubber operation. Ball milling uses water as a vehicle for the enamel slip ingredients, as cooling water, and for equipment cleanup. Coating application uses water as a trap for the excess enamel particles during the spray step. Wastewater constituents in significant concentrations in the streams emanating from this subcategory include suspended solids, aluminum, iron, copper, lead, manganese, nickel, titanium, zinc, and cobalt. All of these metals are the result of the enamel carryover via spray booth blowdown or ball mill washdown.

Table 8.3 presents wastewater characterization data for the streams in this cast iron subcategory.

8.4.3 Wastewater from the Porcelain Enameling on Aluminum Subcategory

Wastewaters from this subcategory come from surface preparation, enamel application, ball milling, and related operations. Constituents of this wastewater include aluminum and components of the surface preparation solutions and the enamels being applied.[3–6]

Water is used in this subcategory as solution makeup and for rinsing in the surface preparation process, as the vehicle for the coating in the application process (normally done by spray coating), and for cooling and cleanup in the ball milling operation.

The surface preparation process contributes pollutants to the wastewater by the continuous overflow of the cleaning bath (if a continuous process), by the batch dumping of spent solutions, and by the rinsing steps directly following the process. Generally, significant quantities of dirt and grease are removed during this cleaning process. Also entering the wastestream is a considerable amount of aluminum. When an alkaline cleaning process is used, the wastewater contains significant concentrations of suspended solids, phosphorus, and aluminum. Acids used to deoxidize the surface normally remove a larger amount of aluminum than alkaline treatments and, therefore, increase the dissolved aluminum concentration. The enamel preparation and application steps contribute significant amounts of suspended solids and metals, particularly cadmium, lead, titanium, zinc, aluminum, barium, iron, selenium, and antimony due to use of these metals in the enamel itself. There are also high levels of fluorides and phosphorus.

Table 8.4 presents classical and toxic pollutant concentrations for the porcelain enameling on aluminum subcategory.

8.4.4 Wastewater from the Porcelain Enameling on Copper Subcategory

Wastewater from this subcategory is generated as in the previous subcategories, by surface preparation, enamel application, ball milling, and related operations. Wastewater constituents generally consist of copper and the components used to form the enamel.

TABLE 8.2
Wastewater Characterization of the Porcelain Enameling on Steel Subcategory

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections	Number of Samples	Number of Detections	Range of Detections	Average of Detections
	Alkaline Cleaning				Acid Etch			
Classical Pollutants (mg/L)								
TSS	20	20	6–650	140	19	19	1.9–310	32
Total phosphorus	20	19	0.29–92	15	9	9	0.56–12	7.0
Total phenols	20	19	0.006–0.69	0.08	19	15	0.005–0.95	0.38
Oil and grease	11	11	3–63	17	10	10	1–17	4.5
pH (pH units)	38	38	2–11.7	7.9	26	26	2–7.5	2.9
Fluorides	21	21	0.23–1.8	0.80	21	21	0.14–1.1	0.58
Aluminum	21	16	0.08–3.2	0.43	21	15	0.05–3.2	0.4
Iron	18	18	0.028–1500	90	21	21	13–10,000	2100
Manganese	19	14	0.005–4.5	0.50	21	20	0.06–53	8.8
Titanium	21	0	—	—	21	1	0.05	—
Cobalt	21	2	0.001–0.11	0.05	21	18	0.017–0.38	0.11
Toxic Pollutants (μg/L)								
Metals and inorganics								
Antimony	21	0	—	—	21	0	—	—
Arsenic	21	0	—	—	21	0	—	—
Beryllium	21	0	—	—	21	0	—	—
Cadmium	21	3	BDL–84	36	21	1	14	—
Chromium	21	9	BDL–260	47	21	21	11–3100	590
Copper	21	19	BDL–220	63	21	21	BDL–380	75
Cyanide	8	0	—	—	7	0	—	—
Lead	21	0	—	—	21	5	50–130	85
Nickel	19	7	14–25,000	3600	21	17	87–25,000	5000
Selenium	21	19	BDL–210	110	21	1	210	—
Zinc	20	18	13–810	90	21	21	17–250	110

Continued

TABLE 8.2 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections	Number of Samples	Number of Detections	Range of Detections	Average of Detections
	← Nickel Flash			→	← Neutralization			→
Classical Pollutants (mg/L)								
TSS	10	10	2–310	56	6	6	8.0–57	30
Total phosphorus	6	6	1.1–8.3	4.5	7	6	0.04–7.5	1.7
Total phenols	10	8	0.008–0.095	0.04	6	6	0.004–0.50	0.10
Oil and grease	7	7	1–18	5.1	6	6	1–3.8	2.7
pH (pH units)	20	20	2.0–6.2	3.0	14	14	6–9.7	8.4
Fluorides	12	12	0.27–0.82	0.55	7	7	0.32–1.1	0.69
Aluminum	12	6	0.04–0.33	0.19	7	2	0.04–0.34	0.19
Iron	12	12	57–1500	640	7	7	1.8–44	13
Manganese	12	12	0.27–7.6	3.2	7	7	0.016–0.25	0.09
Titanium	12	0	—	—	7	0	—	—
Cobalt	12	12	0.01–0.46	0.18	7	0	—	—
Toxic Pollutants (µg/L)								
Metals and inorganics								
Antimony	12	0	—	—	7	0	—	—
Arsenic	12	0	—	—	7	0	—	—
Beryllium	12	0	—	—	7	0	—	—
Cadmium	12	1	12	—	7	0	—	—
Chromium	12	12	19–260	88	7	3	12–32	25
Copper	12	11	8–79	33	7	3	10–14	11
Cyanide	7	0	—	—	6	0	—	—
Lead	12	0	—	—	7	0	—	—
Nickel	12	12	2900–280,000	76,000	7	7	75–9500	1700
Selenium	12	1	210	—	7	0	—	—
Zinc	12	12	36–1300	200	7	7	BDL–25	13
Silver	3	2	8–54	31	—	—	—	—

	Coating				Total Raw Waste			
Classical Pollutants (mg/L)								
TSS	21	21	360–320,000	29,000	18	18	66–16,000	2800
Total phosphorus	19	19	0.49–9.8	2.7	9	9	0.82–13	5.3
Total phenols	21	16	0.005–0.066	0.019	18	17	0.006–0.29	0.05
Oil and grease	15	15	1–98	23	10	16	2.3–38	13
pH (pH units)	30	30	5.8–12.5	8.5	36	36	2–12.5	6.2
Fluorides	21	21	1.9–120	37	20	20	0.61–30	8.3
Aluminum	21	21	5.2–1500	180	20	20	0.45–210	26
Iron	21	21	0.45–620	56	17	17	1.5–670	270
Manganese	21	21	0.45–400	58	18	18	0.08–61	9.1
Titanium	21	21	4.3–1600	270	20	20	0.17–1200	88
Cobalt	21	21	0.31–350	38	20	20	0.17–9.2	2.9
Toxic Pollutants (μg/L)								
Metals and inorganics								
Antimony	21	10	920–1.0 × 10^6	10,000	20	9	52–22,000	4600
Arsenic	21	9	52–3500	840	20	9	BDL–2500	550
Beryllium	21	8	14–120	50	20	8	BDL–BDL	BDL
Cadmium	21	13	BDL–54,000	6600	20	16	BDL–5300	440
Chromium	21	21	BDL–37000	2100	20	20	22–840	160
Copper	21	21	160–55000	5400	20	20	34–2200	600
Cyanide	12	1	55		7	0		
Lead	21	19	47–11,000	3100	20	19	BDL–830	320
Nickel	21	21	390–360,000	33000	18	18	82–32,000	1700
Selenium	21	14	120–17,000	2900	20	15	BDL–13,000	1700
Zinc	21	21	1100–1.3 × 10^6	13,0000	19	19	78–45,000	12,000
Organics								
Toluene	3	0	—		2	0	—	—
1,2-Dichlorobenzene	1	0	—		0	—	—	—
Chloroform	3	3	BDL–BDL	BDL	0	—	—	—
Dichlorobromomethane	3	2	BDL–BDL	BDL	0	—	—	—
1,1,2,2-Tetrachloroethane	2	2	BDL–BDL	BDL	0	—	—	—
Tetrachloroethylene	3	2	BDL–BDL	BDL	0	—	—	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr467_03.html, 2008.

BDL, below detection limit.

TABLE 8.3
Wastewater Characterization of the Porcelain Enameling on Cast Iron Subcategory

	Coating			
Pollutant	**Number of Samples**	**Number of Detections**	**Range of Detections**	**Average of Detections**
Classical Parameters (mg/L)				
TSS	7	7	6600–81,000	27,000
Total phosphorus	7	6	0.49–2.1	1.1
Total phenols	6	6	0.008–0.038	0.02
Oil and grease	3	3	1.0–9.5	4.7
pH (pH units)	14	14	7.9–11.4	9.5
Fluorides	7	7	2.0–120	41
Aluminum	7	7	0.38–1200	340
Iron	6	5	18–150	56
Manganese	7	7	0.003–65	15
Titanium	7	4	0.02–100	44
Cobalt	7	7	0.044–95	24
Toxic Pollutants (μg/L)				
Metals and inorganics				
Antimony	7	1	6000	
Arsenic	7	3	1900–2800	2400
Beryllium	7	4	BDL–120	49
Cadmium	7	4	14–9600	2700
Chromium	7	7	BDL–1100	430
Copper	7	7	BDL–8800	2600
Cyanide	3	1	BDL	—
Lead	7	7	490–880,000	170,000
Nickel	7	4	250–67,000	33,000
Selenium	7	7	430–160,000	29,000
Zinc	7	6	680–650,000	130,000

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.
BDL, below detection limit.

Water is used to rinse the workpieces after various operations, as a constituent of the enamel slip, in spray booths, and in cleaning, cooling, and air scrubbing. Pollutants such as dirt and grease enter the wastestream from the surface preparation and rinsing steps. Acid pickling adds dissolved copper to the wastestreams. Enamel preparation and application may add high concentrations of aluminum, titanium, manganese, nickel, zinc, and cobalt, as well as fluorides, antimony, copper, lead, and iron for the porcelain enameling on copper subcategory on a stream basis, as shown in Table 8.5.

8.5 SPECIFIC DESCRIPTIONS OF PORCELAIN ENAMELING INDUSTRIAL PLANTS

Only a limited amount of information is available on specific plants within this industry. This section describes the treatment practice and wastewater composition at nine plants: three that enamel on steel, three on aluminum, two on cast iron, and one on copper. The major treatment operation used is a settling technique. Treatment operations are not necessarily listed in this narrative in the same order that they are used at the plants. Wastewater composition data were obtained from verification sampling.[3–6]

TABLE 8.4
Wastewater Characterization of the Porcelain Enameling on Aluminum Subcategory

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections
	←	**Alkaline Cleaning**	→	
Classical Pollutants (mg/L)				
TSS	8	8	1.0–180	40
Total phosphorus	8	8	0.41–24	8.5
Total phenols	8	7	0.005–0.02	0.008
Oil and grease	8	4	3–11	6.8
pH (pH units)	16	16	6.3–11	8.7
Fluorides	8	8	0.72–0.98	0.88
Aluminum	8	7	0.68–26	6.6
Barium	8	0	—	—
Iron	8	8	0.01–0.33	0.1
Manganese	8	3	0.02–0.18	0.11
Titanium	8	0	—	—
Cobalt	8	0	—	—
Toxic Pollutants (μg/L)				
Metals and inorganics				
Antimony	8	0	—	—
Arsenic	8	0	—	—
Beryllium	8	0	—	—
Cadmium	8	1	BDL	—
Chromium	8	2	BDL–18	12
Copper	8	2	21–56	38
Cyanide	8	2	15–180	95
Lead	8	2	40–4300	2200
Nickel	8	0	—	—
Selenium	8	0	—	—
Zinc	8	7	19–540	210
Organics				
Bis(2-ethylhexyl)phthalate	8	0	—	—
Di-n-octyl phthalate	8	0	—	—
Toluene	3	0	—	—
	←	**Coating**	→	
Classical Pollutants (mg/L)				
TSS	8	8	55–650	330
Total phosphorus	8	8	0.38–65	9.8
Total phenols	8	5	0.005–0.02	0.01
Oil and grease	8	3	2.3–4.7	3.4
pH (pH units)	16	16	7.0–10	8.9
Fluorides	8	8	0.92–1.9	1.2
Aluminum	8	8	0.25–2.1	0.62
Barium	8	8	0.11–1.4	0.59
Iron	8	8	0.11–0.94	0.33
Manganese	8	2	0.003–0.01	0.007
Titanium	8	8	3.1–30	10
Cobalt	8	1	0.03	—
Toxic Pollutants (μg/L)				
Metals and inorganics				
Antimony	8	2	210–360	280
Arsenic	8	0	—	—

Continued

TABLE 8.4 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections
Beryllium	8	0	—	—
Cadmium	8	7	290–54,000	11,000
Chromium	8	8	BDL–39	24
Copper	8	6	BDL–180	57
Cyanide	8	1	BDL	—
Lead	8	8	3500–38,000	15,000
Nickel	8	0	—	—
Selenium	8	4	530–7100	2200
Zinc	8	8	150–2000	740
Organics				
Bis(2-ethylhexyl)phthalate	8	0	—	—
Di-n-octyl phthalate	8	0	—	—
Toluene	3	0	—	—
	←	**Total Raw Waste**		→
Classical Pollutants (mg/L)				
TSS	8	8	12–190	110
Total phosphorus	8	8	0.88–24	9.3
Total phenols	8	8	0.001–0.015	0.007
Oil and grease	8	5	1.7–11	5.8
pH (pH units)	16	16	6.3–10.4	8.7
Fluorides	8	8	0.74–0.98	0.89
Aluminum	8	8	0.08–10	3.8
Barium	8	8	0.01–0.24	0.10
Iron	8	8	0.02–0.71	0.24
Manganese	8	5	0.002–0.13	0.04
Titanium	8	8	0.09–6.1	2.6
Cobalt	8	1	0.005	—
Toxic Pollutants (μg/L)				
Metals and inorganics				
Antimony	8	2	150–260	210
Arsenic	8	0	—	—
Beryllium	8	0		
Cadmium	8	7	BDL–5200	2200
Chromium	8	8	BDL–13	BDL
Copper	8	6	BDL–130	48
Cyanide	8	2	BDL–140	73
Lead	8	8	150–12,000	3900
Nickel	8	0	—	—
Selenium	8	4	110–630	400
Zinc	8	8	120–530	300
Organics				
Bis(2-ethylhexyl)phthalate	8	0	—	—
Di-n-octyl phthalate	8	0	—	—
Toluene	3	0	—	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

BDL, below detection limit.

TABLE 8.5
Wastewater Characterization of the Porcelain Enameling on Copper Subcategory

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections
	←	Acid Etch		→
Classical Pollutants (mg/L)				
TSS	2	2	14–24	19
Total phosphorus	2	1	0.52	—
Total phenols	2	1	0.006	—
Oil and grease	1	1	200	—
pH (pH units)	5	5	1.8–6.6	5.7
Fluorides	2	2	0.11–0.12	0.12
Aluminum	3	3	0.0002–0.17	0.073
Iron	3	3	0.15–51	27
Manganese	3	3	0.01–0.26	0.09
Titanium	3	0	—	—
Cobalt	3	0	—	—
Toxic Pollutants (μg/L)				
Metals and inorganics				
Antimony	3	0	—	—
Arsenic	3	1	BDL	—
Beryllium	3	0	—	—
Cadmium	3	1	22	—
Chromium	3	3	BDL–60	26
Copper	3	3	9700–820,000	280,000
Cyanide	2	0	—	—
Lead	3	1	770	—
Nickel	3	1	120	—
Selenium	3	1	BDL	—
Zinc	3	3	49–2400	890
Organics				
Carbon tetrachloride	1	0	—	—
1,1,1-Trichloroethane	1	1	BDL	—
1,1,2-Trichloroethane	1	0	—	—
1,1-Dichloroethylene	1	0	—	—
Methylene chloride	1	0	—	—
Methyl chloride	1	0	—	—
Trichloroethylene	1	1	BDL	—
Toluene	2	0	—	—
Chloroform	3	2	BDL–BDL	BDL
Dichlorobromomethane	2	2	BDL–BDL	BDL
1,1,2,2-Tetrachloroethane	2	2	BDL–BDL	BDL
Tetrachloroethylene	4	0	—	—
	←	Coating		→
Classical Pollutants (mg/L)				
TSS	3	3	14,000–94,000	46,000
Total phosphorus	2	2	1–71	36
Total phenols	3	0	—	—
Oil and grease	3	3	2.0–98	37
pH (pH units)	7	7	7.6–10	8.8

Continued

TABLE 8.5 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections
Fluorides	3	3	46–66	56
Aluminum	4	4	96–200	140
Iron	4	4	15–29	22
Manganese	4	4	6.2–120	68
Titanium	4	4	3.6–560	220
Cobalt	4	4	20–64	46
Toxic Pollutants (*µg/L*)				
Metals and inorganics				
Antimony	4	4	1600–3500	2300
Arsenic	4	2	420–3800	2100
Beryllium	4	3	BDL–59	34
Cadmium	4	4	97–2800	830
Chromium	4	4	200–3000	1000
Copper	4	4	4700–10,000	6900
Cyanide	3	1	55	—
Lead	4	4	2300–440,000	110,000
Nickel	4	4	20,000–49,000	37,000
Selenium	4	4	200–810	570
Zinc	4	4	1100–200,000	84,000
Organics				
1,2-Dichlorobenzene	1	0	—	—
Toluene	3	0	—	—
Carbon tetrachloride	1	1	BDL	—
1,1,1-Trichloroethane	1	1	BDL	—
1,1,2-Trichloroethane	1	0	—	—
1,1-Dichloroethylene	1	0	—	—
Methylene chloride	1	0	—	—
Methyl chloride	1	0	—	—
Trichloroethylene	1	1	BDL	—
Chloroform	4	4	BDL–BDL	BDL
Dichlorobromomethane	3	2	BDL–BDL	BDL
1,1,2,2-Tetrachloroethane	2	2	BDL–BDL	BDL
Tetrachloroethylene	4	2	BDL–BDL	BDL
	← **Total Raw Waste** →			
Classical Pollutants (mg/L)				
TSS	3	3	1100–94,000	33,000
Total phosphorus	1	1	0.08	—
Total phenols	3	1	0.006	—
Oil and grease	2	2	2–190	96
pH (pH units)	7	7	1.8–10	7.7
Fluorides	3	3	3.8–56	22
Aluminum	4	4	0.12–200	55
Iron	4	4	1.4–48	27
Manganese	4	4	0.27–120	33
Titanium	4	4	0.004–560	150
Cobalt	4	4	0.024–64	18

Continued

TABLE 8.5 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Average of Detections
Toxic Pollutants (μg/L)				
Metals and inorganics				
Antimony	4	4	BDL–2400	690
Arsenic	4	2	BDL–420	210
Beryllium	4	3	BDL–35	13
Cadmium	4	4	BDL–220	69
Chromium	4	4	23–630	190
Copper	4	4	7100–810,000	210,000
Cyanide	t3	1	BDL	—
Lead	4	4	190–4800	1700
Nickel	4	4	140–49,000	14,000
Selenium	4	4	BDL–810	230
Zinc	4	4	2400–200,000	53,000
Organics				
Toluene	3	0	—	—
Chloroform	4	4	BDL–BDL	BDL
Dichlorobromomethane	3	3	BDL–BDL	BDL
1,1,1-Trichloroethane	1	1	BDL	—
1,1,2-Trichloroethane	1	0	—	—
1,1-Dichloroethylene	1	0	—	—
Methylene chloride	1	0	—	—
Methyl chloride	1	0	—	—
Trichloroethylene	1	1	BDL	—
1,1,2,2-Tetrachloroethane	2	2	BDL–BDL	BDL
Tetrachloroethylene	4	2	BDL–BDL	BDL
Carbon tetrachloride	1	1	BDL	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

BDL, below detection limit.

8.5.1 INDUSTRIAL PLANTS OF PORCELAIN ENAMELING ON STEEL SUBCATEGORY

8.5.1.1 Plant 40053

This facility is involved with porcelain enameling on both steel and cast iron. Data presented in Tables 8.6 and 8.7 are for the coating on steel subcategory only.

8.5.1.2 Plant 41062

This plant produces 130 m^2/h of enameled steel and operates 3500 h/yr. It uses 0.0036 m^3 water/m^2 of product to coat the steel. Average process water flow is 0.144 m^3/h for coating operations and 0.734 m^3/h for metal preparation. The primary treatment in-place for process wastewater is clarification and settling. Other water treatment practices employed are pH adjustment with lime or acid, sludge applied to landfill, polyelectrolyte coagulation, and inorganic coagulation.

8.5.1.3 Plant 36030

This facility produces 110 m^2/h of enameled steel and operates 4000 h/yr. It uses 0.0042 m^3 water/m^2 of product in coating operations. Average process water flow is 1.69 m^3/h for coating operations and 0.466 m^3/h for metal preparation. The primary in-place treatment is chemical coagulation and clarification. Clarification can be either settling or dissolved air flotation.

TABLE 8.6
Water Use (m^3 Water/m^2 Product) in the Porcelain Enameling on Steel Subcategory

	Plant Identification					
Process[a]	**33617**	**40063**	**47033**	**40053**	**36030**	**41062**
Alkaline cleaning	0.00094	0.0032	0.10	0.0056	0.010	0.029
Acid etch	0.00014	0.0026	0.038	0.012	0.0051	0.0071
Nickel flash	0.00033	0.0027	0.021	[c]	[c]	[e]
Neutralization	0.00011	0.0016	0.0056	[c]	0.00075	[c]
Ball milling	0.00004	0.017	0.0010	0.0013	0.0031	0.0053
Coating	0.00066	0.011	[b]	[d]	0.0013	[d]

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

[a] Because of differences in area prepared and coated, these data cannot be added directly for each process to obtain overall subcategory water usage.

[b] Uses dip coating and spray coating with a dry booth.

[c] No rinsing involved.

[d] Dry spray booths.

[e] Nickel flash not used at this plant.

Table 8.6 gives the water use for each process in the production of porcelain enameled steel for the above plants. Pollutant concentrations for treated effluents are presented in Table 8.7.[3–6]

8.5.2 INDUSTRIAL PLANTS OF THE PORCELAIN ENAMELING ON ALUMINUM SUBCATEGORY

8.5.2.1 Plant 11045

This facility produces 210 m^2/h of enameled aluminum and uses 0.015 m^3 water/m^2 of product for coating operations. The average process flow rate is 1.33 m^3/h for metal preparation operations and 0.716 m^3/h for coating operations. The primary in-place treatment for process wastewater is chemical coagulation and clarification (i.e., settling).

8.5.2.2 Plant 47051

This plant produces 290 m^2/h of enameled aluminum for 6400 h/yr. It uses 0.018 m^3 water/m^2 product for coating and ball milling purposes. The average process flow rate is 12.5 m^3/h for metal preparation and 1.59 m^3/h for coating and ball milling. In-place treatment consists primarily of chemical coagulation, clarification (settling), and final pH adjustment.

8.5.2.3 Plant 33077

This facility produces 360 m^2/h of porcelain enameled aluminum for 4000 h/yr, and uses 0.038 m^3 of process water/m^2 of product coated. The mixed wastewater stream is treated by equalization (settling), pH adjustment (lime or acid), polyelectrolyte coagulation, clarification, and contractor removal of the resulting sludge prior to discharge to a surface stream. Process water flow for this production consists of 8.12 m^3/h and 4.37 m^3/h for surface preparation and coating operations, respectively.[3–6]

Table 8.8 gives the water use for each process in the production of porcelain enameled aluminum for the above plants. Pollutant concentrations for treated effluents are presented in Tables 8.9 and 8.10.[10]

TABLE 8.7
Effluent Concentrations of Pollutants Found in Steel Subcategory Plants

	Plant Identification		
Pollutant (mg/L)	**40053[a]**	**41062[b]**	**36030[b]**
Aluminum	190	2100	130,000
Antimony	—	—	9700
Arsenic	—	ND	—
Cadmium	ND	75	550
Chromium	12	10	630
Cobalt	22	ND	32,000
Copper	52	13	3500
Fluoride	930	2300	58,000
Iron	250,000	240	630,000
Lead	ND	ND	3500
Manganese	910	BDL	51,000
Nickel	2700	14	29,000
Phenols, total	24	36	—
Phosphorus	11,000	770	3600
Selenium	ND	ND	590
Titanium	ND	160	660,000
Zinc	140	230	180,000
Oil and grease	—	1700	—
TSS	51,000	11,000	57,000,000[c]
pH (pH units)	2.1–3.2	8.1–9.1	—

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

Dashes indicate data not available.

BDL, below detection limit; ND, not detected.

[a] In-place treatment not available.

[b] In-place treatment consists of clarification/settling.

[c] As reported in reference; currently under review.

TABLE 8.8
Water Use (m^3 Water/m^2 Product) in the Porcelain Enameling on Aluminum Subcategory

	Plant Identification		
Process[a]	**11045**	**33077**	**47051**
Surface preparation	0.029	0.140	0.042
Ball milling	0.041	0.014	0.0029
Coating	0.019	0.014	—[b]

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

[a] Because of differences in area prepared and coated, these data cannot be added for each process to obtain overall subcategory water usage.

[b] This plant employs dry spray booths.

TABLE 8.9
Effluent Concentrations of Pollutants Found in Aluminum Subcategory Plants

	Plant Identification		
Pollutant (μg/L)	**11045**[a]	**33077**[a]	**47051**[a]
Aluminum	3600	76	6800
Antimony	—	ND	—
Arsenic	—	ND	—
Barium	240	200	300
Cadmium	1100	350	BDL
Chromium, total	BDL	BDL	57
Chromium-hexavalent	—	ND	ND
Cobalt	—	—	BDL
Copper	84	ND	52
Fluoride	930	1800	390
Iron	460	24	360
Lead	5300	210	97
Manganese	28	ND	80
Nickel	—	—	57
Phenols, total	BDL	BDL	BDL
Phosphorus	1900	1900	—
Selenium	—	28	—
Titanium	3900	130	ND
Zinc	210	390	290
Oil and grease	3300	ND	72,000
TSS	140,000	13,000	310
pH (pH units)	7.3–9.3	9–9.3	7.1–10.2

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

Dashes indicate data not available.

BDL, below detection limit; ND, not detected.

[a] In-place treatment consists of clarification/settling.

8.5.3 INDUSTRIAL PLANTS OF THE PORCELAIN ENAMELING ON CAST IRON SUBCATEGORY

8.5.3.1 Plant 15712

This facility produces 9.1 m^2/yr of porcelain enameled cast iron. The primary in-place treatment for process wastewater is chemical coagulation, clarification (settling), and skimming.

8.5.3.2 Plant 40053

This facility is involved with porcelain enameling on both steel and cast iron. Data presented in Tables 8.11 and 8.12 are for the coating on cast iron subcategory only. Table 8.11 gives the water use for each process in the production of porcelain enameled cast iron for the above plants. Pollutant concentrations in the treated effluent are presented in Table 8.12.

8.5.4 INDUSTRIAL PLANTS OF THE PORCELAIN ENAMELING ON COPPER SUBCATEGORY

Plant 36030 enamels both copper and steel. It uses 0.042 m^3 water/m^2 product in all coating operations. Process wastewater flow is 0.466 m^3/h for metal preparation and 1.69 m^3/h for coating

TABLE 8.10
Full Scale Treatment of Porcelain Enameling on Aluminum Subcategory Wastewater by Equalization and Chemical Precipitation Using Lime and Polymer

Removal Data Sampling: [16-h Composite, Flow Proportion (1 h)]

	Concentration		Percent Removal	Detection Limit
	Influent	Effluent		
Classical Pollutants (mg/L)				
pH, minimum	8.9	9.4	—	—
pH, maximum	10.5	10.0	—	—
Fluorides	1.8	2.0	NM	0.1
Phosphorus	12	0.89	92	0.003
TSS	53	ND	>99	5.0
Iron	2.0	0.038	98	0.005
Titanium	1.2	ND	>99	—
Manganese	0.017	ND	>99	0.005
Phenols, total	0.006	ND	>99	0.005
Aluminum	1.2	ND	>99	0.04
Barium	0.23	0.20	13	—
Toxic Pollutants (μg/L)				
Cadmium	2900	57	98	2.0
Chromium, total	11	ND	>99	3.0
Copper	4.0	ND	>99	1.0
Lead	1200	ND	>99	30
Zinc	220	540	NM	1.0
Cyanide, total	160	ND	>99	5.0
Selenium	300	ND	>99	—

Source: U.S. EPA, References 5 and 7.

Dashes indicate data not available.

ND, not detected; NM, not meaningful.

Plant: 33077

Wastewater flow rate: 965 m^3/d

Chemical dosage(s): lime: 47,200 kg/yr; polymer: 320 kg/yr

Unit configuration: continuous operation (16 h/day)

TABLE 8.11
Water Use (m^3 Water/m^2 Product) in the Porcelain Enameling on Cast Iron Subcategory

	Plant Identification	
Process	**15712**	**40053**
Surface preparation	[a]	[a]
Ball milling	0.00001	0.0013
Coating application	0.00028	[b]

Source: U.S. EPA, References 5 and 7.

[a] Surface preparation consists of dry operations.

[b] This plant uses dry spray booths.

TABLE 8.12
Effluent Concentrations of Pollutants Found in Cast Iron Subcategory Plants

	Plant Identification	
Pollutant (μg/L)	**15712**[a]	**40053**[b]
Aluminum	190,000	190,000
Cadmium	—	3600
Chromium, total	19	740
Cobalt	6200	50,000
Copper	BDL	6000
Fluoride	2200	89,000
Iron	13,000	80,000
Lead	110,000	5600
Manganese	BDL	35,000
Nickel	—	44,000
Phenols, total	20	20
Phosphorus	1200	980
Selenium	63,000	590
Titanium	—	58,000
Zinc	470	250,000
TSS	16,000,000	21,000,000
pH (pH units)	8.8–10.7	8.8–9.0

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

Analytic methods: V.7.3.16, Data set 2.

Dashes indicate data not available.

BDL, below detection limit.

[a] In-place treatment consists of clarification/settling.

[b] In-place treatment not available.

and ball milling. The production rate for porcelain enameling on copper is 10 m^2/h for 4000 h/yr. The primary in-place treatment is clarification and settling.

Table 8.13 gives the water use for each process in the production of porcelain enameled copper for two plants. Pollutant concentrations in the treated effluent are given in Table 8.14.

TABLE 8.13
Water Use (m^3 Water/m^2 Product) in the Porcelain Enameling on Copper Subcategory

	Plant Identification	
	36030	**06031**
Acid etch	0.057	0.087
Ball milling	0.0037	[a]
Coating	0.0015	0.00017

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

[a] Ball milling operations at this facility generated no wastewater.

TABLE 8.14
Effluent Concentrations of Pollutants Found in Copper Subcategory Plants

	Plant Identification
Pollutant (μg/L)	**36030**[a]
Aluminum	130,000
Antimony	6400
Cadmium	550
Chromium, total	1100
Cobalt	32,000
Copper	3500
Fluoride	58,000
Iron	630,000
Lead	2100
Manganese	51,000
Nickel	29,000
Phosphorus	3600
Selenium	590
Titanium	660,000
Zinc	180,000
TSS	57,000,000

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, 2008.

[a] In-place treatment consists of clarification/settling.

8.6 POLLUTANT REMOVABILITY OF PORCELAIN ENAMELING INDUSTRY WASTEWATER

Treatment technologies used in the porcelain enameling industry are generally chosen to remove the major wastewater components, such as suspended solids and toxic metals. Table 8.15 presents a summary of the treatment and disposal techniques used by this industry. Usually more than one treatment methods will be used at each facility.[3–6,10]

Some type of clarification technology is used in a large portion of the plants. Clarification can be either sedimentation or dissolved air flotation.[10–12] pH adjustment by chemical addition is another common treatment that is used to neutralize the alkaline or acid wastes. Coagulants are sometimes used to aid settling or flotation. Once the clarification (either settling or flotation) nears completion, filtration techniques are used to concentrate the sludge, which is then landfilled or contractor hauled.[13–15] Oils may be treated in a similar manner. Tables 8.8, 8.10, 8.12, 8.14, and 8.15 in the plant-specific section give treated effluent concentrations. Table 8.15 is a summary of the common wastewater treatment technologies used in porcelain enameling industry. Brief descriptions of the common treatment practices and the water reuse and recycle techniques follow.

8.6.1 EQUALIZATION AND NEUTRALIZATION

Raw wastewaters are commonly collected in equalization basins to even out the flow and the pollutant contaminant load. This permits uniform and controlled operation of subsequent treatment facilities. Wastes in this industry generally require pH adjustment, which can be performed in mixed equalization basins or in separate neutralization reactor basins following equalization.[10]

TABLE 8.15
Treatment Technologies in Current Use in the Porcelain Enameling Industry

	Number of Plants Using the Method by Subcategory				
Treatment Method	**Steel**	**Iron**	**Aluminum**	**Copper**	**Total Plants**
Skimming	2	—	—	—	2
Settling tank	33	7	5	1	46
Clarifier	17	—	2	—	19
Sedimentation lagoon	10	—	—	—	10
Tube/plate settler	3	—	—	—	3
Equalization	24	2	2	—	28
pH adjustment—lime	15	1	2	—	18
pH adjustment—caustic	6	2	—	—	8
pH adjustment—acid	6	—	1	—	7
pH adjustment—carbonate	2	—	1	—	3
pH adjustment—final	5	—	1	—	6
Coagulant—polyelectrolyte	10	1	1	—	12
Coagulant—inorganic	3	1	—	—	4
Chrome reduction	2	—	1	—	3
Emulsion breaking	1	—	—	—	1
Chlorination	1	—	—	—	1
Ultrafiltration	2	—	—	—	2
Pressure filtration	5	1	—	—	6
Vacuum filtration	5	—	—	—	5
Filtration	3	—	—	—	3
Aeration	2	—	—	—	2
Trickling filter	1	—	—	—	1
Centrifugation sludge	1	—	—	—	1
Material recovery	1	2	—	—	3
Air pollution control	1	—	—	—	1
Process reuse—oil	1	—	—	—	1
Contract removal—oil	7	—	—	—	7
Contract removal—sludge	5	—	1	—	6
Landfill—oil	2	—	—	—	2
Landfill—sludge	20	2	—	—	22
Sludge drying bed	3	—	—	—	3
Sludge thickening	—	—	1	—	1

Source: U.S. EPA, References 5 and 7.
Dashes indicate no plants using this method.

8.6.2 CLARIFICATION BY SEDIMENTATION (SETTLING) OR FLOTATION

Sedimentation and dissolved air flotation are the most common clarification processes for removal of precipitates. Either sedimentation or flotation is often preceded by chemical coagulation or precipitation, which converts dissolved pollutants to a suspended form, and by flocculation, which enhances clarification by flocculating suspended solids into larger, more easily separating particles. Simple sedimentation normally requires a long retention time to adequately reduce the solids content. The detention time of dissolved air flotation, however, is much shorter. When chemicals are used, retention times are reduced and clarification removal efficiency of either sedimentation or flotation is increased. A properly operated clarification system is capable of efficient removal of suspended solids, metal hydroxides, and other wastewater impurities.[10–12]

8.6.3 Chemical Addition, Precipitation, Coagulation, and Flocculation

Chemical precipitation is used in porcelain enameling to precipitate dissolved metals and phosphates. Chemical precipitation can be utilized to permit removal of metal ions such as iron, lead, tin, copper, zinc, cadmium, aluminum, mercury, manganese, cobalt, antimony, arsenic, beryllium, molybdenum, and trivalent chromium. Removal efficiency can approach 100% for the reduction of heavy metal ions. Porcelain enameling plants commonly use lime, caustic, and carbonate for chemical precipitation and pH adjustment. Coagulants used in the industry include alum, ferric chloride, ferric sulfate, and polymers.[10–12]

8.6.4 Granular Bed Filtration, Granular Activated Carbon Filtration, and Membrane Filtration

Granular bed filters are used in porcelain enameling wastewater treatment to remove residual solids from clarifier effluent (sedimentation effluent or flotation effluent). Filtration polishes the effluent and reduces suspended solids and insoluble precipitated metals to very low levels. Fine sand and coal are media commonly utilized in granular bed filtration. The filter is backwashed after becoming loaded with solids and the backwash is returned to the treatment plant influent for removal of solids in the clarification step.[10–12]

When granular activated carbons (GAC) are used as the filter media, the GAC filter can also remove dissolved organics (such as TTO, total toxic organics; or VOC, volatile organic compounds).[10,11]

Recently, membrane filtration has become popular for treating industrial effluent. Membrane filtration includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).[11,12]

8.6.5 Sludge Concentration and Dewatering

Sludges from clarifiers can be thickened in gravity thickeners or mechanically thickened by centrifuges. Thickened sludges can be further dewatered on one of a number of dewatering operations including vacuum filters, pressure filters, and belt filter presses. Dewatered sludges are disposed generally to landfills that must be properly constructed to conform to provisions of the Resource Conservation and Recovery Act (RCRA) and regulations governing disposal of hazardous wastes.[13–15]

8.7 POLLUTION PREVENTION AND CLEANER PRODUCTION IN THE PORCELAIN ENAMELING INDUSTRY

Many facilities in this industry use in-plant technology to reduce or eliminate the waste load, requiring end-of-pipe treatment and thereby improve the quality of the effluent discharge and reduce treatment costs. In-plant technology involves water reuse, process material conservation, reclamation of waste enamel, process modifications, material substitutions, improved rinse techniques, and good housekeeping practices.[3–6,15]

Water reuse is practiced at several plants in this industry. Water that may be reused for such purposes as rinse water, makeup water, and cleanup water includes air conditioning water, acid treatment rinsewater, and noncontact cooling water. Reuse of acid rinsewater in alkaline rinses has been demonstrated at many electroplating plants.

Process material conservation is practiced by the recovery, reuse, or purification of the materials used in the processes. In the nickel deposition process the nickel solution is filtered to reduce its iron content, giving a longer life to the solution. Because the bath is dumped less often, the pollutant load is reduced.

The use of dry spray booths can also reduce the wastewater volume from the plant as well as increasing excess enamel recovery and reuse. Overspray is captured on filter screens and then swept up and reused in the enamel slip. Several plants use this and other, similar processes to recover the enamel raw material.

Process modifications, material substitutions, improved rinsing techniques, and good housekeeping procedures may also significantly reduce the amount of wastewater released.

8.8 COSTS FOR TREATMENT OF PORCELAIN ENAMELING INDUSTRIAL WASTEWATERS

The investment cost, operating and maintenance costs, and energy costs for the application of control technologies to the wastewater of the porcelain enameling industry have been analyzed. These costs were developed to reflect the conventional use of technologies in this industry. The detailed presentation of the cost methodology and cost information is characterized as follows.[3–6,16]

Unit operation and unit process configurations have been analyzed for the cost of application to the wastewater of this industry. Recommended unit process configurations for BPT (best practicable control technology) and BAT (best available technology) level of treatment and their costs are summarized briefly in the following sections.

8.8.1 BPT Level Treatment

8.8.1.1 Suggested BPT for Treating Porcelain Enameling Industrial Wastes

The BPT treatment for the steel, aluminum, and copper subcategories of this industry consists of settling the coating waste separately, chemical reduction of hexavalent chromium in the metal preparation stream, equalization of all other enameling wastewaters by combining the wastewater streams, and using chemical precipitation and sedimentation to remove metals and solids. For the purpose of the BPT system cost estimates, chromium reduction was included for the aluminum subcategory, because aluminum is the only subcategory that has chromium in the wastewater. The treatment for the cast iron subcategory consists of presettling of coating wastewaters, and chemical precipitation and sedimentation (or dissolved air flotation or membrane filtration) to remove metals and solids.[3–6,10–12]

8.8.1.2 Suggested BPT System Components for Treating Porcelain Enameling Industrial Wastes

A reinforced concrete sump and associated pumping equipment is required for sedimentation of coating wastewaters. Chromium reduction for the aluminum subcategory wastewater is achieved either by batch treatment or continuous treatment. The continuous treatment system consists of a single reaction tank, sulfur dioxide and sulfuric acid storage and feeding equipment, and mixers and controls. The batch treatment system consists of dual reaction tanks, chemical feed equipment, and mixers and controls. Chemical precipitation and sedimentation is either by batch or continuous treatment. The continuous treatment system includes lime storage and feed equipment, a flocculator, and a clarification basin with sludge rakes and pumps. The batch treatment system includes only reaction settling tanks and sludge pumps. The sludge from settling tanks is dewatered with vacuum filters and hauled away for offsite disposal.[10–12]

8.8.1.3 BPT Unit Cost for Treating Porcelain Enameling Industrial Wastes

Total annual unit costs consisting of annual cost of capital, depreciation, operation, and maintenance cost, and energy cost for average, low, and high flow rates are summarized in Table 8.16. The total capital cost for the treatment system includes the cost of the components discussed above and subsidiary costs including engineering, line segregation, administration, and interest expenses during construction.

TABLE 8.16
Total Annual Unit Cost for BPT Level of Wastewater Treatment[a] in 2008 U.S. Dollars[b]

Subcategory	Flow (L/min)	Cost ($/m^3)	Flow (L/min)	Cost ($/m^3)	Flow (L/min)	Cost ($/m^3)
Steel	63	7.72	315	3.74	946	2.81
Aluminum	64	6.08	202	3.04	317	2.34
Copper	3	82.6	6	48.7	10	36.0
Cast iron	0.3	511	4	72.1	22	21.1

Source: U.S. EPA, References 5 and 7.

[a] For flows less than 315 L/min treatment is by batch system.

[b] Cost was updated to 2008 using U.S. ACE Cost Index for Utilities.[16]

8.8.2 BAT Level Treatment

8.8.2.1 Suggested BAT for Treating Porcelain Enameling Industrial Wastes

The BAT level of treatment consists of all components of BPT and the addition of a multimedia filter to treat the effluent from the sedimentation process.

8.8.2.2 Suggested BAT System Components for Treating Porcelain Enameling Industrial Wastes

The filtration system consists of a granular bed multimedia filter unit, a GAC filter unit, and/or a membrane filtration unit.[10–12]

8.8.2.3 BAT Unit Cost for Treating Porcelain Enameling Industrial Wastes

The total annual unit cost for the complete BAT system, which includes components described in the BPT system for those different flow rates, is summarized in Table 8.17.

8.9 PORCELAIN ENAMELING POINT SOURCE DISCHARGE EFFLUENT LIMITATIONS, PERFORMANCE STANDARDS, AND PRETREATMENT STANDARDS

8.9.1 U.S. Environmental Regulations for the Steel Basis Material Subcategory

Table 8.18 documents the current (May 2008) effluent limitations of the steel basis material subcategory that represent the degree of effluent reduction attainable by the application of the BPT currently available.[3–7]

TABLE 8.17
Total Annual Unit Cost for BAT Level of Wastewater Treatment[a] in 2008 U.S. Dollars[b]

Subcategory	Flow (L/min)	Cost ($/m^3)	Flow (L/min)	Cost ($/m^3)	Flow (L/min)	Cost ($/m^3)
Steel	32	14.0	189	5.15	631	3.51
Aluminum	49	8.89	153	4.21	272	3.04
Copper	3	122	5	63.9	8	45.6
Cast iron	0.3	165	4	82.1	22	23.2

Source: U.S. EPA, References 5 and 7.

[a] For flows less than 189 L/min treatment is by batch system.

[b] Costs was updated to 2008 using U.S. ACE Cost Index for Utilities.[16]

TABLE 8.18

Effluent Limitations of the Steel Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

Pollutant	Maximum for Any 1 Day		Maximum for Monthly Average	
	Metal Preparation	Coating Operation	Metal Preparation	Coating Operation
		(mg/m^2 of Area Processed or Coated)		
Chromium	16.82	3.41	6.81	1.38
Lead	6.01	1.21	5.21	1.06
Nickel	56.46	11.43	40.05	8.11
Zinc	53.26	10.78	22.43	4.54
Aluminum	182.20	36.87	74.47	15.07
Iron	112.12	22.69	56.06	11.34
Oil and grease	800.84	162.10	480.51	97.23
TSS	1642.00	332.20	800.90	162.00
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]
		(lb/10^6 ft^2 of Area Processed or Coated)		
Chromium	3.45	0.07	1.40	0.29
Lead	1.23	0.25	1.07	0.22
Nickel	11.57	2.34	8.20	1.66
Zinc	10.91	2.21	4.60	0.93
Aluminum	37.32	7.55	15.26	3.09
Iron	22.96	4.65	11.48	2.32
Oil and grease	164.03	33.19	98.42	19.92
TSS	337.00	68.10	164.00	33.20
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr466_03.html, 2008.

[a] Within this range at all times.

Table 8.19 documents the current (May 2008) effluent limitations of the steel basis material subcategory that represent the degree of effluent reduction attainable by the application of the BAT economically achievable.

Table 8.20 presents the new source performance standards (NSPS) of the steel basis material subcategory. Any new source must achieve the NSPS.

Any existing source of the steel basis material subcategory that introduces pollutants into a POTW must achieve the pretreatment standards listed in Table 8.21A. In cases where a POTW finds it necessary to impose mass effluent pretreatment standards, the equivalent mass pretreatment standards are provided in Table 8.21B.[3–7]

Any new source of the steel basis material subcategory that introduces pollutants into a POTW must achieve the pretreatment standards listed in Table 8.22.

8.9.2 U.S. Environmental Regulations for the Cast Iron Basis Material Subcategory

There shall be no discharge of process wastewater pollutants from any metal preparation operations in the cast iron basis material subcategory. The discharge of process wastewater pollutants

TABLE 8.19
Effluent Limitations of the Steel Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
		(mg/m² of Area Processed or Coated)		
Chromium	16.82	0.53	6.81	0.22
Lead	6.01	0.19	5.21	0.16
Nickel	56.50	1.78	40.05	1.26
Zinc	53.30	1.68	22.43	0.71
Aluminum	182.00	5.74	74.48	2.35
Iron	112.12	3.53	56.06	1.77
		(lb/10⁶ ft² of Area Processed or Coated)		
Chromium	3.45	0.11	1.4	0.05
Lead	1.23	0.04	1.07	0.03
Nickel	11.57	0.37	8.20	0.26
Zinc	10.91	0.35	4.60	0.15
Aluminum	37.32	1.18	15.26	0.48
Iron	22.96	0.72	11.48	0.36

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr466_03.html, 2008.

from all porcelain enameling coating operations shall not exceed the values set forth in Tables 8.23 through 8.27.

Table 8.23 documents the current (May 2008) effluent limitations of the cast iron basis material subcategory that represent the degree of effluent reduction attainable by the application of the BPT currently available.

Table 8.24 documents the current (May 2008) effluent limitations of the cast iron basis material subcategory that represent the degree of effluent reduction attainable by the application of the best available technology (BAT) economically achievable.

Table 8.25 presents the NSPS of the cast iron basis material subcategory. Any new source must achieve the NSPS.

Any existing source of the cast iron basis material subcategory that introduces pollutants into a POTW must achieve the pretreatment standards listed in Table 8.26A. In cases where a POTW finds it necessary to impose mass effluent pretreatment standards, the equivalent mass pretreatment standards are provided in Table 8.26B.[7]

Any new source of the cast iron basis material subcategory that introduces pollutants into a POTW must achieve the pretreatment standards listed in Table 8.27.

8.9.3 U.S. ENVIRONMENTAL REGULATIONS FOR THE ALUMINUM BASIS MATERIAL SUBCATEGORY

Table 8.28 documents the current (May 2008) effluent limitations of the aluminum basis material subcategory that represent the degree of effluent reduction attainable by the application of the BPT currently available.

Table 8.29 documents the current (May 2008) effluent limitations of the aluminum basis material subcategory that represent the degree of effluent reduction attainable by the application of the BAT economically achievable.

TABLE 8.20
New Source Performance Standards (NSPS) of the Steel Basis Material Subcategory

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
	(mg/m² of Area Processed or Coated)			
Chromium	3.37	0.47	1.5	0.19
Lead	1.0	0.13	0.9	0.11
Nickel	12.0	1.51	6.3	0.79
Zinc	10.2	1.29	4.2	0.53
Aluminum	30.3	3.82	12.4	1.56
Iron	28.0	3.53	14.0	1.77
Oil and grease	100.0	12.60	100.0	12.60
TSS	150.0	18.91	120.0	15.12
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]
	(lb/10⁶ ft² of Area Processed or Coated)			
Chromium	0.76	0.10	0.31	0.04
Lead	0.21	0.03	0.19	0.03
Nickel	2.46	0.31	1.29	0.16
Zinc	2.09	0.27	0.86	0.11
Aluminum	6.21	0.78	2.54	0.32
Iron	5.74	0.72	2.87	0.36
Oil and grease	20.48	2.58	20.48	2.58
TSS	30.72	3.87	24.58	3.10
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr466_03.html, 2008.

Note: Any new source must achieve the NSPS.

[a] Within this range at all times.

Table 8.30 presents the NSPS of the aluminum basis material subcategory. Any new source must achieve the NSPS.

Any existing source of the aluminum basis material subcategory that introduces pollutants into a publicly owned treatment works (POTW) must achieve the pretreatment standards listed in Table 8.31A. In cases where POTW find it necessary to impose mass effluent pretreatment standards, the equivalent mass pretreatment standards are provided in Table 8.31B.[7]

Any new source of the aluminum basis material subcategory that introduces pollutants into a POTW must achieve the pretreatment standards listed in Table 8.32.

TABLE 8.21A
Effluent Pretreatment Standards of an Existing Source of the Steel Basis Material Subcategory that Introduces Pollutants into a POTW

Pollutant	**Maximum for Any 1 Day (mg/L)**	**Maximum for Monthly Average (mg/L)**
Chromium	0.42	0.17
Lead	0.15	0.13
Nickel	1.41	1.00
Zinc	1.33	0.56

TABLE 8.21B
Mass Effluent Pretreatment Standards of an Existing Source of the Steel Basis Material Subcategory that Introduces Pollutants into a POTW

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
		(mg/m^2 of Area Processed or Coated)		
Chromium	16.82	0.53	6.81	0.22
Lead	6.01	0.19	5.21	0.16
Nickel	56.5	1.78	40.1	1.26
Zinc	53.3	1.68	22.5	0.71
		(lb/10^6 ft^2 of Area Processed or Coated)		
Chromium	3.45	0.11	1.4	0.05
Lead	1.23	0.04	1.07	0.03
Nickel	11.6	0.37	8.20	0.26
Zinc	10.9	0.35	4.6	0.15

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr466_03.html, 2008.

8.9.4 U.S. ENVIRONMENTAL REGULATIONS FOR THE COPPER BASIS MATERIAL SUBCATEGORY

Table 8.33 presents the NSPS of the copper basis material subcategory. Any new source must achieve the NSPS.

Any new source of the copper basis material subcategory that introduces pollutants into a POTW must achieve the pretreatment standards listed in Table 8.34.[7]

TABLE 8.22
Effluent Pretreatment Standards of a New Source of the Steel Basis Material Subcategory that Introduces Pollutants into a POTW

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
		(mg/m^2 of Area Processed or Coated)		
Chromium	3.7	0.47	1.5	0.19
Lead	1.0	0.13	0.9	0.11
Nickel	12.0	1.51	6.3	0.79
Zinc	10.2	1.29	4.2	0.53
		(lb/10^6 ft^2 of Area Processed or Coated)		
Chromium	0.76	0.10	0.31	0.04
Lead	0.2	0.03	0.19	0.002
Nickel	2.46	0.31	1.29	0.16
Zinc	2.09	0.27	0.86	0.11

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Porcelain Enameling Point Source Category*, Washington, DC, 1982; U.S. EPA, *Porcelain Enameling Point Source Category*, available at http://www.access.gpo.gov/nara/cfr/waisidx_03/40cfr466_03.html, 2008.

TABLE 8.23

Effluent Limitations of the Cast Iron Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

Pollutant	Maximum for Any 1 Day [mg/m^2 (lb/10^6 ft^2) of Area Coated]		Maximum for Monthly Average [mg/m^2 (lb/10^6 ft^2) of Area Coated]	
Chromium	0.29	(0.06)	0.12	(0.024)
Lead	0.11	(0.02)	0.09	(0.02)
Nickel	0.98	(0.02)	0.7	(0.15)
Zinc	0.93	(0.19)	0.39	(0.08)
Aluminum	3.16	(0.65)	1.29	(0.27)
Iron	0.86	(0.18)	0.44	(0.09)
Oil and grease	13.86	(2.84)	8.32	(1.71)
TSS	28.42	(5.82)	13.86	(2.84)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA, References 5 and 7.

[a] Within this range at all times.

TABLE 8.24

Effluent Limitations of the Cast Iron Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

Pollutant	Maximum for Any 1 Day [mg/m^2 (lb/10^6 ft^2) of Area Coated]		Maximum for Monthly Average [mg/m^2 (lb/10^6 ft^2) of Area Coated]	
Chromium	0.53	(0.11)	0.22	(0.05)
Lead	0.19	(0.04)	0.16	(0.03)
Nickel	1.78	(0.37)	1.26	(0.26)
Zinc	1.68	(0.35)	0.71	(0.15)
Aluminum	5.74	(1.18)	2.35	(0.48)
Iron	1.55	(0.32)	0.79	(0.16)

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36543, Sept. 6, 1985].

TABLE 8.25

New Source Performance Standards (NSPS) of the Cast Iron Basis Material Subcategory. Any New Source Must Achieve the NSPS

Pollutant	Maximum for Any 1 Day [mg/m^2 (lb/10^6 ft^2) of Area Coated]		Maximum for Monthly Average [mg/m^2 (lb/10^6 ft^2) of Area Coated]	
Chromium	0.47	(0.10)	0.19	(0.04)
Lead	0.13	(0.03)	0.11	(0.02)
Nickel	0.69	(0.14)	0.47	(0.10)
Zinc	1.29	(0.27)	0.53	(0.11)
Aluminum	3.82	(0.78)	1.56	(0.32)
Iron	1.55	(0.32)	0.79	(0.16)
Oil and grease	12.60	(2.58)	12.60	(2.58)

Continued

TABLE 8.25 (continued)

Pollutant	Maximum for Any 1 Day [mg/m^2 (lb/10^6 ft^2) of Area Coated]		Maximum for Monthly Average [mg/m^2 (lb/10^6 ft^2) of Area Coated]	
TSS	18.91	(3.87)	15.12	(3.10)
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36544, Sept. 6, 1985].

[a] Within this range at all times.

TABLE 8.26A
Effluent Pretreatment Standards of an Existing Source of the Cast Iron Basis Material Subcategory that Introduces Pollutants into a POTW

Pollutant	Maximum for Any 1 Day (mg/L)	Maximum for Monthly Average (mg/L)
Chromium	0.42	0.17
Lead	0.15	0.13
Nickel	1.41	1.00
Zinc	1.33	0.56

Source: U.S. EPA, References 5 and 7.

TABLE 8.26B
Mass Effluent Pretreatment Standards of an Existing Source of the Cast Iron Basis Material Subcategory that Introduces Pollutants into a POTW

Pollutant	Maximum for Any 1 Day [mg/m^2 (lb/10^6 ft^2) of Area Coated]		Maximum for Monthly Average [mg/m^2 (lb/10^6 ft^2) of Area Coated]	
Chromium	0.53	(0.11)	0.22	(0.05)
Lead	0.19	(0.04)	0.16	(0.03)
Nickel	1.78	(0.37)	1.26	(0.26)
Zinc	1.68	(0.35)	0.71	(0.15)

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36544, Sept. 6, 1985].

TABLE 8.27
Effluent Pretreatment Standards of a New Source of the Cast Iron Basis Material Subcategory that Introduces Pollutants into a POTW

Pollutant	Maximum for Any 1 Day [mg/m^2 (lb/10^6 ft^2) of Area Coated]		Maximum for Monthly Average [mg/m^2 (lb/10^6 ft^2) of Area Coated]	
Chromium	0.47	(0.10)	0.19	(0.04)
Lead	0.13	(0.03)	0.11	(0.02)
Nickel	0.69	(0.14)	0.47	(0.10)
Zinc	1.29	(0.27)	0.53	(0.11)

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36544, Sept. 6, 1985].

TABLE 8.28
Effluent Limitations of the Aluminum Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BPT Currently Available

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
	(mg/m^2 of Area Processed or Coated)			
Chromium	16.34	6.32	6.63	2.56
Lead	5.84	2.26	5.06	1.96
Nickel	54.85	21.21	38.90	15.04
Zinc	51.73	20.01	21.79	8.43
Aluminum	176.98	68.44	72.35	27.98
Iron	47.85	18.50	24.51	9.48
Oil and grease	777.92	300.84	466.76	108.50
TSS	1594.74	616.68	777.92	300.82
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]
	(lb/10^6 ft^2 of Area Processed or Coated)			
Chromium	3.35	1.30	1.37	0.53
Lead	1.20	0.47	1.04	0.40
Nickel	11.24	4.35	7.97	3.08
Zinc	10.6	4.10	4.46	1.73
Aluminum	36.25	14.02	14.82	5.73
Iron	9.80	3.79	5.02	1.94
Oil and grease	159.33	61.61	95.60	36.97
TSS	326.62	126.33	159.33	61.61
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

[a] Within this range at all times.

TABLE 8.29
Effluent Limitations of the Aluminum Basis Material Subcategory that Represent the Degree of Effluent Reduction Attainable by the Application of the BAT Economically Achievable

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
	(mg/m^2 of Area Processed or Coated)			
Chromium	16.34	0.53	6.62	0.22
Lead	5.84	0.19	5.06	0.16
Nickel	54.85	1.78	38.90	1.26
Zinc	51.74	1.68	21.79	1.71
Aluminum	176.98	5.74	72.35	2.35
Iron	47.85	1.55	24.51	0.80
	(lb/10^6 ft^2 of Area Processed or Coated)			
Chromium	3.35	0.11	1.36	0.05
Lead	1.20	0.04	1.04	0.03
Nickel	11.24	0.37	7.97	0.26
Zinc	10.60	0.35	4.46	0.35

Continued

TABLE 8.29 (continued)

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
Aluminum	36.25	1.18	14.82	0.48
Iron	9.80	0.32	5.02	0.16

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36544, Sept. 6, 1985].

TABLE 8.30
New Source Performance Standards (NSPS) of the Aluminum Basis Material Subcategory

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
		(mg/m^2 of Area Processed or Coated)		
Chromium	3.60	0.47	1.46	0.19
Lead	0.97	0.13	0.88	0.11
Nickel	5.35	0.69	3.60	0.47
Zinc	9.92	1.29	4.09	0.53
Aluminum	29.46	3.82	12.06	1.56
Iron	11.96	1.55	6.13	0.79
Oil and grease	97.24	12.60	97.24	12.60
TSS	145.86	18.91	116.69	15.12
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]
		(lb/10^6 ft^2 of Area Processed or Coated)		
Chromium	0.74	0.10	0.30	0.04
Lead	0.20	0.03	0.18	0.20
Nickel	1.10	0.14	0.74	0.10
Zinc	2.03	0.27	0.84	0.11
Aluminum	6.03	0.78	2.47	0.32
Iron	2.45	0.32	1.26	0.16
Oil and grease	19.92	2.58	19.92	2.58
TSS	29.88	3.87	23.90	3.10
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Note: Any new source must achieve the NSPS.

[a] Within this range at all times.

TABLE 8.31A
Effluent Pretreatment Standards of an Existing Source of the Aluminum Basis Material Subcategory that Introduces Pollutants into a POTW

Pollutant	**Maximum for Any 1 Day (mg/L)**	**Maximum for Monthly Average (mg/L)**
Chromium	0.42	0.17
Lead	0.15	0.13
Nickel	1.41	1.00
Zinc	1.33	0.56

TABLE 8.31B
Mass Effluent Pretreatment Standards of an Existing Source of the Aluminum Basis Material Subcategory that Introduces Pollutants into a POTW

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
	(mg/m^2 of Area Processed or Coated)			
Chromium	16.34	0.53	6.62	0.22
Lead	5.84	0.19	5.06	0.16
Nickel	54.85	1.78	38.9	1.26
Zinc	51.74	1.68	21.79	1.71
	(lb/10^6 ft^2 of Area Processed or Coated)			
Chromium	3.35	0.11	1.36	0.05
Lead	1.20	0.04	1.04	0.03
Nickel	11.24	0.37	7.97	0.25
Zinc	10.6	0.35	4.46	0.35

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36544, Sept. 6, 1985].

TABLE 8.32
Effluent Pretreatment Standards of a New Source of the Aluminum Basis Material Subcategory that Introduces Pollutants into a POTW

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
	(mg/m^2 of Area Processed or Coated)			
Chromium	3.60	0.47	1.46	0.19
Lead	0.97	0.13	0.88	0.11
Nickel	5.35	0.69	3.60	0.47
Zinc	9.92	1.29	4.09	0.53
	(lb/10^6 ft^2 of Area Processed or Coated)			
Chromium	0.74	0.10	0.30	0.04
Lead	0.20	0.03	0.18	0.02
Nickel	1.10	0.14	0.74	0.10
Zinc	2.03	0.27	0.84	0.11

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36545, Sept. 6, 1985].

8.10 TECHNICAL TERMINOLOGIES USED IN THE PORCELAIN ENAMELING INDUSTRY

1. *Porcelain enameling.* This is the entire process of applying a fused vitreous enamel coating to a metal basis material. Usually this includes metal preparation and coating operations.[3–7]
2. *Basis material.* This is the metal part or base onto which porcelain enamel is applied.
3. *Area processed.* This is the total basis material area exposed to processing solutions.

TABLE 8.33
New Source Performance Standards (NSPS) of the Copper Basis Material Subcategory

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
		(mg/m^2 of Area Processed or Coated)		
Chromium	6.23	0.46	2.52	0.19
Lead	1.69	0.13	1.52	0.11
Nickel	9.25	0.69	6.23	0.47
Zinc	17.16	1.29	7.07	0.53
Aluminum	50.97	3.82	20.86	1.56
Iron	20.69	1.55	10.60	0.79
Oil and grease	168.23	12.60	168.23	12.60
TSS	252.35	18.91	201.88	15.12
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]
		(lb/10^6 ft^2 of Area Processed or Coated)		
Chromium	1.28	0.10	0.52	0.04
Lead	0.35	0.03	0.31	0.03
Nickel	1.90	0.14	1.28	0.10
Zinc	3.52	0.27	1.45	0.11
Aluminum	10.44	0.78	4.27	0.32
Iron	4.24	0.32	2.17	0.16
Oil and grease	34.46	2.58	34.46	2.58
TSS	51.69	3.87	41.35	3.10
pH	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]	7.5–10.0[a]

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36545, Sept. 6, 1985].

Note: Any new source must achieve the NSPS

[a] Within this range at all times.

TABLE 8.34
Effluent Pretreatment Standards of a New Source of the Copper Basis Material Subcategory that Introduces Pollutants into a POTW

	Maximum for Any 1 Day		Maximum for Monthly Average	
Pollutant	**Metal Preparation**	**Coating Operation**	**Metal Preparation**	**Coating Operation**
		(mg/m^2 of Area Processed or Coated)		
Chromium	6.23	0.46	2.52	0.19
Lead	1.69	0.13	1.52	0.11
Nickel	9.25	0.69	6.23	0.47
Zinc	17.16	1.29	7.07	0.53
		(lb/10^6 ft^2 of Area Processed or Coated)		
Chromium	1.28	0.10	0.52	0.04
Lead	0.35	0.03	0.31	0.02
Nickel	1.90	0.14	1.28	0.10
Zinc	3.52	0.27	1.45	0.11

Source: U.S. EPA; *Porcelain Enameling Point Source Category, Code of Federal Regulations*, Title 40, Volume 27, Part 466, Washington, DC, July 1, 2003 [47 FR 53184, Nov. 24, 1982, as amended at 50 FR 36545, Sept. 6, 1985].

4. *Area coated*. This is the area of basis material covered by each coating of enamel.
5. *Coating operations*. This includes all of the operations associated with preparation and application of the vitreous coating. Usually this incorporates ball milling, slip transport, application of slip to the workpieces, cleaning and recovery of faulty parts, and firing (fusing) of the enamel coat.
6. *Metal preparation*. This comprises any and all of the metal processing steps preparatory to applying the enamel slip. Usually this includes cleaning, pickling, and applying a nickel flash or chemical coating.
7. *Control authority*. This is defined as the POTW if it has an approved pretreatment program; in the absence of such a program, this is the NPDES State if it has an approved pretreatment program or U.S. EPA if the State does not have an approved program.
8. *Precious metal*. This means gold, silver, or platinum group metals, and the principal alloys of those metals.

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9 Treatment and Management of Metal Finishing Industry Wastes

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CONTENTS

9.1 INDUSTRY DESCRIPTION

The metal finishing industry is one of many industries subject to regulation under the Resource Conservation and Recovery Act (RCRA)[1,2] and the Hazardous and Solid Waste Amendments (HSWA).[3] It has also been subject to extensive regulation under the Clean Water Act (CWA).[4] Compliance with these regulations requires highly coordinated regulatory, scientific, and engineering analyses to minimize costs.[5]

9.1.1 GENERAL DESCRIPTION

The metal finishing industry comprises 44 unit operations involving the machining, fabrication, and finishing of metal products [Standard Industrial Classification (SIC) groups 34–39]. There are approximately 160,000 manufacturing facilities in the United States that are classified as being part of the metal finishing industry.[6] These facilities are engaged in the manufacturing of a variety of products that are constructed primarily by using metals. The operations performed usually begin with a raw stock in the form of rods, bars, sheets, castings, forgings, and so on, and can progress to sophisticated surface finishing operations. The facilities vary in size from small job shops employing fewer than 10 people to large plants employing thousands of production workers. Wide variations also exist in the age of the facilities, and in the number and type of operations performed within facilities. Because of the differences in size and processes, production facilities are custom-tailored to the specific needs of each plant. The possible variations in unit operations within the metal finishing industry are extensive. Some complex products could require the use of nearly all of the 44 possible unit operations, while a simple product might require only a single operation. Each of the 44 individual unit operations is listed with a brief description below.[7]

1. *Electroplating* is the production of a thin coating of one metal upon another by electrodeposition.
2. *Electroless plating* is a chemical reduction process that depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of metal without the use of external electric energy.
3. *Anodizing* is an electrolytic oxidation process that converts the surface of the metal to an insoluble oxide.
4. *Chemical conversion coatings* are applied to previously deposited metal or basis material for increased corrosion protection, lubricity, preparation of the surface for additional coatings, or formulation of a special surface appearance. This operation includes chromating, phosphating, metal coloring, and passivating.
5. *Etching and chemical milling* are used to produce specific design configurations and tolerances on parts by controlled dissolution with chemical reagents or etchants.

6. *Cleaning* involves the removal of oil, grease, and dirt from the surface of the basis material using water with or without a detergent or other dispersing material.
7. *Machining* is the general process of removing stock from a workpiece by forcing a cutting tool through the workpiece, removing a chip of basis material. Machining operations such as turning, milling, drilling, boring, tapping, planing, broaching, sawing and cutoff, shaving, threading, reaming, shaping, slotting, hobbing, filing, and chamfering are included in this definition.
8. *Grinding* is the process of removing stock from a workpiece by the use of a tool consisting of abrasive grains held by a rigid or semirigid binder. The processes included in this unit operation are sanding (or cleaning to remove rough edges or excess material), surface finishing, and separating (as in cutoff or slicing operations).
9. *Polishing* is an abrading operation used to remove or smooth out surface defects (scratches, pits, tool marks, etc.) that adversely affect the appearance or function of a part. The operation usually referred to as buffing is included in the polishing operation.
10. *Barrel finishing* or tumbling is a controlled method of processing parts to remove burrs, scale, flash, and oxides as well as to improve surface finish.
11. *Burnishing* is the process of finish sizing or smooth finishing a workpiece (previously machined or ground) by displacement, rather than removal, of minute surface irregularities. It is accomplished with a smooth point or line-contact and fixed or rotating tools.
12. *Impact deformation* is the process of applying an impact force to a workpiece such that the workpiece is permanently deformed or shaped. Impact deformation operations include shot peening, forging, high energy forming, heading, and stamping.
13. *Pressure deformation* is the process of applying force (at a slower rate than an impact force) to permanently deform or shape a workpiece. Pressure deformation includes operations such as roiling, drawing, bending, embossing, coining, swaging, sizing, extruding, squeezing, spinning, seaming, staking, piercing, necking, reducing, forming, crimping, coiling, twisting, winding, flaring, or weaving.
14. *Shearing* is the process of severing or cutting a workpiece by forcing a sharp edge or opposed sharp edges into the workpiece, stressing the material to the point of shear failure and separation.
15. *Heat treating* is the modification of the physical properties of a workpiece through the application of controlled heating and cooling cycles. Operations such as tempering, carburizing, cyaniding, nitriding, annealing, normalizing, austenizing, quenching, austempering, siliconizing, martempering, and malleabilizing are included in this definition.
16. *Thermal cutting* is the process of cutting, slotting, or piercing a workpiece using an oxyacetylene oxygen lance or electric arc cutting tool.
17. *Welding* is the process of joining two or more pieces of material by applying heat, pressure, or both, with or without filler material, to produce a localized union through fusion or recrystallization across the interface. Included in this process are gas welding, resistance welding, arc welding, cold welding, electron beam welding, and laser beam welding.
18. *Brazing* is the process of joining metals by flowing a thin, capillary thickness layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term brazing is used where the temperature exceeds 425°C (800°F).
19. *Soldering* is the process of joining metals by flowing a thin, capillary thickness layer of nonferrous filler metal into the space between them. Bonding results from the intimate contact produced by the dissolution of a small amount of base metal in the molten filler metal, without fusion of the base metal. The term soldering is used where the temperature range falls below 425°C (800°F).

20. *Flame spraying* is the process of applying a metallic coating to a workpiece using finely powdered fragments of wire and suitable fluxes, which are projected together through a cone of flame onto the workpiece.
21. *Sand blasting* is the process of removing stock, including surface films, from a workpiece by the use of abrasive grains pneumatically impinged against the workpiece. The abrasive grains used include sand, metal shot, slag, silica, pumice, or natural materials such as walnut shells.
22. *Abrasive jet machining* is a mechanical process for cutting hard, brittle materials. It is similar to sand blasting but uses much finer abrasives carried at high velocities [150–910 m/s (500–3000 ft/s)] by a liquid or gas stream. Uses include frosting glass, removing metal oxides, deburring, and drilling and cutting thin sections of metal.
23. *Electrical discharge machining* is a process that can remove metal with good dimensional control from any metal. It cannot be used for machining glass, ceramics, or other nonconducting materials. Electrical discharge machining is also known as spark machining or electronic erosion. The operation was developed primarily for machining carbides, hard nonferrous alloys, and other hard-to-machine materials.
24. *Electrochemical machining* is a process based on the same principles used in electroplating except that the workpiece is the anode and the tool is the cathode. Electrolyte is pumped between the electrodes and a potential is applied, resulting in rapid removal of metal.
25. *Electron beam machining* is a thermoelectric process in which heat is generated by high-velocity electrons impinging the workpiece, converting the beam into thermal energy. At the point where the energy of the electrons is focused, the beam has sufficient thermal energy to vaporize the material locally. The process is generally carried out in a vacuum. The process results in x-ray emission, which requires that the work area be shielded to absorb radiation. At present the process is used for drilling holes as small as 0.05 mm (0.002 in.) in any known material, cutting slots, shaping small parts, and machining sapphire jewel bearings.
26. *Laser beam machining* is the process of using a highly focused, monochromatic collimated beam of light to remove material at the point of impingement on a workpiece. Laser beam machining is a thermoelectric process, and material removal is largely accomplished by evaporation, although some material is removed in the liquid state at high velocity. Since the metal removal rate is very small, this process is used for such jobs as drilling microscopic holes in carbides or diamond wire drawing dies and for removing metal in the balancing of high-speed rotating machinery.
27. *Plasma arc machining* is the process of material removal or shaping of a workpiece by a high-velocity jet of high-temperature ionized gas. A gas (nitrogen, argon, or hydrogen) is passed through an electric arc causing it to become ionized and raising its temperatures in excess of 16,000°C (30,000°F). The relatively narrow plasma jet melts and displaces the workpiece material in its path.
28. *Ultrasonic machining* is a mechanical process designed to remove material by the use of abrasive grains that are carried in a liquid between the tool and the work and that bombard the work surface at high velocity. This action gradually chips away minute particles of material in a pattern controlled by the tool shape and contour. Operations that can be performed include drilling, tapping, coining, and the making of openings in all types of dies.
29. *Sintering* is the process of forming a mechanical part from a powdered metal by fusing the particles together under pressure and heat. The temperature is maintained below the melting point of the basis metal.
30. *Laminating* is the process of adhesive bonding of layers of metal, plastic, or wood to form a part.

31. *Hot dip coating* is the process of coating a metallic workpiece with another metal by immersion in a molten bath to provide a protective film. Galvanizing (hot dip zinc) is the most common hot dip coating.
32. *Sputtering* is the process of covering a metallic or nonmetallic workpiece with thin films of metal. The surface to be coated is bombarded with positive ions in a gas discharge tube, which is evacuated to a low pressure.
33. *Vapor plating* is the process of decomposition of a metal or compound upon a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting point of either the deposit or the basis material.
34. *Thermal infusion* is the process of applying fused zinc, cadmium, or other metal coatings to a ferrous workpiece by imbuing the surface of the workpiece with metal powder or dust in the presence of heat.
35. *Salt bath descaling* is the process of removing surface oxides or scale from a workpiece by immersion of the workpiece in a molten salt bath or a hot salt solution. The workpiece is immersed in the molten salt [temperatures range from 400°C to 540°C (750–1000°F)], quenched with water, and then dipped in acid. Oxidizing, reducing, and electrolytic baths are available, and the particular type needed depends on the oxide to be removed.
36. *Solvent degreasing* is a process for removing oils and grease from the surfaces of a workpiece by the use of organic solvents, such as aliphatic petroleum, aromatics, oxygenated hydrocarbons, halogenated hydrocarbons, and combinations of these classes of solvents. However, ultrasonic vibration is sometimes used with liquid solvent to decrease the required immersion time with complex shapes. Solvent cleaning is often used as a precleaning operation such as prior to the alkaline cleaning that precedes plating, as a final cleaning of precision parts, or as a surface preparation for some painting operations.
37. *Paint stripping* is the process of removing an organic coating from a workpiece. The stripping of such coatings is usually performed with caustic, acid, solvent, or molten salt.
38. *Painting* is the process of applying an organic coating to a workpiece. This process includes the application of coatings such as paint, varnish, lacquer, shellac, and plastics by methods such as spraying, dipping, brushing, roll coating, lithographing, and wiping. Other processes included under this unit operation are printing, silk screening, and stenciling.
39. *Electrostatic painting* is the application of electrostatically charged paint particles to an oppositely charged workpiece followed by thermal fusing of the paint particles to form a cohesive paint film. Both waterborne and solvent-borne coatings can be sprayed electrostatically.
40. *Electropainting* is the process of coating a workpiece by either making it anodic or cathodic in a bath that is generally an aqueous emulsion of the coating material. The electrodeposition bath contains stabilized resin, dispersed pigment, surfactants, and sometimes organic solvents in water.
41. *Vacuum metalizing* is the process of coating a workpiece with metal by flash heating metal vapor in a high-vacuum chamber containing the workpiece. The vapor condenses on all exposed surfaces.
42. *Assembly* is the fitting together of previously manufactured parts or components into a complete machine, unit of a machine, or structure.
43. *Calibration* is the application of thermal, electrical, or mechanical energy to set or establish reference points for a component or complete assembly.
44. *Testing* is the application of thermal, electrical, or mechanical energy to determine the suitability or functionality of a component or complete assembly.

Table 9.1 presents an industry summary for the metal finishing industry including the total number of subcategories, number of subcategories studied, and the type and number of dischargers.

TABLE 9.1
Metal Finishing Industry Summary

Item	Number
Total subcategories	51
Subcategories studied	28
Discharges in industry	98,418
Direct	20,632
Indirect	77,586
Zero discharge	200

Source: U.S. EPA, *Treatability Manual, Volume II Industrial Descriptions*, Report EPA-600/2-82-001b, U.S. Environmental Protection Agency, Washington, DC, September 1981.

9.1.2 SUBCATEGORY DESCRIPTIONS

The primary purpose of subcategorization is to establish groupings within the metal finishing industry such that each subcategory has a uniform set of quantifiable effluent limitations. Several bases were considered in establishing subcategories within the metal finishing industry. These included the following:

1. Raw waste characteristics
2. Manufacturing processes
3. Raw materials
4. Product type or production volume
5. Size and age of facility
6. Number of employees
7. Water usage
8. Individual plant characteristics.

After these subcategorization bases were evaluated, raw waste characterization was selected as the basis for subcategorization. The raw waste characterization is divided into two components, inorganic and organic wastes. These components are further subdivided into the specific types of wastes that occur within the components. Inorganics include common metals, precious metals, complexed metals, hexavalent chromium, and cyanide. Organics include oils and solvents.

Table 9.2 lists the unit operations associated with each of the seven industry subcategories (raw waste characteristics). Common metals are found in the raw waste of all 44 unit operations. Precious metals are found in only seven unit operations; complexed metals are found in three unit operations; hexavalent chromium is found in seven unit operations; and cyanide is found in eight unit operations. Within the organics, oils are found in 22 unit operations and solvents are found in nine unit operations. A unit operation will often be found in more than one subcategory.

9.2 WASTEWATER CHARACTERIZATION

In this section, the uses of water in the metal finishing industry are presented and the waste constituents are identified and quantified.

Water is used for rinsing workpieces, washing away spills, air scrubbing, process fluid replenishment, cooling and lubrication, washing of equipment and workpieces, quenching, spray booths, and assembly and testing. Unit operations with significant water usage include electroplating, electroless

TABLE 9.2
Subcharacterization of Unit Operations

Industry Subcategory (Raw Waste Characteristics)	Unit Operations	
Common metals		
All 44 unit operations		
Precious metals		
Electroplating	Etching	Burnishing
Electroless plating	Cleaning	
Conversion coating	Polishing	
Complexed metals		
Electroless plating		
Etching		
Cleaning		
Hexavalent chromium		
Electroplating	Etching	Electrostatic painting
Anodizing	Cleaning	
Conversion coating	Tumbling	
Cyanide		
Electroplating	Cleaning	Heat treating
Electroless plating	Tumbling	Electrochemical machining
Conversion coating	Burnishing	
Oils		
Cleaning	Pressure deformation	Solvent degreasing
Machining	Shearing	Paint stripping
Grinding	Heat treating	Painting
Polishing	Other abrasive jet machining	Assembly
Tumbling	Electrostatic painting	Calibration
Burnishing	Electrical discharge machining	Testing
Impact deformation	Electrochemical machining	
Solvents		
Cleaning	Solvent degreasing	Electrostatic painting
Heat treating	Paint stripping	Electropainting
Electrochemical machining	Painting	Assembly

Source: U.S. EPA, *Treatability Manual, Volume II Industrial Descriptions*, Report EPA-600/2-82-001b, U.S. Environmental Protection Agency, Washington, DC, September 1981.

plating, anodizing, conversion coating, etching, cleaning, machining, grinding, tumbling, heat treating, welding, sand blasting, salt bath descaling, paint stripping, painting, electrostatic painting, electroplating, and testing. Unit operations with zero discharge are electron beam machining, laser beam machining, plasma arc machining, ultrasonic machining, sintering, sputtering, vapor plating, thermal infusion, vacuum metalizing, and calibration.[7]

Table 9.3 displays the ranges of flows in the metal finishing industry. Approximately 81% of the plants have flows between 1.9 and 57 m^3/h (67–2000 ft^3/h). For those plants with common metals waste streams, the average contribution of these streams to the total wastewater flow within a

TABLE 9.3
Wastewater Flow Characterization of the Metal Finishing Industry

Flow of Plants (m^3/h)	Percentage of Plants Represented by this Flow
<0.38	2.8
0.38–1.9	5.0
1.9–3.8	13
3.8–9.5	17
9.5–19	20.7
19–28	10.7
28–38	10.7
38–57	9.1
57–95	5.0
95–190	3.8
190–380	0.7
>380	1.5

Source: U.S. EPA, *Treatability Manual, Volume II Industrial Descriptions*, Report EPA-600/2-82-001b, U.S. Environmental Protection Agency, Washington, DC, September 1981.

particular plant is 62.4% (range of 0.007–100%). All of the plants have a waste stream requiring common metals treatment.

Of the plants, 4.8% have production processes, which generate precious metals wastewater. The average precious metals wastewater flow is 21.5% of total plant flow.

The average contribution of the complexed metal streams to total plant flow is 22.2%. The percentage was computed from data for plants whose complexed metal streams could be segregated from the total stream.

Of the plants, 42.5% have segregated hexavalent chromium waste streams. The average flow contribution of these waste streams to the total wastewater stream is 28.7%. At those plants with cyanide wastes, the average contribution of the cyanide-bearing stream to the total wastewater generated is 28.8% (range of 0.1–100%). Of the plants, 31.2% have segregated cyanide-bearing wastes.

Segregated oily wastewater is defined as oil waste collected from machine sumps and process tanks. The water is segregated from other wastewaters until it has been treated by an oily waste removal system. Of the plants, 12.4% are known to segregate their oily wastes. The average contribution of these wastes to the total plant wastewater flow is 6.6% (range of approximately 0.0–55.4%).

In order to characterize the waste streams in each subcategory, raw waste data were collected. Discrete samples of raw wastes were taken for each subcategory and analyses on the samples were performed. The results of these analyses are presented for each subcategory in Tables 9.4 through 9.9. In each table, data on the number of detections of a pollutant, the number of samples analyzed, the median concentration, the range in concentrations, and the mean concentration of those samples detected are presented. The minimum detection limit for the toxic pollutants in the sampling program was 1 μg/L and any value below this is listed in Tables 9.4 through 9.9 as BDL, below detection limit.

9.2.1 COMMON METALS SUBCATEGORY

Pollutant parameters found in the common metals subcategory raw waste stream from sampled plants are shown in Table 9.4. The major constituents shown are parameters, which originate in process solutions (such as from plating or galvanizing) and enter wastewaters by drag-out to rinses. These metals appear in waste streams in widely varying concentrations.

TABLE 9.4
Concentrations of Pollutants Found in the Common Metals Subcategory of Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Toxic Pollutants (Concentrations Shown in μg/L)					
Metals and inorganics					
Antimony	106	22	1–430	6	34
Arsenic	105	31	2–64	10	16
Beryllium	27	23	1–44	5	9
Cadmium	108	60	BDL–19,000	8	1000
Chromium	105	89	3–35,000	180	16,000
Copper	108	105	3–500,000	180	16,000
Lead	108	73	3–42,000	120	1400
Mercury	99	32	BDL–400	10	18
Nickel	108	88	4–420,000	200	24,000
Selenium	26	21	1–60	5	9
Thallium	26	21	1–62	3	10
Zinc	108	107	9–330,000	290	19,000
Phthalates					
Bis(2-ethylhexyl)phthalate	93	91	BDL–1900	6	57
Butyl benzyl phthalate	65	38	BDL–10	BDL	1
Di-*n*-butyl phthalate	89	79	BDL–10	BDL	BDL
Di-*n*-octyl phthalate	65	25	BDL–10	BDL	BDL
Diethyl phthalate	83	66	BDL–240	5	31
Dimethyl phthalate	65	7	BDL–10	BDL	2
Nitrogen compounds					
3,3-Dichlorobenzidene	4	1	BDL		
N-nitroso-di-*n*-propylamine	4	1	570		
Phenols					
2-Nitrophenol	4	1	24		
Phenol	23	15	BDL–1000	45	240
Aromatics					
Benzene	6	4	BDL–16	7	8
Ethylbenzene	37	9	BDL–1200	250	340
Toluene	39	17	2–690	77	140
Polycyclic aromatic hydrocarbons					
Fluoranthene	4	1	74		
Isophorone	4	4	13–310	180	170
Napthalene	89	61	BDL–2000	1	83
Anthracene	82	56	BDL–30	1	2
Fluorene	2	2	BDL–160		80
Phenanthrene	71	55	BDL–30	1	2
Pyrene	4	1	190		
Halogenated aliphatics					
Carbon tetrachloride	57	37	BDL–1	BDL	BDL
1,2-Dichloroethane	4	1	3		
1,1,1-Trichloroethane	57	43	BDL–550	BDL	18
1,1,2-Trichloroethane	57	21	BDL–3	BDL	BDL

continued

TABLE 9.4 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Toxic Pollutants (Concentrations Shown in μg/L)					
Chloroform	65	48	BDL–140	BDL	5
1,1-Dichloroethylene	58	4	BDL–110	BDL	20
1,2-*trans*-dichloroethylene	5	3	1–5	2	3
1,2-Dichloropropylene	4	1	2		
Methylene chloride	80	27	BDL–570	BDL	53
Methyl chloride	74	3	BDL–60	3	21
Methyl bromide	4	1	2		
Dichlorobromomethane	5	2	3–8		6
Chlorodibromomethane	4	1	8		
Tetrachloroethylene	59	23	BDL–66	BDL	6
Trichloroethylene	77	49	BDL–480	BDL	22
Pesticides and metabolites					
Dieldrin	4	1	BDL		
Endosulfan	4	1	9		
Endrin aldehyde	4	1	BDL		
BHC	4	1	BDL		
BHC	4	1	4		
BHC	4	1	BDL		
Classical Pollutants (Concentrations Shown in mg/L)					
TSS	107	104	0.56–11,000	63	520
Aluminum	8	6	0.03–200	0.29	62
Barium	4	3	0.027–0.071	0.03	0.043
Calcium	3	3	25–76	52	51
Cobalt	4	4	0.009–0.023	0.02	0.017
Fluorides	7	3	0.021–36	1.1	5.3
Iron	85	76	0.035–490	1.9	28
Magnesium	88	87	5.6–31	14	16
Manganese	4	4	0.059–0.5	0.085	0.22
Molybdenum	7	7	0.031–0.3	0.27	0.2
Phosphorus	4	3	0.007–77	3	7.9
Sodium	4	3	17–310	140	160
Tin	4	4	0.002–15	0.86	3.7
Titanium	5	2	0.006–0.08	0.03	0.039
Vanadium	7	3	0.01–0.22	0.036	0.087
Yttrium	4	3	0.002–0.02	0.018	0.013

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*, Report EPA-440/1-80/091, U.S. Environmental Protection Agency, Washington, DC, 1980.

9.2.2 PRECIOUS METALS SUBCATEGORY

Table 9.5 shows the concentrations of pollutant parameters found in the precious metals subcategory raw waste streams. The major constituents are silver and gold, which are much more commonly used in metal finishing industry operations than palladium and rhodium. Because of their high cost, precious metals are of special interest to metal finishers.

TABLE 9.5
Concentrations of Pollutants Found in the Precious Metals Subcategory of Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
			Classical Pollutants (Concentrations Shown in mg/L)		
Silver	15	12	0.033–600	0.38	86
Gold	15	9	0.56–43	0.86	15
Palladium	13	3	0.09–0.12	0.09	0.10
Rhodium	12	1	0.22		

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*, Report EPA-440/1-80/091, U.S. Environmental Protection Agency, Washington, DC, 1980.

9.2.3 COMPLEXED METALS SUBCATEGORY

The concentrations of metals found in complexed metals subcategory raw waste streams are presented in Table 9.6. Complexed metals may occur in a number of unit operations but come primarily from electroless and immersion plating. The most commonly used metals in these operations are copper, nickel, and tin. Wastewaters containing complexing agents must be segregated and treated independently of other wastes in order to prevent further complexing of free metals in the other streams.

TABLE 9.6
Concentrations of Pollutants Found in the Complexed Metals Subcategory of Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
			Toxic Pollutants (Concentrations Shown in μg/L)		
Cadmium	31	9	1–3600	67	850
Copper	31	28	10–63,000	6700	11,000
Lead	31	10	2–3600	420	1200
Nickel	31	25	26–290,000	3200	28,000
Zinc	31	31	23–18,000	210	3000
			Classical Pollutants (Concentrations Shown in μg/L)		
Aluminum	1	1	0.1		
Calcium	1	1	17		
Iron	31	31	0.038–99	0.74	9.9
Magnesium	1	1	2		
Manganese	1	1	0.1		
Phosphorus	31	31	0.023–100	8.2	23
Sodium	1	1	110		
Tin	31	10	0.013–6	0.68	1.6

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*, Report EPA-440/1-80/091, U.S. Environmental Protection Agency, Washington, DC, 1980.

9.2.4 CYANIDE SUBCATEGORY

Cyanide has been used extensively in the surface finishing industry for many years; however, it is a hazardous substance that must be handled with caution. The use of cyanide in plating and stripping solutions stems from its ability to weakly complex many metals typically used in plating. Metal deposits produced from cyanide plating solutions are finer grained than those plated from an acidic solution. In addition, cyanide-based plating solutions tend to be more tolerant of impurities than other solutions, offering preferred finishes over a wide range of conditions.

1. Cyanide-based strippers are used to selectively remove plated deposits from the base metal without attacking the substrate.
2. Cyanide-based electrolytic alkaline descalers are used to remove heavy scale from steel.
3. Cyanide-based dips are often used before plating or after stripping processes to remove metallic smuts on the surface of parts.

Cyanide-based metal finishing solutions usually operate at basic pH levels to avoid decomposition of the complexed cyanide and the formation of highly toxic hydrogen cyanide gas.

The cyanide concentrations found in cyanide subcategory raw waste streams are shown in Table 9.7. The levels of cyanide range from 0.045 to 500 μg/L. Streams with high cyanide concentrations normally originate in electroplating and heat treating processes. Cyanide-bearing waste streams should be segregated and treated before being combined with other raw waste streams.

9.2.5 HEXAVALENT CHROMIUM SUBCATEGORY

Concentrations of hexavalent chromium from metal finishing raw wastes are shown in Table 9.8. Hexavalent chromium enters wastewater as a result of many unit operations and can be very concentrated. Because of its high toxicity, it requires separate treatment so that it can be efficiently removed from wastewater.

9.2.6 OILS SUBCATEGORY

Pollutant parameters and their concentrations found in the oily waste subcategory streams are shown in Table 9.9. The oily waste subcategory for the metal finishing industry is characterized by both concentrated and dilute oily waste streams that consist of a mixture of free oils, emulsified oils, greases, and other assorted organics. Applicable treatment of oily waste streams is dependent on the concentration levels of the wastes, but oily wastes normally receive specific treatment for oil removal prior to solids removal waste treatment.

TABLE 9.7
Concentrations of Pollutants Found in the Cyanide Subcategory of Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
		Toxic Pollutants (Concentrations Shown in μg/L)			
Cyanide	20	20	45–500,000	45,000	110,000
Cyanide, amenable to chlorination	19	18	5–460,000	4500	86,000

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*, Report EPA-440/1-80/091, U.S. Environmental Protection Agency, Washington, DC, 1980.

TABLE 9.8
Concentrations of Pollutants Found in the Hexavalent Chromium Subcategory of Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
		Toxic Pollutants (Concentrations Shown in μg/L)			
Chromium, hexavalent	49	41	5–13,000,000	20,000	420,000

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*, Report EPA-440/1-80/091, U.S. Environmental Protection Agency, Washington, DC, 1980.

TABLE 9.9
Concentrations of Pollutants Found in the Oils Subcategory of Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detection	Median of Detections	Mean of Detections
		Toxic Pollutants (Concentrations Shown in μg/L)			
Phthalates					
Bis(2-ethylhexyl) phthalate	37	20	2–9300	73	820
Butyl benzyl phthalate	37	9	1–10,000	130	1600
Di-*n*-butyl phthalate	37	19	1–3100	16	270
Di-*n*-octyl phthalate	37	3	4–120	—	62
Diethyl phthalate	37	9	1–1900	40	420
Dimethyl phthalate	37	34	1–1200	1	400
Ethers					
Bis(chloromethyl)ether	37	1	9	—	—
Bis(2-chloroethyl)ether	37	2	4–10	—	7
Bis(2-chloroisopropyl)ether	37	1	4	—	—
Bis(2-chloroethoxy)methane	37	1	3	—	—
Nitrogen compounds					
1,2-Diphenylhydrazine	37	2	5–12	—	8
Phenols					
2,4,6-Trichlorophenol	37	3	10–1000	10	610
Perachlorometacresol	37	8	4–800,000	2300	100,000
2-Chlorophenol	37	2	76–620	—	350
2,4-Dichlorophenol	37	2	10–68	—	39
2,4-Dimethylphenol	37	6	1–31,000	10	5200
2-Nitrophenol	37	3	10–320	35	120
4-Nitrophenol	37	1	10	—	—
2,4-Dinitrophenol	37	3	10–10,000	13	3300
N-nitrosodiphenylamine	37	5	4–900	750	490

continued

TABLE 9.9 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detection	Median of Detections	Mean of Detections
			Toxic Pollutants (Concentrations Shown in μg/L)		
Pentachlorophenol	37	3	10–50,000	5200	18,000
Phenol	27	3	3–6600	440	1700
4,6-Dinitro-*o*-cresol	37	2	10–5700	—	2800
Aromatics					
Benzene	37	18	1–110	8	12
Chlorobenzene	37	2	11–610	—	310
Nitrobenzene	37	2	1–10	—	5
Toluene	37	25	1–37,000	33	1800
Ethylbenzene	37	16	1–5500	12	380
Polynuclear aromatic hydrocarbons					
Acenaphthane	37	2	57–5700	—	2900
2-Chloronaphthalene	37	1	130	—	—
Fluoranthene	37	8	1–55,000	110	8300
Naphthalene	37	10	1–260	100	36
Benzo(*a*)pyrene	37	1	10	—	—
Chrysene	37	3	1–73	2	25
Acenaphthalene	37	3	77–1000	140	410
Anthracene	43	7	3–2000	34	360
Fluorine	37	7	1–760	75	180
Phenanthrene	37	8	2–2000	28	400
Pyrene	37	5	31–150	75	79
Halogenated hydrocarbons					
Carbon tetrachloride	37	5	1–10,000	97	2600
1,2-Dichloroethane	37	6	9–2100	1400	1100
1,1,1-Trichloroethane	37	18	1–1,300,000	260	75,000
1,1-Dichloroethane	37	11	2–1100	600	460
1,1,2-Trichloroethane	37	4	6–1300	10	330
1,1,2,2-Tetrachloroethane	37	2	6–570	—	290
Chloroform	37	19	2–690	10	58
1,1-Dichloroethylene	37	12	2–10,000	200	1500
1,2-*trans*-Dichloroethylene	43	9	8–1700	88	510
Methylene chloride	37	29	5–7600	92	600
Methyl chloride	37	4	1–4700	9	1200
Bromoform	37	1	10	—	—
Dichlorobromomethane	37	2	1–10	—	5
Trichlorofluoromethane	37	2	260–290	—	280
Chlorodibromomethane	37	3	1–10	2	4
Tetrachloroethylene	37	18	1–110,000	10	8900
Trichloroethylene	37	11	1–130,000	110	23,000

continued

TABLE 9.9 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detection	Median of Detections	Mean of Detections
Toxic Pollutants (Concentrations Shown in μg/L)					
Pesticides and metabolites					
Aldrin	37	2	4–11	—	7
Dialdrene	37	1	3	—	—
Chlordane	37	2	1–13	—	7
4,4-DDT	37	2	2–10	—	6
4,4-DDE	37	4	BDL–53	2	14
4,4-DDD	37	3	1–10	4	5
α-Endosulfan	37	2	8–28	—	18
β-Endosulfan	37	2	BDL–6	—	3
Endosulfan sulfate	37	4	1–16	11	10
Endrin	37	2	7–10	—	8
Endrin aldehyde	37	2	10–14	—	12
Heptachlor	37	1	BDL	—	—
Heptachlor epoxide	37	1	BDL	—	—
α-BHC	37	3	4–18	13	12
γ-BHC	37	3	1–9	7	6
δ-BHC	37	2	4–11	—	7
Polychlorinated biphenyls					
Aroclor 1254	37	2	76–1100	—	590
Aroclor 1248	37	2	160–1800	—	580
Classical Pollutants (Concentrations Shown in mg/L)					
Ammonia	37	10	0.46–270	7.9	46
Biochemical oxygen demand (BOD)	37	21	10–17,000	1400	3200
Chemical oxygen demand (COD)	37	16	310–1,500,000	12,000	120,000
Oil and grease	37	37	65–800,000	6100	41,000
Phenols, total	37	34	0.002–49	0.24	2.5
Total dissolved solids (TDS)	37	9	250–4900	1600	2000
Total organic carbon (TOC)	37	37	3–560,000	1600	28,000
Total suspended solids (TSS)	37	35	35–18,000	680	2700

Source: U.S. EPA, *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*, Report EPA-440/1-80/091, U.S. Environmental Protection Agency, Washington, DC, 1980.

The majority of the pollutants listed in Table 9.9 are priority organics that are used either as solvents or as oil additives to extend the useful life of the oils. Organic priority pollutants, such as solvents, should be segregated and disposed of or reclaimed separately. However, when they are present in wastewater streams they are most often at the highest concentration in the oily waste stream because organic pollutants generally have a higher solubility in hydrocarbons than in water. Oily wastes will normally receive treatment for oil removal before being directed to waste treatment for solids removal.

9.2.7 SOLVENT SUBCATEGORY

The solvent subcategory raw wastes are generated in the metal finishing industry by the dumping of spent solvents from degreasing equipment (including sumps, water traps, and stills). These solvents predominately comprise compounds classified by the U.S. Environmental Protection Agency (U.S. EPA) as toxic pollutants. Spent solvents should be segregated, hauled for disposal or reclamation, or reclaimed on-site. Solvents that are mixed with other wastewaters tend to appear in the common metals or the oily wastes stream.

9.3 SOURCE REDUCTION

It is not currently feasible to achieve a zero discharge of chemical pollutants from metal finishing operations. However, substantial reductions in the type and volume of hazardous chemicals wasted from most metal finishing operations are possible.[8] Because end-of-pipe waste detoxification is costly for small- and medium-sized metal finishers, and the cost and liability of residuals disposal have increased for all metal finishers, management and production personnel may be more willing to consider production process modifications to reduce the amount of chemicals lost to waste.

This section provides guidance for reducing waterborne wastes from metal finishing operations in order to avoid or reduce the need for waste detoxification and the subsequent off-site disposal of detoxification residuals. Waste reduction practices may take the form of[5]:

1. Chemical substitution
2. Waste segregation
3. Process modifications to reduce drag-out loss
4. Capture/concentration techniques

9.3.1 CHEMICAL SUBSTITUTION

The incentive for substituting process chemicals containing nonpolluting materials has only been present in recent years with the advent of pollution control regulations. Chemical manufacturers are gradually introducing such substitutes. By eliminating polluting process materials such as hexavalent chromium and cyanide-bearing cleaners, and deoxidizers, the treatments required to detoxify these wastes are also eliminated. It is particularly desirable to eliminate processes employing hexavalent chromium and cyanide, since special equipment is needed to detoxify both.

Substituting nonpolluting cleaners for cyanide cleaners can avoid cyanide treatment entirely. For a 7.6 L/min rinsewater flow, this means a savings of about USD 18,400 in equipment costs and USD 10/kg of cyanide treatment chemical costs. In this case, treatment chemical costs are about four times the cost of the raw sodium cyanide cleaner.

There can be disadvantages in using nonpolluting chemicals. Before making a decision, the following questions should be asked of the chemical supplier[5]:

- Are substitutes available and practical?
- Will substitution solve one problem but create another?
- Will tighter chemical controls be required of the bath?
- Will product quality and/or production rate be affected?
- Will the change involve any cost increases or decreases?

Based on a survey of chemical suppliers and electroplaters who use nonpolluting chemicals, some commonly used chemical substitutes are summarized in Table 9.10.

TABLE 9.10
Chemical Substitutes

Polluting	Substitute	Comments
Fire dip (NaCN)	Muriatic acid with additives	Slower acting than + H_2O_2 traditional fire dip
Heavy copper cyanide plating bath	Copper sulfate	Excellent throwing power with a bright, smooth, rapid finish A copper cyanide strike may still be necessary for steel, zinc, or tin–lead base metals Requires good preplate cleaning Noncyanide process eliminates carbonate buildup in tanks
Chromic acid pickles, deoxidizers, and bright dips	Sulfuric acid and hydrogen perioxide	Nonchrome substitute Nonfuming
Chrome-based antitarnish	Benzotriazole (0.1–1.0% solution in methanol) or water-based proprietaries	Nonchrome substitute Extremely reactive, requires ventilation
Cyanide cleaner	Trisodium-phosphate or ammonia	Noncyanide cleaner Good degreasing when hot and in an ultrasonic bath Highly basic May complex with soluble metals if used as an intermediate rinse between plating baths where metal ion may be dragged into the cleaner and cause wastewater treatment problems
Tin cyanide	Acid tin chloride	Works faster and better

Source: U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

The chemical supplier can also identify any regulated pollutants in the facility's treatment chemicals and offer available substitutes. The federally regulated pollutants are cyanide, chrome, copper, nickel, zinc, lead, cadmium, and silver. Local and/or state authorities may regulate other substances, such as tin, ammonia, and phosphate. The current status of cyanide and noncyanide substitute plating processes is shown in Table 9.11

TABLE 9.11
Cyanide and Noncyanide Plating Processes

Metal	Cyanide	Noncyanide
Brass	Proven	No
Bronze	Proven	No
Cadmium	Proven	Yes
Copper	Proven	Proven
Gold	Proven	Developing
Indium	Proven	Yes
Silver	Proven	Developing
Zinc	Proven	Proven

Source: U.S. EPA, *Managing Cyanide in Metal Finishing*, Capsule Report EPA 625/R-99/009, U.S. Environmental Protection Agency, Cincinnati, OH, December 2000.

9.3.2 WASTE SEGREGATION

After eliminating as many pollutants as possible, the next step is for polluting streams to be segregated from nonpolluting streams. Nonpolluting streams can go directly to the sewer, although pH adjustment may be necessary. The segregation process will likely require some physical relayout and/or repiping of the shop. These potentially nonpolluting rinse streams represent about one-third of all plating process water. Caution must be exercised to make certain that so-called nonpolluting baths contain no dissolved metal. The cost savings in segregating polluting from nonpolluting streams is realized through wastewater treatment equipment and operating costs. The remaining polluting sources, which require some form of control, include all dumped spent solutions, including tumble finishing and burnishing washes, cyanide cleaner rinses, plating rinses, rinses after "bright dips," and aggressive cleaning solutions.

9.3.3 PROCESS MODIFICATIONS TO REDUCE DRAG-OUT LOSS

Plating solution that is wasted by being carried over into the rinsewater as a workpiece emerges from the plating bath is defined as drag-out, and is the largest volume source of chemical pollutant in the electroplating shop. Numerous techniques have been developed to control drag-out; the effectiveness of each method varies as a function of the plating process, operator cooperation, racking, barrel design, transfer dwell time, and plated part configuration.

Wetting agents and longer workpiece withdrawal/drainage times are two techniques that significantly control drag-out. These and other techniques are discussed below.

9.3.3.1 Wetting Agents

Wetting agents lower the surface tension of process baths. To remove plating solution dragged out with the plated part, gravity-induced drainage must overcome the adhesive force between the solution and the metal surface. The drainage time required for racked parts is a function of the surface tension of the solution, part configuration, and orientation. Lowering the surface tension reduces the drainage time and also minimizes the edge effect (the bead of liquid adhering to the part edge); thus there is less drag-out. Plating baths such as nickel and heavy copper cyanide also use wetting agents to maintain grain quality and provide improved coverage. The chemical supplier should be asked if the baths he supplies contain wetting agents and, if not, whether wetting agents can be added. In some baths the use of wetting agents has the potential to reduce drag-out by 50%.

9.3.3.2 Longer Drain Times

With slower withdrawal rates and/or longer drain times, drag-out of process solutions can be reduced by up to 50%. Where high-temperature plating solutions are used, slow withdrawal of the rack may also be necessary to prevent evaporative "freezing," which can actually increase drag-out. In the extreme case, too rapid a withdrawal rate causes "sheeting," where huge volumes of drag-out are lost to waste. Figure 9.1 shows the drainage rates for plain and bent-shaped pieces. Drainage for all shapes is almost complete within 15 s after withdrawal, indicating that this is an optimum drain time for most pieces.

One of the best ways to control drag-out loss from rack plating on hand lines is to provide drain bars over the tank from which the rack can be hung to drain for a brief period. Hanging and removing the racks from the drain bars ensures an adequate drain time. Slightly jostling the racks helps shake off adhering solution.

In barrel plating, the barrel should be rotated for a time just above the plating tank in order to reduce the volume of dragged-out chemical. Holes in the barrels should be as large as possible to improve solution drainage while still containing the pieces. A fog spray directed at the barrel or its

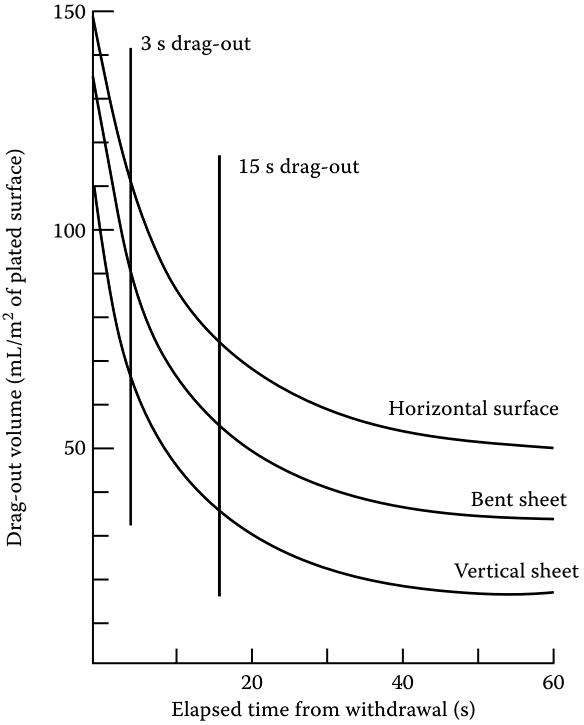

FIGURE 9.1 Typical drag-out drainage rates. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

contents can also help drag-out drainage. Deionized water is recommended to minimize bath contamination.

The combined application of wetting agents and longer withdrawal/drainage times can significantly reduce the amount of drag-out for many cleaning or plating processes. For example, a typical nickel drag-out can be reduced from 1 to 1/4 L/h by these techniques.

9.3.3.3 Other Drag-Out Reduction Techniques

9.3.3.3.1 Rinse Elimination

The rinse between a soak cleaner and an electrocleaner may be eliminated if the two baths are compatible.

9.3.3.3.2 Low-Concentration Plating Solutions

Low-concentration plating solutions reduce the total mass of chemicals being dragged-out. The mass of chemicals removed from a bath is a function of the solution concentration and the volume of solution carried from the bath. Traditionally, the bath concentration is maintained at a midpoint within a range of operating conditions. With the high cost of replacement, treatment, and disposal of dragged-out chemicals, the economics of low-concentration baths are favorable.

As an illustration, a typical nickel plating operation with five nickel tanks has an annual nickel drag-out of about 10,000 L. Assuming the nickel baths are maintained at the midpoint operating concentration, as shown in Table 9.12, the annual cost of chemical replacement, treatment, and disposal is about USD 20,700 in terms of 2007 USD. If the bath is converted to the modified operating condition as shown in the table, the annual cost of chemical replacement, treatment, and disposal are approximately USD 18,700, a savings of about USD 2000/yr. Generally, any percent

TABLE 9.12
Standard Nickel Solution Concentration Limits

Chemical	Concentration Range (g/L)	Midpoint Operating Condition (g/L)	Modified Operating Condition (g/L)
Nickel sulfate			
$NiSO_4$-$6H_2O$	300–375	338	308
as $NiSO_4$	—	200	182
Nickel chloride			
$NiCl_2$-$6H_2O$	60–90	75	64
as $NiCl_2$	—	41	35
Boric acid, H_3BO_3	45–49	47	46

Source: U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

decrease in bath chemical concentration results in the same percent reduction in the mass of chemicals lost in the drag-out. The disadvantage of low-concentration baths may be lowered plating efficiencies, which may require higher current densities and closer process control. The reduction in plating chemical replacement, treatment, and disposal costs could be partially offset by the added labor and power costs associated with the use of the lower concentration baths.

9.3.3.3.3 Clean Plating Baths

Contaminated plating baths, for example, carbonate buildup in cyanide baths, can increase drag-out as much as 50% by increasing the viscosity of the bath. Excessive impurities also make the application of recovery technology difficult, if not impossible.

9.3.3.3.4 Low-Viscosity Conducting Salts

Bath viscosity indexes are available from chemical suppliers. As the bath viscosity increases, drag-out volume also increases.

9.3.3.3.5 High-Temperature Baths

High-temperature baths reduce surface tension and viscosity, thus decreasing drag-out volume. Disadvantages to be considered are more rapid solution decomposition, higher energy consumption, and possible dry-on pattern on the workpiece.

9.3.3.3.6 No Unnecessary Components

Additional bath components (chemicals) tend to increase both viscosity and drag-out.

9.3.3.3.7 Fog Sprays or Air Knives

Fog sprays or air knives may be used over the bath to remove drag-out from workpieces as they are withdrawn. The spray of deionized water or air removes plating solution from the part and returns as much as 75% of the drag-out back to the plating tank. Fog sprays, located just above the plating bath surface, dilute and drain the adhering drag-out solution, thus reducing the concentration and mass of chemicals lost. Fog sprays are best when tank evaporation rates are sufficient to accommodate the added volume of spray water. Air knives, also located just above the plating bath surface, reduce the volume of drag-out by mechanically scouring the adhering liquid from the workpiece. The drag-out concentration remains constant, but the mass of chemicals lost is reduced. Air knives are best when the surface evaporation rates of the bath are too low to allow additional spray water. In some cases, use of supplementary atmospheric evaporators may be justified by economic considerations.

Air knives can be installed for about USD 750–800 per bath if an oil-free, compressed air source is available. Fog sprays can be installed also for about USD 750–800 per bath if a deionized water source is available. The spray should be actuated only when work is in the spraying position. Properly designed spray nozzles distribute the water evenly over the work, control the volume of water used, and avoid snagging workpieces as they are withdrawn from the tank.

9.3.3.3.8 Proper Racking

Every workpiece has at least one racking position in which drag-out will be at a minimum. In general, to minimize drag-out

- Parts should be racked with major surfaces vertically oriented.
- Parts should not be racked directly over one another.
- Parts should be oriented so that the smallest surface area of the piece leaves the bath surface last.

The optimum orientation will provide faster drainage and less drag-out per piece. However, in some cases this may reduce the number of pieces on a rack, or the optimum draining configuration may not be the optimum plating configuration. In addition, the user should maintain rack coatings, replace rack contacts when broken, strip racks before plating buildup becomes excessive, and ensure that all holes on racks are covered or filled.

9.3.3.4 Capture/Concentration Techniques

9.3.3.4.1 Capture/Concentration with Full Reuse of Drag-Out

The pioneer in simple, low-cost methods of reducing waste in the plating shop was Dr. Joseph B. Kushner.[9] In *Water and Waste Control for the Plating Shop* (1972), he describes a "simple waste recovery system" that captures drag-out in a static tank or tanks for return to the plating bath. The drag-out tanks are followed by a rinse tank that flows to the sewer with only trace amounts of polluting salts and is often in compliance with sewer discharge standards. A simplified diagram of this reuse system is shown in Figure 9.2. It is not difficult to automate the direct drag-out recovery process, and commercial units are available.

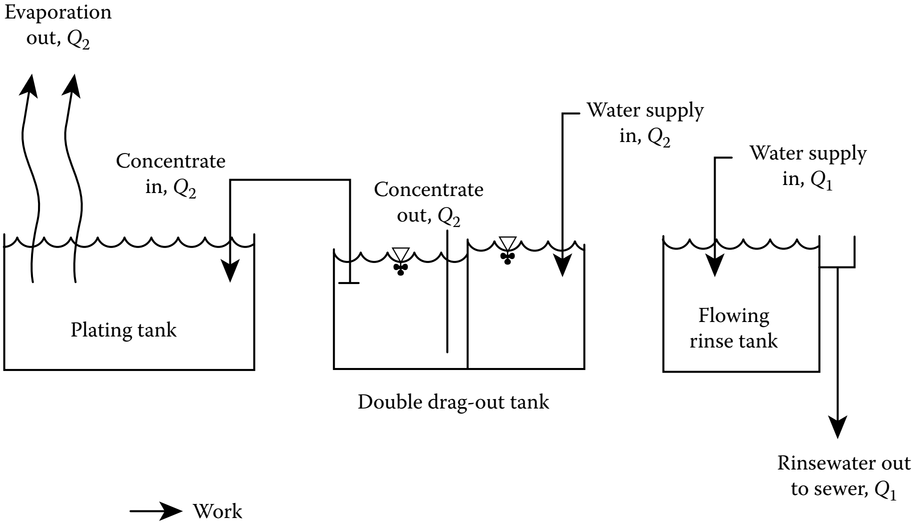

FIGURE 9.2 Kushner method of double drag-out for full reuse. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

The Kushner concept is easily applicable to hot plating baths where the bath evaporation rate equals or exceeds the pour-back rate, Q_2. The drag-out concentration depends on the bath drag-out rate, the number of drag-out tanks, the rinsewater flow rate, Q_2, the plating bath evaporation rate, and drag-out return rate. The number of drag-out tanks must be based on the available space. The higher the number of counterflowed drag-out tanks, the smaller will be the return rate necessary to obtain good rinsing. The Kushner multiple drag-outs are not feasible if there is no room for the required drag-out tanks. If there is little or no evaporation from the bath, supplementary evaporation should be considered. Bath contamination must be minimized by using purified (RO) water for Q_2.

9.3.3.4.2 Capture/Concentration with Partial Reuse of Drag-Out

By adding a trickling water supply and drain, Q_3, to the drag-out tank, the application of Kushner's concept can be extended to other metal finishing processes that may not be amenable to full reuse but can allow partial reuse. Figure 9.3 depicts the partial reuse scheme. The trickle concentrate can also be batch treated in a small volume on-site, recycled at a central facility, or mixed with Q_1, for discharge, if the combined metal content is below sewer discharge standards.

9.3.4 WASTE REDUCTION COSTS AND BENEFITS

The benefits of waste reduction in the metal finishing shop include the following:

1. Reduced chemical cost
2. Reduced water cost
3. Reduced volume of "hazardous" residuals
4. Reduced pretreatment cost.

The benefits of saving valuable chemicals and water and reducing sludge disposal costs can best be illustrated by an example. An electroplating operation discharges 98,400 L/d of wastewater containing 0.91 kg of copper, 1.14 kg of nickel, and 0.91 kg of cyanide. The shop can reduce its

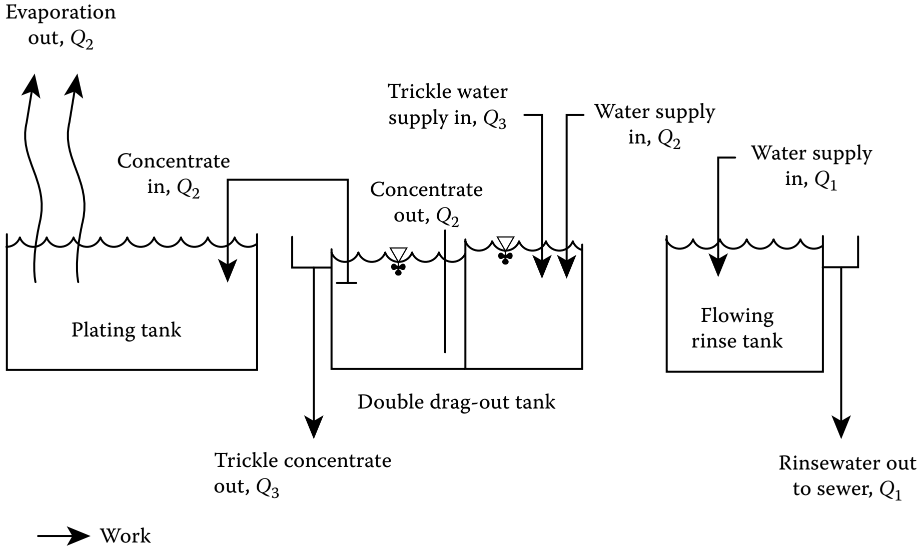

FIGURE 9.3 Modified method of double drag-out for partial reuse. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

TABLE 9.13
Chemical Costs of Treatment and Disposal in 2007 USD

	Chemical Cost (2007 USD/kg)[a]	
Pollutant	**Treatment**[b]	**Disposal**[c]
Nickel	2.73	6.70
Copper	2.73	6.70
Cyanide	17.63	NA

Source: U.S. EPA, Meeting Hazardous Waste Requirements for Metal Finishers, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

[a] Costs were converted from 1979 USD to 2007 USD using U.S. ACE Yearly Average Cost Index for Utilities.[10]

[b] Cost of NaOH @ USD1.00/kg and NaOCL @ USD2.35/kg.

[c] Cost of disposal @ USD1.84 /kg of sludge (USD400/drum) @ 30% solids content.

generation of cyanide and copper waste by about 50% by eliminating cyanide cleaners and utilizing pour-back of copper cyanide solution; generation of nickel waste can be reduced 90% by pour-back of the nickel solution. Reducing wasted salts also allows a reduced rinsewater flow rate, thus saving water and sewer use fees. The chemical costs of treatment are given in Table 9.13 and the annual replacement costs of chemicals are given in Figure 9.4. Calculations of the annual dollar savings are shown in Table 9.14. All costs have been converted into 2007 USD using U.S. ACE Yearly Average Cost Index for Utilities.[10]

9.4 POLLUTANT REMOVABILTY

This section reviews the technologies currently available and used to remove or recover pollutants from the wastewater generated in the metal finishing industry.[5–7,11] Treatment options are presented

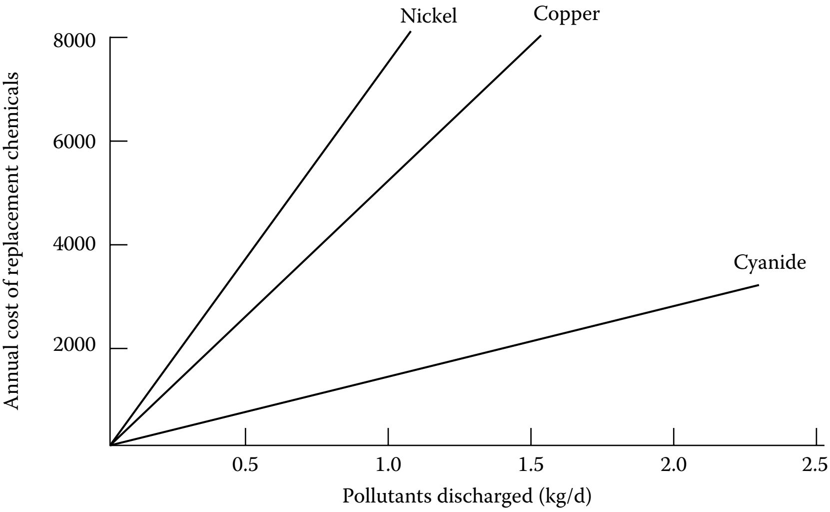

FIGURE 9.4 Annual replacement cost of chemicals in 2007 USD. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

TABLE 9.14
Illustration of Annual Cost Savings for Waste Reduction

Item	Cost Saving[a] (2007 USD)
Process chemical savings[b]	
Copper	2425
Cyanide	485
Nickel	7760
Treatment chemical saving[c]	
Copper	310
Cyanide	2000
Nickel	700
Reduced treatment sludge disposal[c]	
Copper	760
Cyanide	0
Nickel	1700
Water and sewer use fee reduction[d]	4360
Total annual savings	20,500

Source: U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

[a] Costs were converted from 1979 USD to 2007 USD using U.S. ACE Yearly average Cost Index for Utilities.[10]

[b] From Figure 9.4.

[c] From Table 9.12 and Figure 9.4.

[d] USD 0.77/m^3.

for each subcategory within the metal finishing industry. Table 9.15 lists the treatment techniques available for treating wastes from each subcategory.

9.4.1 COMMON METALS

The treatment methods used to treat wastes within the common metals subcategory fall into two groupings:

1. Recovery techniques
2. Solids removal techniques.

Recovery techniques are treatment methods used for the purpose of recovering or regenerating process constituents, which would otherwise be discarded. Included in this group are[5–7]

1. Evaporation
2. Ion exchange
3. Electrolytic recovery
4. Electrodialysis
5. Reverse osmosis.

Solids removal techniques are employed to remove metals and other pollutants from process wastewaters to make these waters suitable for reuse or discharge. These methods include[5–7]

1. Hydroxide and sulfide precipitation
2. Sedimentation

TABLE 9.15
Treatment Methods in Current Use or Available for Use in the Metal Finishing Industry

Subcategory/Technology	Number of Plants
Common metals	
Hydroxide followed by sedimentation	103
Hydroxide followed by sedimentation and filtration	30
Evaporation (metal recovery, bath concentrates, rinse waters)	41
Ion exchange	63
Electrolytic recovery	11
Electrodialysis	3
Reverse osmosis	8
Post-adsorption	0
Insoluble starch xanthate	2
Sulfide precipitation	3
Flotation	29
Membrane flotation	7
Precious metals	
Evaporation	1
Ion exchange	NR
Electrolytic recovery	NR
Complexed metals	
High-pH precipitation with sedimentation	NR
High-pH precipitation with sedimentation	NR
Hexavalent chromium	
Chemical chrome reduction	343
Electrochemical chromium reduction	2
Electrochemical chromium regeneration	0
Advanced electrodialysis	NR
Evaporation	1
Ion exchange	1
Cyanide	
Oxidation by chlorine	201
Oxidation by ozone	2
Oxidation by ozone with UV radiation	NR
Oxidation by hydrogen peroxide	3
Electrochemical cyanide oxidation	4
Chemical precipitation	3
Reverse osmosis	NR
Evaporation	NR
Oils (segregated)	
Emulsion breaking	28
Skimming	94
Emulsion breaking and skimming	NR
Ultrafiltration	20
Reverse osmosis	3
Carbon adsorption	10
Coalescing	3
Flotation	29

continued

TABLE 9.15 (continued)

Subcategory/Technology	Number of Plants
Centrifugation	5
Integrated adsorption	0
Resin adsorption	0
Ozonation	0
Chemical oxidation	0
Aerobic decomposition	14
Thermal emulsion breaking	0
Solvent waste	
Segregation	NR
Contract handling	NR
Sludges	
Gravity thickening	78
Pressure filtration	66
Vacuum filtration	68
Centrifugation	55
Sludge bed drying	77
In-process control	
Flow reduction	NR

Source: U.S. EPA, *Treatability Manual, Volume II, Industrial Descriptions*, Report EPA-600/2-82-001b, U.S. Environmental Protection Agency, Washington, DC, September 1981.

Note: NR, not reported.

3. Diatomaceous earth filtration
4. Membrane filtration
5. Granular bed filtration
6. Peat adsorption
7. Insoluble starch xanthate treatment
8. Flotation.

Three treatment options are used in treating common metals wastes:

- *Option 1* system consists of hydroxide precipitation[12] followed by sedimentation.[13] This system accomplishes the end-of-pipe metals removal from all common metals-bearing wastewater streams that are present at a facility. The recovery of precious metals, the reduction of hexavalent chromium, the removal of oily wastes, and the destruction of cyanide must be accomplished prior to common metals removal.
- *Option 2* system is identical to the Option 1 treatment system with the addition of filtration devices[14] after the primary solids removal devices. The purpose of these filtration units is to remove suspended solids such as metal hydroxides that do not settle out in the clarifiers. The filters also act as a safeguard against pollutant discharge should an upset occur in the sedimentation device. Filtration techniques applicable to Option 2 systems are diatomaceous earth and granular bed filtration.[15,16]
- *Option 3* treatment system for common metal wastes consists of the Option 2 end-of-pipe treatment system plus the addition of in-plant controls for lead and cadmium. In-plant controls would include evaporative recovery, ion exchange, and recovery rinses.[16]

In addition to these three treatments, there are several alternative treatment technologies applicable to the treatment of common metals wastes. These technologies include electrolytic recovery, electrodialysis, reverse osmosis, peat adsorption, insoluble starch xanthate treatment, sulfide precipitation, flotation, and membrane filtration.[15,16]

9.4.2 PRECIOUS METALS

Precious metal wastes can be treated using the same treatment alternatives as those described for treatment of common metal wastes. However, due to the intrinsic value of precious metals, every effort should be made to recover them. The treatment alternatives recommended for precious metal wastes are the recovery techniques—evaporation, ion exchange, and electrolytic recovery.

9.4.3 COMPLEXED METAL WASTES

Complexed metal wastes within the metal finishing industry are a product of electroless plating, immersion plating, etching, and printed circuit board manufacture. The metals in these waste streams are tied up or complexed by particular complexing agents whose function is to prevent metals from coming out of solution. This counteracts the technique employed by most conventional solids removal methods. Therefore, segregated treatment of these wastes is necessary. The treatment method well suited to treating complexed metal wastes is high-pH precipitation. An alternative method is membrane filtration[17] that is primarily used in place of sedimentation for solids removal.

9.4.4 HEXAVALENT CHROMIUM

Hexavalent chromium-bearing wastewaters are produced in the metal finishing industry in chromium electroplating, in chromate conversion coatings, in etching with chromic acid, and in metal finishing operations carried out on chromium as a basis material.

The selected treatment option involves the reduction of hexavalent chromium to trivalent chromium either chemically or electrochemically. The reduced chromium can then be removed using a conventional precipitation–solids removal system. Alternative hexavalent chromium treatment techniques include chromium regeneration, electrodialysis, evaporation, and ion exchange.[16]

9.4.5 CYANIDE

Cyanides are introduced as metal salts for plating and conversion coating or as active components in plating and cleaning baths. Cyanide is generally destroyed by oxidation. Chlorine, in either elemental or hypochlorate form, is the primary oxidation agent used in industrial waste treatment to destroy cyanide. Alternative treatment techniques for the destruction of cyanide include oxidation by ozone, ozone with ultraviolet (UV) radiation (oxyphotolysis), hydrogen peroxide, and electrolytic oxidation.[18] Treatment techniques, which remove cyanide but do not destroy it, include chemical precipitation, reverse osmosis, and evaporation.[16,18]

9.4.6 OILS

Oily wastes and toxic organics that combine with the oils during manufacturing include process coolants and lubricants, wastes from cleaning operations, wastes from painting processes, and machinery lubricants. Oily wastes are generally of three types: free oils, emulsified or water-soluble oils, and greases. Oil removal techniques commonly employed in the metal finishing industry include skimming, coalescing, emulsion breaking, flotation, centrifugation, ultrafiltration, reverse osmosis, carbon adsorption, and aerobic decomposition.[18–20]

Because emulsified oils and processes that emulsify oils are used extensively in the metal finishing industry, the exclusive occurrence of free oils is nearly nonexistent.

Treatment of oily wastes can be carried out most efficiently if oils are segregated from other wastes and treated separately. Segregated oily wastes originate in the manufacturing areas and are collected in holding tanks and sumps. Systems for treating segregated oily wastes consist of separation of oily wastes from the water. If oily wastes are emulsified, techniques such as emulsion breaking or dissolved air flotation (DAF)[21] with the addition of chemicals are necessary to remove oil. Once the oil–water emulsion is broken, the oily waste is physically separated from the water by decantation or skimming. After the oil–water separation has been carried out, the water is sent to the precipitation/sedimentation unit used for metals removal. There are three options for oily waste removal:

- *Option 1* system incorporates the emulsion breaking process followed by surface skimming (gravity separation is adequate if only free oils are present).
- *Option 2* system consists of the Option 1 system followed by ultrafiltration.
- *Option 3* treatment system consists of the Option 2 system with the addition of either carbon adsorption or reverse osmosis.

In addition to these three treatment options, several alternative technologies are applicable to the treatment of oily wastewater. These include coalescing, flotation, centrifugation, integrated adsorption, resin adsorption, ozonation, chemical oxidation, aerobic decomposition, and thermal emulsion breaking.[18–20]

9.4.7 Solvents

Spent degreasing solvents should be segregated from other process fluids to maximize the value of the solvents, to preclude contamination of other segregated wastes, and to prevent the discharge of priority pollutants to any wastewaters. This segregation may be accomplished by providing and identifying the necessary storage containers, establishing clear disposal procedures, training personnel in the use of these techniques, and checking periodically to ensure that proper segregation is occurring. Segregated waste solvents are appropriate for on-site solvent recovery or may be contract hauled for disposal or reclamation.

Alkaline cleaning is the most feasible substitute for solvent degreasing. The major advantage of alkaline cleaning over solvent degreasing is the elimination or reduction in the quantity of priority pollutants being discharged. Major disadvantages include high energy consumption and the tendency to dilute oils removed and to discharge these oils as well as the cleaning additive.

9.5 TREATMENT TECHNOLOGIES

9.5.1 Neutralization

One technique used in a number of facilities that utilize molten salt for metal surface treatment prior to pickling is to take advantage of the alkaline values generated in the molten salt bath in treating other wastes generated in the plant. When the bath is determined to be spent, it is in many instances manifested, hauled off-site, and land disposed. One technique is to take the solidified spent molten salt (molten salt is sold at ambient temperatures) and circulate acidic wastes generated in the facility over the material prior to entry into the waste treatment system. This in effect neutralizes the acid wastes and eliminates the requirements of manifesting and land disposal.

9.5.2 Cyanide-Containing Wastes

There are eight methods applicable to the treatment of cyanide wastes for metal finishing[5,22]:

1. Alkaline chlorination
2. Electrolytic decomposition

3. Ozonation
4. UV/Ozonation
5. Hydrogen peroxide
6. Thermal oxidation
7. Acidification and acid hydrolysis
8. Ferrous sulfate precipitation.

Alkaline chlorination is the method most widely applied in the metal finishing industry. A schematic for cyanide reduction via alkaline chlorination is provided in Figure 9.5. This technology is generally applicable to wastes containing less than 1% cyanide, generally present as free cyanide. It is conducted in two stages; the first stage is operated at a pH greater than 10 and the second stage is operated with a pH in the range of 7.5–8. Alkaline chlorination is performed using sodium hypochlorite and chlorine.

Electrolytic decomposition technology was applied to cyanide-containing wastes in the early part of this century. It fell from favor as alkaline chlorination came into use at large-scale facilities. However, as wastes become more concentrated, this technology may find more widespread application in the future. The reason is that it is applicable to wastes containing cyanide in excess of 1%. The basis of this technology is electrolytic decomposition of the cyanide compounds at an elevated temperature (200°F) to yield nitrogen, CO_2, ammonia, and amines (Figure 9.6).

Ozonation treatment can be used to oxidize cyanide, thereby reducing the concentration of cyanide in wastewater. Ozone, with an electrode potential of +1.24 V in alkaline solutions, is one of the most powerful oxidizing agents known. Cyanide oxidation with ozone is a two-step reaction similar to alkaline chlorination.[22] Cyanide is oxidized to cyanate, with ozone reduced to oxygen as per the following equation:

$$CN^- + O_3 \rightarrow CNO^- + O_2. \tag{9.1}$$

$$NaCN + Cl_2 \rightarrow CNCl + NaCl$$

$$CNCl + 2NaOH \rightarrow NaCNO + H_2O + NaCl$$

$$2NaCNO + 3Cl_2 + 4NaOH \rightarrow 2CO_2 + N_2 + 6NaCl + 2H_2O$$

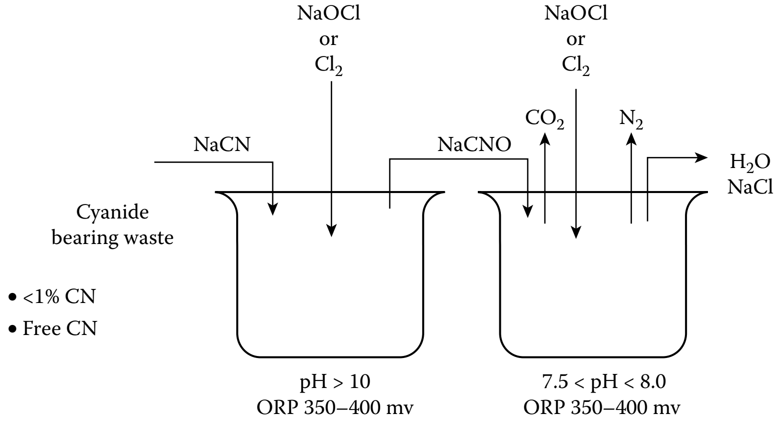

FIGURE 9.5 Cyanide reduction via alkaline chlorination. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

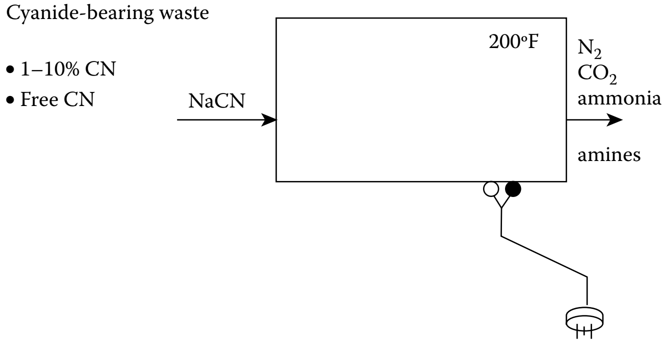

FIGURE 9.6 Cyanide reduction via electrolytic decomposition. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

Then cyanate is hydrolyzed, in the presence of excess ozone, to bicarbonate and nitrogen and oxidized as per the following reaction:

$$2CNO^- + 3O_3 + H_2O \rightarrow N_2 + 2HCO_3^- + 3O_2. \tag{9.2}$$

The reaction time for complete cyanide oxidation is rapid in a reactor system with 10–30 min retention times being typical. The second-stage reaction is much slower than the first-stage reaction. The reaction is typically carried out in the pH range of 10–12 where the reaction rate is relatively constant. Temperature does not influence the reaction rate significantly.

One interesting variation on ozonation technology is augmentation with UV radiation. This is a technology that has been applied to wastes in the coke by-product manufacturing industry. A significant development has been made that has resulted in significantly less ozone consumption through the use of UV radiation. UV absorption has the following effects:

- Ozone and cyanide are raised to higher energy status
- Free radicals are formed
- More rapid reaction
- Less ozone is required.

Cyanide reduction with hydrogen peroxide is effective in reducing cyanide. It has been applied on a less frequent basis within this industry, due to the fact that there are high operating costs associated with hydrogen peroxide generation. The reduction of cyanide with peroxide occurs in two steps and yields CO_2 and ammonia:

$$NaCN + H_2O_2 \rightarrow NaCNO + H_2O, \tag{9.3}$$

$$NaCNO + 2H_2O \rightarrow CO_2 + NH_3 + NaOH. \tag{9.4}$$

Thermal oxidation is another alternative for destroying cyanide. Thermal destruction of cyanide can be accomplished through either high-temperature hydrolysis or combustion. At temperatures between 140°C and 200°C and a pH of 8, cyanide hydrolyzes quite rapidly to produce formate and ammonia.[23] Pressures up to 100 bar are required, but the process can effectively treat waste streams over a wide concentration range and is applicable to both rinsewater and concentrated solutions[22]:

$$CN^- + 2H_2O \rightarrow HCOO^- + NH_3. \tag{9.5}$$

In the presence of nitrates, formate and ammonia can be destroyed in another reactor at 150°C, according to the following equations:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O, \tag{9.6}$$

$$3HCOOH + 2NO_2^- + 2H^+ \rightarrow 3CO_2 + 4H_2O + N_2. \tag{9.7}$$

Direct acidification of cyanide waste streams was once a relatively common treatment. Cyanide is acidified in a sealed reactor that is vented to the atmosphere through an air emission control system. Cyanide is converted to gaseous hydrogen cyanide, treated, vented, and dispersed.

Acid hydrolysis of cyanates is still commonly used, following a first-stage cyanide oxidation process. At pH 2 the reaction proceeds rapidly, while at pH 7 cyanate may remain stable for weeks.[24] This treatment process requires specially designed reactors to assure that HCN is properly vented and controlled. The hydrolysis mechanisms are as follows[22]:

In acid medium

$$2HOCN + 3H^+ \rightarrow NH_4{}^+ + CO_2\ (\text{rapid}) + HCN, \tag{9.8}$$

$$2HOCN + H_2O \rightarrow NH_3 + CO_2\ (\text{slow}) + HCN. \tag{9.9}$$

In strongly alkaline medium

$$NCO^- + 2H_2O \rightarrow NH_3 + HCO_3^-\ (\text{very slow}). \tag{9.10}$$

Each of the technologies described above is effective in treating wastes containing free cyanides, that is, cyanides present as CN in solution. There are instances in metal finishing facilities where complex cyanides are present in wastes. The most common are complexes of iron, nickel, and zinc. A technology that has been applied to remove complex cyanides from aqueous wastes is ferrous sulfate precipitation. The technology involves a two-stage operation in which ferrous sulfate is first added at a pH of 9 to complex any trace amounts of free cyanide. In the second stage, the complex cyanides are precipitated through the addition of ferrous sulfate or ferric chloride at a pH in the range of 2–4.[5]

9.5.3 CHROMIUM-CONTAINING WASTES

There are three treatment methods applicable to wastes containing hexavalent chromium. Wastes containing trivalent chromium can be treated using chemical precipitation and sedimentation, which is discussed below. The three methods applicable to treatment of hexavalent chromium are

1. Sulfur dioxide
2. Sodium metabisulfite
3. Ferrous sulfate.

Hexavalent chromium reduction through the use of sulfur dioxide and sodium metabisulfite has found the widest application in the metal finishing industry. It is not truly a treatment step, but a conversion process in which the hexavalent chromium is converted to trivalent chromium. The hexavalent chromium is reduced through the addition of the reductant at a pH in the range of 2.5–3 with a retention time of approximately 30–40 min (Figure 9.7).

Ferrous sulfate has not been as widely applied. However, it is particularly applicable in facilities where ferrous sulfate is produced as part of the process, or is readily available. The basis for this

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2H_2CrO_4 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 5H_2O$$

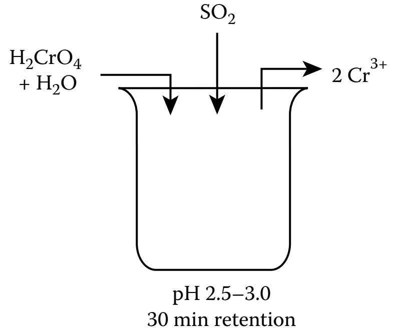

FIGURE 9.7 Hexavalent chromium reduction. (Adapted from U.S. EPA, *Meeting Hazardous Waste Requirements for Metal Finishers*, Report EPA/625/4-87/018, U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

technology is that the hexavalent chromium is reduced to trivalent chromium and the ferrous iron is oxidized to ferric iron.

9.5.4 ARSENIC- AND SELENIUM-CONTAINING WASTES

It may be necessary to segregate waste streams containing elevated concentrations of arsenic and selenium, especially waste streams with concentrations in excess of 1mg/L for these pollutants. Arsenic and selenium form anionic acids in solution (most other metals act as cations) and require special preliminary treatment prior to conventional metals treatment. Lime, a source of calcium ions, is effective in reducing arsenic and selenium concentrations when the initial concentration is below 1mg/L. However, preliminary treatment with sodium sulfide at a low pH (i.e., 1–3) may be required for waste streams with concentrations in excess of 1mg/L.[22] The sulfide reacts with the anionic acids to form insoluble sulfides that are readily separated by means of filtration.

9.5.4.1 Chemical Precipitation and Sedimentation

The most important technology in metals treatment is chemical precipitation and sedimentation. It is accomplished through the addition of a chemical reagent to form metal precipitants, which are then removed as solids in a sedimentation step. The options available to a facility as precipitation reagents are lime $Ca(OH)_2$, caustic NaOH, carbonate $CaCO_3$ and Na_2CO_3, sulfide NaHS and FeS, and sodium borohydride $NaBH_4$. The advantages and disadvantages of these reagents are summarized below[22]:

1. Lime
    - Least expensive precipitation reagent
    - Generates highest sludge volume
    - Sludges generally cannot be sold to smelter/refiners.

2. Caustic
    - More expensive than lime
    - Generates smaller volume of sludge
    - Sludges can be sold to smelter/refiners.

3. Carbonates
    - Applicable for metals where solubility within a pH range is not sufficient to meet treatment standards.

Lime is the least expensive reagent; however, it generates the highest volume of residue. It also generates a residue which cannot be resold to smelters and refiners for reclaiming because of the presence of the calcium ion. Caustic is more expensive than lime; however, it generates a smaller volume of residue. One key advantage of caustic is that the resulting residues can be readily reclaimed. Carbonates are particularly appropriate for metals where solubility within a pH range is not sufficient to meet a given set of treatment standards. The sulfides offer the benefit of achieving effective treatment at lower concentrations due to lower solubilities of the metal sulfides. Sodium borohydride has application where small volumes of sludge that are suitable for reclamation are desired.

It is appropriate to look at reagent use in the context of the current regulatory framework under HSWA. Historically, lime has been the reagent of choice. It was relatively inexpensive and simple to handle. The phrase “lime and settle” refers to the application of lime precipitation and sedimentation technology. In the 1970s, new designs made use of caustic as the precipitation reagent because of the reduction in residue volume realized and the ability for reclamation. In the 1980s, a return to lime and the use of combined reagent techniques have come into use.

One obvious question is why return to lime as a treatment reagent, given that caustic results in a smaller residue volume and a waste that can undergo reclamation? The answer lies in the three points that result from the implementation of the HSWA hierarchy. As source reduction and material reuse and recovery techniques are applied, facilities will be generating

- More concentrated wastes
- Wastes with a varied array of constituents
- Wastes with a greater degree of complexation.

9.5.4.2 Complexation

Complexation is a phenomenon that involves a coordinate bond between a central atom (the metal) and a ligand (the anions). In a coordinate bond, the electron pair is shared between the metal and the ligand. A complex containing one coordinate bond is referred to as a monodentate complex. Multiple coordinate bonds are characteristic of polydentate complexes. Polydentate complexes are also referred to as chelates. An example of a monodentate-forming ligand is ammonia. Examples of chelates are oxylates (bidentates) and EDTA (hexadentates).

The reason for the return to lime is due to the calcium ion present in lime. The calcium ion present in solution through the addition of lime is very effective in competing with the ligand for the metal ion. The sodium ion contributed by caustic is not effective. As such, lime dramatically reduces complexation and is more effective in treating complexed wastes. The term “high-lime treatment” has been applied in cases where excess calcium ions are introduced into solution. This is accomplished through the addition of lime to raise the pH to approximately 11.5 or through the addition of calcium chloride (which has a greater solubility than lime).

The use of combinations of precipitation reagents has been most effective in taking advantage of the attributes of caustic as well as the advantages of lime. As an example, a system may use caustic in a first stage to make a coarse pH adjustment followed by the addition of lime to make a fine adjustment. This achieves an overall reduction in the sludge volume through the use of the caustic and more effective metal removal through the use of lime. Sulfide reagents are used in a similar fashion in combination with caustic or lime to provide additional metal removal, due to the lower solubility of the metal sulfides. Sulfides are also applicable to wastes containing elevated concentrations (i.e., in excess of 2 mg/L) of selenium and arsenic compounds.[22]

9.5.5 OTHER METALS WASTES

There are three techniques applicable to managing solids generated in metal finishing. These are

1. Dewatering
2. Stabilization
3. Incineration.

There are four dewatering techniques that have been applied in metal processing. The most widely applied techniques are vacuum and belt filtration.[25] They have a higher relative capital cost but generally have a lower relative operating cost. Plate and frame filter presses have experienced less widespread application. Belt filters generally have a lower relative capital cost and have higher relative operating costs. The higher operating costs are due to the fact that the units are more labor intensive. Centrifuges[25] have been applied in specific instances, but are more difficult to operate when a widely varying mix of wastes is treated.

Experience has shown that companies are most successful in applying a dewatering technique that they have successfully designed and operated in similar applications within the company. As an example, many companies operate plate and frame filter presses as a part of metal manufacturing operations. The knowledge gained in metal processing had been successfully transferred to treatment of metal finishing wastes.

There are six stabilization techniques currently available; however, only two of them have found widespread application. These are cementation and stabilization through the addition of lime and fly ash.[25,26] There is currently developmental work being undertaken to make use of bitumen, paraffin, and polymeric materials to reduce the degree to which metals can be taken into solution. Encapsulation with inert materials is also under development.

9.6 COSTS

The investment, operation and maintenance,[27,28] and energy costs for the application of control technologies to the wastewaters of the metal finishing industry have been analyzed. These costs were developed to reflect the conventional use of technologies in this industry. The detailed presentation of the cost methodology and cost data is available in a U.S. EPA publication.[6] The available industry-specific cost information is characterized below.

9.6.1 TYPICAL TREATMENT OPTIONS

Many waste treatment options are available.[28–32] Only several unit operation/unit process configurations have been analyzed for the cost of application to the wastewater of this industry. The components included in these configurations are

- *Option 1*: Emulsion breaking and oil separation by skimming, cyanide oxidation, chromium reduction, chemical precipitation and sedimentation, and sludge drying beds.
- *Option 2*: All of Option 1 plus multimedia filtration.
- *Option 3*: All of Option 2 plus ultrafiltration and carbon adsorption for oily waste, zero discharge of any processes using either cadmium or lead by using an evaporative system.

The flow diagram for suggested Option 1 is shown in Figure 9.8. The flow diagram for the other options would be similar.

9.6.2 COSTS

The cost estimates prepared for the treatment technologies commonly used in this industry are described below in a brief fashion. More details of the factors considered in the cost analysis are available in the source.[6]

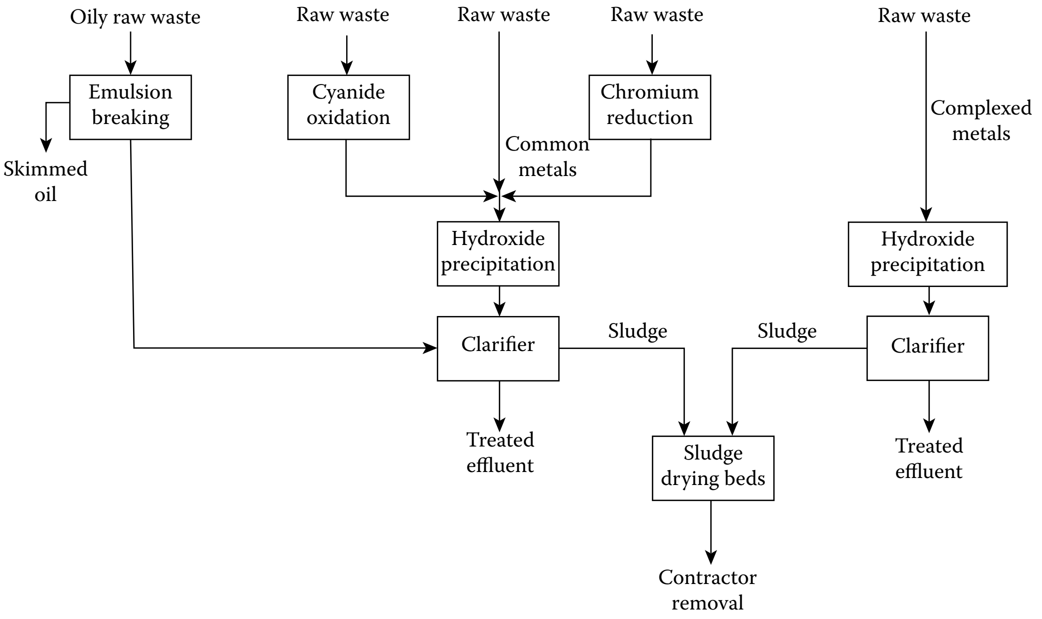

FIGURE 9.8 Metal finishing wastewater treatment flow diagram. (Adapted from U.S. EPA, *Treatability Manual, Volume II Industrial Descriptions*, Report EPA-600/2-82-001b, U.S. Environmental Protection Agency, Washington, DC, September 1981.)

9.6.2.1 Emulsion Breaking and Oil Separation

Method: Emulsion broken by mixing oily waste with alum and a chemical emulsion breaker, followed by gravity oil separation in a tank.

System component: A small mixing tank, two chemical feed tanks, a mixer, and a large tank equipped with an oil skimmer and a sludge pump. The mixing tank has a retention time of 15 min and the oil skimming tank has a retention time of 2.5 h.

9.6.2.2 Cyanide Oxidation

Method: Cyanide is destroyed by reaction with sodium hypochlorite under alkaline conditions.

System component: Reaction tanks, a reagent storage and feed system, mixers, sensors, and controls: two identical reaction tanks sized as the above-ground cylindrical tank with a retention time of 4 h. Chemical storage consists of covered concrete tanks to store 60 d supply of sodium hypochlorite and 90 d supply of sodium hydroxide.

9.6.2.3 Chromium Reduction

Method: Chemical reduction of hexavalent chromium by sulfur dioxide under acid conditions for the continuous operating system and by sodium bisulfite under acid conditions for the batch operating system. The reduced trivalent form of chromium is subsequently removed by precipitation as the hydroxide.

System component: Reaction tanks, a reagent storage and feed system, mixers, sensors, and controls for continuous chromium reduction. A single above-ground concrete tank with retention time of 45 min is provided. For batch operation, dual above-ground concrete tanks with 4 h retention time are provided.

9.6.2.4 Lime Precipitation and Sedimentation

Method: Chemical precipitation of dissolved and complexed metals by reaction with lime and subsequent removal of the precipitated solids by gravity settling in a clarifier. Alum and polyelectrolyte are added for coagulation and flocculation.

System component: The continuous treatment system includes reagent storage and feed equipment, a mix tank for reagent feed addition, sensors and controls, and clarification basin with associated sludge rakes and pumps. Lime is fed as 30% lime slurry prepared by using hydrated lime. The mix tank is sized for a retention time of 45 min and the clarifier is sized for hydraulic loading of 1360 L/m^2 and a retention time of 4 h. Batch treatment includes dual reaction-settling tanks sized for 8 h retention time and sludge pumps.

9.6.2.5 Sludge Drying Beds

Method: Sludge dewatered by means of gravity drainage and natural evaporation.
System component: Beds of highly permeable gravel and sand underlain by drain pipes.[29]

9.6.2.6 Multimedia Filter

Method: Polishing treatment after chemical precipitation and sedimentation by filtration through a bed of particles of several distinct size ranges.
System component: Filter beds, media, backwash mechanism, pumps, and controls. The filter beds were sized for hydraulic loading of 81 L/min/m^2 (2 gpm/ft^2).

9.6.2.7 Ultrafiltration

Method: The process used for oily waste stream after emulsion breaking–gravity oil separation.
System component: Filter modules sized on the basis of hydraulic loading of 1 L/min/m^2.

9.6.2.8 Carbon Adsorption

Method: A packed-bed throwaway system to remove organic pollutants from oily waste stream.
System component: A contactor system, and a pump station designed for a contact time of 30 min and hydraulic loading of 162 L/min/m^2 (4 gpm/ft^2).

Unit costs shown in Table 9.16 are for the complete treatment options described previously. Unit costs are computed for a model plant where flows are contributed by several waste streams as follows:

- 30% oily waste stream
- 4% cyanide waste stream
- 9% chromium waste stream

TABLE 9.16
Total Annual Unit Cost (USD/m^3 in 2007 Dollars)[a]

	Option 1		Option 2		Option 3	
Flow (m^3/h)	Continuous	Batch	Continuous	Batch	Continuous	Batch
2.36	—	14.28	—	23.94	—	28.35
11.81	6.09	5.04	9.66	8.4	11.34	10.29
59.07	2.52	—	4.62	—	5.25	—
118.16	2.10	2.10	3.57	3.78	4.20	4.41

Source: U.S. EPA, *Treatability Manual, Volume II Industrial Descriptions*, Report EPA-600/2-82-001b, U.S. Environmental Protection Agency, Washington, DC, September 1981.

[a] Costs were converted from 1979 USD to 2007 USD using U.S. ACE Yearly Average Cost Index for Utilities.[9]

- 52.5% common metals stream
- 4.5% complex metal stream.

9.7 U.S. CODE OF FEDERAL REGULATIONS FOR METAL FINISHING EFFLUENT DISCHARGE MANAGEMENT

This section introduces the U.S. Code of Federal Regulations (CFR) Title 40, Part 433 (40 CFR part 433) for effluent discharge management of metal finishing point source category.

The topics introduced in this section include (a) the applicability, description of the metal finishing point source category; (b) the monitoring requirements of metal finishing effluent discharges; (c) the effluent limitations representing the degree of effluent reduction attainable by applying the best practicable control technology currently available (BPT); (d) the effluent limitations representing the degree of effluent reduction attainable by applying the best available technology economically achievable (BAT); (e) the pretreatment standards for existing sources (PSES); (f) the new source performance standards (NSPS); and (g) the pretreatment standards for new sources (PSNS).

9.7.1 Applicability, Description of the Metal Finishing Point Source Category

Except as noted in the next two paragraphs of this section, the provisions of this subpart apply to plants that perform any of the following six metal finishing operations on any basis material: electroplating, electroless plating, anodizing, coating (chromating, phosphating, and coloring), chemical etching and milling, and printed circuit board manufacture. If any of those six operations are present, then this part applies to discharges from those operations and also to discharges from any of the following 40 process operations: cleaning, machining, grinding, polishing, tumbling, burnishing, impact deformation, pressure deformation, shearing, heat treating, thermal cutting, welding, brazing, soldering, flame spraying, sand blasting, other abrasive jet machining, electric discharge machining, electrochemical machining, electron beam machining, laser beam machining, plasma arc machining, ultrasonic machining, sintering, laminating, hot dip coating, sputtering, vapor plating, thermal infusion, salt bath descaling, solvent degreasing, paint stripping, painting, electrostatic painting, electropainting, vacuum metalizing, assembly, calibration, testing, and mechanical plating.

In some cases, effluent limitations and standards for the following industrial categories may be effective and applicable to wastewater discharges from the metal finishing operations listed above. In such cases, the 40 CFR part 433 limits shall not apply and the following regulations shall apply:

- Nonferrous metal smelting and refining (40 CFR part 421)
- Coil coating (40 CFR part 465)
- Porcelain enameling (40 CFR part 466)
- Battery manufacturing (40 CFR part 461)
- Iron and steel (40 CFR part 420)
- Metal casting foundries (40 CFR part 464)
- Aluminum forming (40 CFR part 467)
- Copper forming (40 CFR part 468)
- Plastic molding and forming (40 CFR part 463)
- Nonferrous forming (40 CFR part 471)
- Electrical and electronic components (40 CFR part 469).

The 40 CFR part 433 does not apply to (a) metallic platemaking and gravure cylinder preparation conducted within or for printing and publishing facilities and (b) existing indirect discharging job shops and independent printed circuit board manufacturers which are covered by 40 CFR part 413.

9.7.2 MONITORING REQUIREMENTS OF METAL FINISHING EFFLUENT DISCHARGES

In lieu of requiring monitoring for total toxic organics (TTO), the permitting authority (or, in the case of indirect dischargers, the control authority) may allow dischargers to make the following certification statement:

> Based on my inquiry of the person or persons directly responsible for managing compliance with the permit limitation [or pretreatment standard] for total toxic organics (TTO), I certify that, to the best of my knowledge and belief, no dumping of concentrated toxic organics into the wastewaters has occurred since filing of the last discharge monitoring report. I further certify that this facility is implementing the toxic organic management plan submitted to the permitting [or control] authority.

For direct dischargers, this statement is to be included as a "comment" on the Discharge Monitoring Report required by 40 CFR 122.44(i), formerly 40 CFR 122.62(i).

For indirect dischargers, the statement is to be included as a comment to the periodic reports required by 40 CFR 403.12(e). If monitoring is necessary to measure compliance with the TTO standard, the industrial discharger need analyze for only those pollutants that would reasonably be expected to be present.

In requesting the certification alternative, a discharger shall submit a solvent management plan that specifies to the satisfaction of the permitting authority (or, in the case of indirect dischargers, the control authority) the toxic organic compounds used; the method of disposal used instead of dumping, such as reclamation, contract hauling, or incineration; and procedures for ensuring that toxic organics do not routinely spill or leak into the wastewater. For direct dischargers, the permitting authority shall incorporate the plan as a provision of the permit.

Self-monitoring for cyanide must be conducted after cyanide treatment and before dilution with other streams. Alternatively, samples may be taken of the final effluent, if the plant limitations are adjusted based on the dilution ratio of the cyanide waste stream flow to the effluent flow.

9.7.3 EFFLUENT LIMITATIONS BASED ON THE BPT

Except as specifically provided in the U.S. CFR, any existing point source subject to the 40 CFR part 433 must achieve the effluent limitations shown in Table 9.17, which represents the degree of

TABLE 9.17
U.S. BPT Effluent Limitations for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L Except for pH)	Monthly Average shall not Exceed (mg/L Except for pH)
Cadmium (T)	0.69	0.26
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
TTO	2.13	
Oil and grease	52	26
TSS	60	31
PH	6–9	6–9

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

TABLE 9.18
Alternative U.S. BPT Effluent Limitations on Cyanide (A) for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L)	Monthly Average shall not Exceed (mg/L)
Cyanide (A)	0.86	0.32

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

effluent reduction attainable by applying the BPT. Alternatively, for metal finishing industrial facilities with cyanide treatment, and upon agreement between a source subject to those limits and the pollution control authority, the amenable cyanide limit shown in Table 9.18 may apply in place of the total cyanide limit specified in Table 9.17. No user subject to the provisions of these regulations shall augment the use of process wastewater or otherwise dilute the wastewater as a partial or total substitute for adequate treatment to achieve compliance with this limitation.

9.7.4 EFFLUENT LIMITATIONS BASED ON THE BAT

Except as specifically provided in the U.S. CFR, any existing point source subject to this subpart must achieve the effluent limitations shown in Table 9.19 which represents the degree of effluent reduction attainable by applying the BAT. Alternatively, for the metal finishing industrial facilities with cyanide treatment, and upon agreement between a source subject to those limits and the pollution control authority, the amenable cyanide limit shown in Table 9.20 may apply in place of the total cyanide limit specified in Table 9.19. No user subject to the provisions of these regulations shall augment the use of process wastewater or otherwise dilute the wastewater as a partial or total substitute for adequate treatment to achieve compliance with this limitation.

9.7.5 PRETREATMENT STANDARDS FOR EXISTING SOURCES

Except as specifically provided in the U.S. CFR, any existing source subject to this 40 CFR part 433 that introduces pollutants into a publicly owned treatment works must also comply with 40 CFR

TABLE 9.19
U.S. BAT Effluent Limitations for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L Except for pH)	Monthly Average shall not Exceed (mg/L Except for pH)
Cadmium (T)	0.69	0.26
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
TTO	2.13	

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

TABLE 9.20
Alternative U.S. BAT Effluent Limitations on Cyanide (A) for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L)	Monthly Average shall not Exceed (mg/L)
Cyanide (A)	0.86	0.32

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

part 403 and achieve the PSES. Table 9.21 indicates the PSES for all metal finishing plants except job shops and independent printed circuit board manufacturers. Alternatively, for industrial facilities with cyanide treatment, upon agreement between a source subject to those limits and the pollution control authority, the amenable cyanide limit shown in Table 9.22 may apply in place of the total cyanide limit specified in Table 9.21. No user introducing wastewater pollutants into a publicly owned treatment works under the provisions of this subpart shall augment the use of process wastewater as a partial or total substitute for adequate treatment to achieve compliance with this standard. An existing source submitting a certification in lieu of monitoring pursuant to this regulation must implement the toxic organic management plan approved by the control authority. An existing source subject to this subpart shall comply with a daily maximum pretreatment standard for TTO of 4.57 mg/L.

9.7.6 NEW SOURCE PERFORMANCE STANDARDS

Any new metal finishing point source subject to the 40 CFR part 433 regulations must achieve the NSPS shown in Table 9.23. Alternatively, for the metal finishing industrial facilities with cyanide treatment, and upon agreement between a source subject to those limits and the pollution control authority, the amenable cyanide limit shown in Table 9.24 may apply in place of the total cyanide limit specified in Table 9.23. No user subject to the provisions of this subpart shall augment the use

TABLE 9.21
U.S. PSES for All Metal Finishing Plants Except Job Shops and Independent Printed Circuit Board Manufacturers

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L Except for pH)	Monthly Average shall not Exceed (mg/L Except for pH)
Cadmium (T)	0.69	0.26
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
TTO	2.13	

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

TABLE 9.22
Alternative U.S. PSES on Cyanide (A) for All Metal Finishing Plants Except Job Shops and Independent Printed Circuit Board Manufacturers

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L)	Monthly Average shall not Exceed (mg/L)
Cyanide (A)	0.86	0.32

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

TABLE 9.23
U.S. NSPS for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L Except for pH)	Monthly Average shall not Exceed (mg/L Except for pH)
Cadmium (T)	0.11	0.07
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
TTO	2.13	
Oil and grease	52	26
TSS	60	31
pH	6–9	6–9

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

TABLE 9.24
Alternative U.S. NSPS on Cyanide (A) for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L)	Monthly Average shall not Exceed (mg/L)
Cyanide (A)	0.86	0.32

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

of process wastewater or otherwise dilute the wastewater as a partial or total substitute for adequate treatment to achieve compliance with this limitation.

9.7.7 PRETREATMENT STANDARDS FOR NEW SOURCES

Except as provided in the U.S. CFR, any new source subject to this subpart that introduces pollutants into a publicly owned treatment works must comply with 40 CFR part 403 and achieve the

TABLE 9.25
U.S. PSNS for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L Except for pH)	Monthly Average shall not Exceed (mg/L Except for pH)
Cadmium (T)	0.11	0.07
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
TTO	2.13	

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

PSNS, shown in Table 9.25. Alternatively, for industrial facilities with cyanide treatment, and upon agreement between a source subject to these limits and the pollution control authority, the amenable cyanide limit shown in Table 9.26 may apply in place of the total cyanide limit specified in Table 9.25.

No user subject to the provisions of this subpart shall augment the use of process wastewater or otherwise dilute the wastewater as a partial or total substitute for adequate treatment to achieve compliance with this limitation. An existing source submitting a certification in lieu of monitoring pursuant to Section 433.12 (a) and (b) of this regulation must implement the toxic organic management plan approved by the control authority.

9.8 SPECIALIZED DEFINITIONS

The definitions set forth in the U.S. CFR for the metal finishing point source category are incorporated in this section for reference.

1. The term “T,” as in “Cyanide, T,” shall mean total.
2. The term “A,” as in “Cyanide A,” shall mean amenable to alkaline chlorination.
3. The term “job shop” shall mean a facility that owns not more than 50% (annual area basis) of the materials undergoing metal finishing.

TABLE 9.26
Alternative U.S. PSNS on Cyanide (A) for the Metal Finishing Point Source Category

Pollutant or Pollutant Property	Maximum for Any 1 Day (mg/L)	Monthly Average shall not Exceed (mg/L)
Cyanide (A)	0.86	0.32

Source: U.S. EPA, *Code of Federal Regulations, Metal Finishing Point Source Category*, Title 40, Volume 27, Part 433, U.S. Environmental Protection Agency, Washington, DC, Revised as of July 1, 2003.

4. The term "independent" printed circuit board manufacturer shall mean a facility that manufactures printed circuit boards principally for sale to other companies.
5. The term "TTO" shall mean total toxic organics, which is the summation of all quantifiable values greater than 0.01 mg/L for the following toxic organics:

   Acenaphthene
   Acrolein
   Acrylonitrile
   Benzene
   Benzidine
   Carbon tetrachloride (tetrachloromethane)
   Chlorobenzene
   1,2,4-Trichlorobenzene
   Hexachlorobenzene
   1,2-Dichloroethane
   1,1,1-Trichloroethane
   Hexachloroethane
   1,1-Dichloroethane
   1,1,2-Trichloroethane
   1,1,2,2-Tetrachloroethane
   Chloroethane
   Bis(2-chloroethyl)ether
   2-Chloroethyl vinyl ether (mixed)
   2-Chloronaphthalene
   2,4,6-Trichlorophenol
   Parachlorometa cresol
   Chloroform (trichloromethane)
   2-Chlorophenol
   1,2-Dichlorobenzene
   1,3-Dichlorobenzene
   1,4-Dichlorobenzene
   3,3-Dichlorobenzidine
   1,1-Dichloroethylene
   1,2-*trans*-Dichloroethylene
   2,4-Dichlorophenol
   1,2-Dichloropropane
   1,3-Dichloropropylene (1,3-Dichloropropene)
   2,4-Dimethylphenol
   2,4-Dinitrotoluene
   2,6-Dinitrotoluene
   1,2-Diphenylhydrazine
   Ethylbenzene
   Fluoranthene
   4-Chlorophenyl phenyl ether
   4-Bromophenyl phenyl ether
   Bis(2-chloroisopropyl)ether
   Bis(2-chloroethoxy)methane
   Methylene chloride (dichloromethane)
   Methyl chloride (chloromethane)
   Methyl bromide (bromomethane)
   Bromoform (tribromomethane)

Dichlorobromomethane
Chlorodibromomethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Isophorone
Naphthalene
Nitrobenzene
2-Nitrophenol
4-Nitrophenol
2,4-Dinitrophenol
4,6-Dinitro-*o*-cresol
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-*n*-propylamine
Pentachlorophenol
Phenol
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-*n*-butyl phthalate
Di-*n*-octyl phthalate
Diethyl phthalate
Dimethyl phthalate
1,2-Benzanthracene (benzo(*a*)anthracene)
Benzo(*a*)pyrene (3,4-benzopyrene)
3,4-Benzofluoranthene (benzo(*b*)fluoranthene)
11,12-Benzofluoranthene (benzo(*k*)fluoranthene)
Chrysene
Acenaphthylene
Anthracene
1,12-Benzoperylene (benzo(*ghi*)perylene)
Fluorene
Phenanthrene
1,2,5,6-Dibenzanthracene (dibenzo(*ah*)anthracene)
Indeno(1,2,3-cd) pyrene (2,3-*o*-phenlene pyrene)
Pyrene
Tetrachloroethylene
Toluene
Trichloroethylene
Vinyl chloride (chloroethylene)
Aldrin
Dieldrin
Chlordane (technical mixture and metabolites)
4,4-DDT
4,4-DDE (*p*,*p*-DDX)
4,4-DDD (*p*,*p*-TDE)
α-endosulfan
β-endosulfan
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor

Heptachlor epoxide
α-BHC (BHC-hexachloro-cyclohexane)
β-BHC (BHC-hexachloro-cyclohexane)
γ-BHC (BHC-hexachloro-cyclohexane)
δ-BHC (BHC-hexachloro-cyclohexane)

PCB-1242 (Arochlor 1242) (PCB-polychlorinated biphenyls)
PCB-1254 (Arochlor 1254) (PCB-polychlorinated biphenyls)
PCB-1221 (Arochlor 1221) (PCB-polychlorinated biphenyls)
PCB-1232 (Arochlor 1232) (PCB-polychlorinated biphenyls)
PCB-1248 (Arochlor 1248) (PCB-polychlorinated biphenyls)
PCB-1260 (Arochlor 1260) (PCB-polychlorinated biphenyls)
PCB-1016 (Arochlor 1016) (PCB-polychlorinated biphenyls)
Toxaphene
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

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10 A Holistic Approach to Phytofiltration of Heavy Metals: Recent Advances in Rhizofiltration, Constructed Wetlands, Lagoons, and Bioadsorbent-Based Systems

Gloria Sánchez-Galván and Eugenia J. Olguín

CONTENTS

10.1 INTRODUCTION

Surface water and groundwater may become contaminated with hazardous compounds as a consequence of natural and human activities. Pollutants of concern are both inorganic (heavy metals, radionuclides, nitrogen, phosphorous, etc.) and organic compounds (fuels, solvents, explosives, pesticides, herbicides, chemical and petrochemical compounds, etc.).[1] Organic pollutants are mostly man-made and xenobiotic to organisms. They are released into the environment via spills, military activities, agriculture, industry, wood treatment, and so on. Inorganic pollutants occur as natural elements in the earth's crust or atmosphere, and human activities such as mining, industry, traffic, agriculture, and military activities promote their release into the environment.[2] Heavy metals and nutrients such as nitrogen and phosphorous are the inorganic pollutants of major concern worldwide.[3–5]

The release of heavy metals into the environment presents a serious threat. Over recent decades, the annual worldwide release of heavy metals reached 22,000 T for cadmium, 939,000 T for copper, 783,000 T for lead, and 1,350,000 T for zinc.[3] Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms and enter the food chain.[6] Exposure to high levels of these metals has been linked to cytotoxic, mutagenic, and carcinogenic effects on

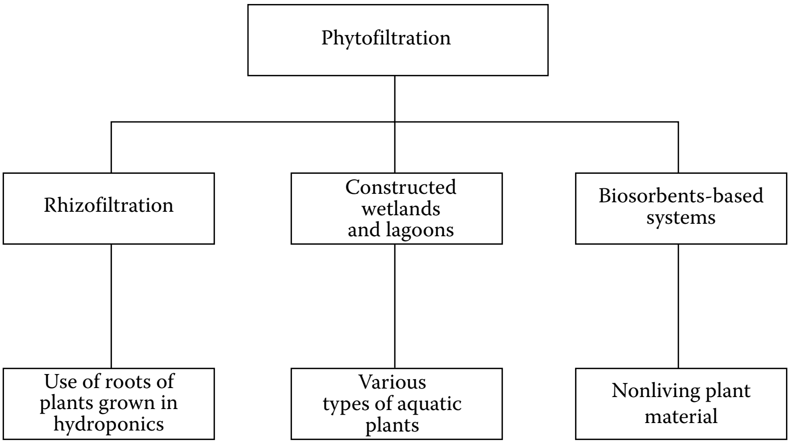

FIGURE 10.1 Different types of systems used in phytofiltration.

human health and wildlife.[7] As a consequence, their elimination from contaminated waters has become a major topic of research in recent years.[8]

Different technologies have been developed in recent years to treat the wastewaters contaminated with heavy metals. Chemical precipitation, coagulation–flocculation, flotation, ion exchange, and membrane filtration can be employed to remove heavy metals from contaminated wastewater.[6] However, they have inherent limitations in application mainly due to the lack of economical feasibility for the treatment of large volumes of water with a low metal concentration. Furthermore, the major disadvantage of conventional technologies is the production of sludge.[9]

Due to the above-mentioned constraints of conventional technologies, the biological treatment of metals, especially phytoremediation, is becoming a more attractive alternative. It is defined as the use of plants and their associated microbes to remove, reduce, degrade, or immobilize environmental pollutants from soil and water, thus restoring contaminated sites to a relatively clean, nontoxic environment. A variety of polluted waters can be phytoremediated, including sewage and municipal wastewater, agricultural runoff/drainage water, industrial wastewater, coal pile runoff, landfill leachate, mine drainage, and groundwater plumes. Phytoremediation includes various strategies and all of them are promising, cost-effective, and environmentally friendly technologies.[10]

Phytofiltration, a specific strategy of phytoremediation, is the use of plants to remove contaminants from water and aqueous waste streams. Three different systems (Figure 10.1) can be considered within this strategy: (a) rhizofiltration (the use of hydroponically cultivated plant roots),[3,11,12] (b) constructed wetlands (CWs) and lagoons, and (c) bioadsorbents-based systems.[1]

It is worth noting that there are preparation stages of the plant biomass before they can be used for pollutants removal, in the case of rhizofiltration and bioadsorbents-based systems (Figure 10.2), which may increase the investment and operational costs. On the contrary, the lagoons and CWs are designed to process the influents in one single stage.

This chapter is aimed at presenting an overview of the state of the art in phytofiltration of heavy metals using any of the three different treatment systems. It has been considered useful to discuss the three alternatives in one single document, since usually, information for each of the systems is reviewed separately, missing the advantages of a holistic discussion.

10.2 RHIZOFILTRATION

The system or process termed rhizofiltration is the use of hydroponically cultivated plant roots of several terrestrial plants to absorb, concentrate, or precipitate toxic metals from polluted effluents

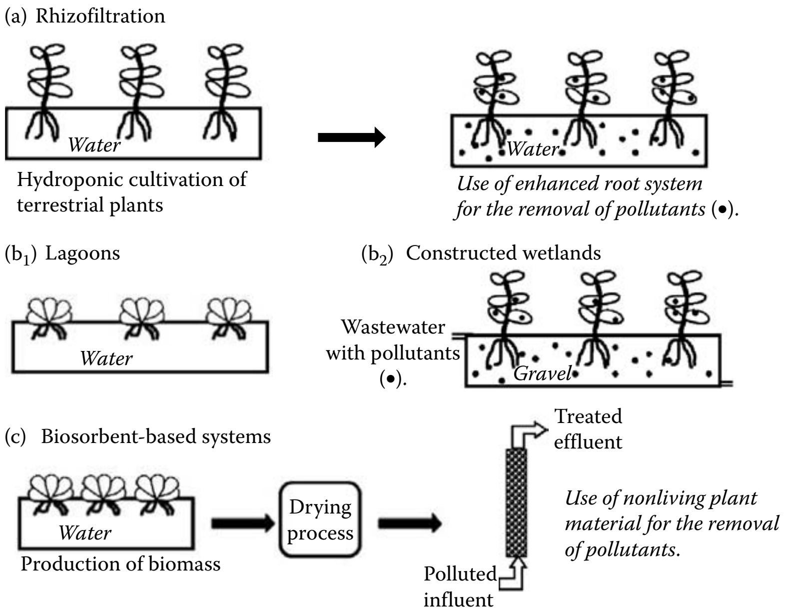

FIGURE 10.2 Preparation and operative stages in rhizofiltration, lagoons, CWs, and biosorbent-based systems.

and was initially promoted by Dushenkov and his group.[13] An extensive review on this topic and the use of various plants for the removal of heavy metals has been already published.[14] More recently, other reviews have been published, mainly related to modeling systems[15] and radionucleotides removal.[12] Thus, in this chapter, an effort has been made in order to refer only to the more recent work related to the removal of heavy metals through rhizofiltration, in the strict sense of the definition described above, and also in relation to the use of terrestrial plant systems for metal removal from aqueous solutions and wastewaters.

During rhizofiltration, the plant roots sorb, concentrate, and/or precipitate the contaminants present in the irrigated wastewater through the soil plant root system into the harvestable parts of the roots and above-ground shoots.[15] Subsequent volatilization of contaminants can also occur. As they become saturated with the contaminants, roots or whole plants are harvested for disposal. Terrestrial plants are preferred over aquatic plants, since they produce long, more substantial, often fibrous root systems with large surface area for pollutant sorption.[3]

Roots of many hydroponically grown terrestrial plants, for example, Indian mustard (*Brassica juncea* (L.) Czern.), sunflower (*Helianthus annuus* L.), and various grasses, have proved to remove effectively toxic metals from aqueous solutions. Sunflower (*Helianthus annuus* L.) is one of the most promising environmental crops that is being used in diverse situations for environmental clean-up.[16] It has been shown to be very efficient in the uptake of Cd(II) and Pb(II).[17] The latter was concentrated in both leaf and stem at the region of vascular bundles with greater amounts in the leaf portion. Lead granules were also found in the root tissue from the epidermis layer to the central axis.[18] The influence of a chelating agent such as (S,S)-N,N0-ethylenediamine disuccinic acid (EDDS) on the accumulation of Cu(II), Zn(II), and Pb(II) by sunflowers from nutrient solution has also been assessed. The uptake of Pb(II) in shoots was enhanced, whereas that of essential metals, such as Cu(II) and Zn(II), was decreased. These results show that synthetic chelating agents do not necessarily increase uptake of heavy metals, when soluble concentrations are equal in the presence and absence of chelates.[19]

Plant groups such as *Brassica* have members with the ability to extract selenium from soil. *Brassica juncea*, in particular, has been the focus of much research due to its relatively large biomass and its fast growth cycle.[20] In hydroponics, it has shown an exceptionally high accumulation of Pb(II) (138 g/kg) being restricted largely to root tissue. Examination using scanning transmission electron microscopy–energy dispersive spectroscopy revealed substantial and predominantly intracellular uptake at the root tip.[21] This plant is also able to remove Hg(II) from contaminated solutions. The main removal mechanism was volatilization that occurred from the roots, while only little Hg(II) was translocated to the shoots (0.7–2% of the total metal accumulated).[22]

Sedum alfredii has proved to be a Zn/Cd-hyperaccumulator[23] and Pb-accumulating plant.[24] Studies developed in hydroponics have suggested that the naturally occurring rhizospheric bacteria may be useful in *S. alfredii* tolerance to heavy metal toxicity, and also accelerate the metal removal from contaminated water.[25] The effect of Pb(II) on hyperaccumulating and nonhyperaccumulating ecotypes of this plant has also been evaluated. Although growth, leaf physiology, and ultrastructure of both the ecotypes were affected by Pb treatment, deleterious effects were more pronounced in the nonhyperaccumulating ecotype.[26]

It is known that lead phytoextraction can be economically feasible only when the developed systems employ high biomass plants that can accumulate >1% of the metal in their shoots. Sahi and coworkers[27] demonstrated that *Sesbania drummondii*, a leguminous shrub occurring in the wild, is able to accumulate >4% of Pb(II) in shoots when it is grown hydroponically in a Pb-contaminated nutrient solution. Pb(II) granules were found in the plasma membrane and cell wall, and also in the vacuoles. *S. drummondii* is also able to accumulate Hg(II) from water in roots (998 mg Hg/kg) and shoots (41,403 mg Hg/kg). It has been suggested that this plant uses effective antioxidative defense mechanisms such as the modulating nonenzymatic antioxidants (glutathione and nonprotein thiols) and enzymatic antioxidants: superoxide dismutase, ascorbate peroxidase, and glutathione reductase.[28]

The potential efficiency of *Fagopyrum esculentum*, common buckwheat, in removing chromium from wastewaters has also been assessed. Plants grown in Cr(III) showed a higher tissue concentration and a higher chromium removal efficiency than those grown in Cr(VI). Buckwheat was able to retain their capacity for Cr removal even though it showed strong toxicity symptoms.[29]

Buddleja asiatica (wild species) and *B. paniculata* (cultivated species) are plants of fast growth, containing an extensive root system. Evaluations under hydroponic conditions were carried out to compare their phytoremediation potential of Cd(II), Zn(II), and Pb(II). *B. asiatica* accumulated more Pb(II) and Cd(II) than *B. paniculata* in both shoots and roots. An extremely high Pb content (12,133–21,667 mg/kg) was observed in roots of both species.[30] On the other hand, *Sesuvium portulacastrum* and *Mesembryanthemum crystallinum* are halophytes from Aizoaceae family that show tolerance to Cd(II) in aqueous solutions. It was found that Cd(II) accumulation was significantly higher in the roots than in the shoots. However, the metal content in the shoots reached values characteristic of Cd hyperaccumulator plants (350–700 μg/g).[31]

Pteris vittata, a terrestrial fern, has been described as an As hyperaccumulator.[32] Additionally, it has been also grown hydroponically to assess its effectiveness in As removal from contaminated groundwater. Several short-term studies have shown that it is able to reduce effectively the arsenic concentration in 3 d (from 46 to <10 μg/L). After this time, reused plants can continue to take up arsenic from the groundwater but at a slower rate.[33] At field scale, Natarajan and coworkers[34] evaluated some factors such as plant density, nitrogen (N) and phosphorous (P) addition, and reuse of plants to improve the effectiveness of *P. vittata* roots system. Results suggested that a higher plant density and lower *P* levels may enhance the As depletion (from 130 to 1.7 μg/L in five weeks). At the same scale, a continuous flow phytofiltration system with the genus *Pteris* consistently produced water having an arsenic concentration less than the detection limit of 2 mg/L, at flow rates as high as 1900 L/d for a total treated water volume of approximately 60,000 L throughout the 84 d demonstration period.[35]

Vetiveria zizanioides is a fast growing, perennial, tussock grass belonging to the family Poaceae. It has the ability to extract metals from the soil and water. Its high tolerance for metals and metalloids is often attributed to its capability to accumulate metals in above-ground tissues that do not affect the roots and shoot growth, and to the mycorrhizal association within its roots that makes it sturdy enough to withstand high toxic metal concentration in soils.[36] Boonyapookana and coworkers[18] reported that after four weeks of growth, a 17-fold increase in shoot Pb(II) content was observed in plants grown in a solution containing 2.5 mmol/L of Pb(II) and in the presence of EDTA. A Bioconcentration Factor (BCF) of 88 was obtained.

10.3 CONSTRUCTED WETLANDS AND LAGOONS

An extensive number of manuals and books related to the different aspects of performance and design of CWs are available in the literature.[37–44] On the contrary, reviews concerning metal removal using lagoons with floating macrophytes are scarce. In this review, brief information about CWs is presented and a major emphasis is given to the use of lagoons with aquatic floating plants for metal removal.

CWs are engineered systems that have been designed to treat wastewaters taking advantage of many of the processes that occur in natural wetlands, although its design allows a more controlled environment. Natural processes involve wetland vegetation, soils, and their associated microbial assemblages.[45] CWs have been used for the purification of domestic, industrial, and agricultural wastewater, and stormwaters. They are furthermore applied to strip nutrients from polluted surface waters before these are discharged into vulnerable nature reserves.[41]

Many are the advantages of CWs for treating wastewater and runoff. They are a cost-effective and technically feasible technology. The expenses of operation and maintenance (energy and supplies) are low, requiring only a periodic, rather than continuous, on-site labor. CWs are tolerant to fluctuations in flow and facilitate water reuse and recycling. Additionally, they provide habitat for many wetland organisms and benefits to wildlife habitat.[37]

In developing countries, additional advantages of using CWs can be obtained. They may provide economic benefits and could encourage small communities to maintain natural wastewater treatment systems. The production of plant biomass can provide economic returns to communities through production of biogas, animal feed, compost, and fiber for paper according to the type of pollutant.[46]

The treatment mechanisms in CWs are numerous and often interrelated. Metals are removed at different stages from the water column by a series of physicochemical and biological processes (Table 10.1).

TABLE 10.1
Mechanisms Involved in the Improvement of the Water Quality in a CW

Mechanism	Type of Process	Pollutant
Settling of suspended particulate matter	Physical	Organic matter
Filtration and chemical precipitation through contact of the water with the substrate and litter	Physicochemical	Metals
Adsorption and ion exchange on the surfaces of plants, substrate, sediment, and litter	Physicochemical	Metals
Direct uptake by plants and microorganisms. Microbial removal of metals	Biological	Metals
Breakdown and transformation of pollutants by microorganisms and plants	Biological	Organics
Uptake and transformation of nutrients by microorganisms and plants	Biological	N, P
Predation and natural die-off of pathogens	Biological	Pathogens

Source: Environmental Protection Agency (EPA), *A Handbook of Constructed Wetlands*. Available at http://www.epa.gov/OWOW/wetlands/pdf/hand.pdf, 2000b and Greenway, M., The role of macrophytes in nutrient removal using constructed wetlands, in *Environmental Bioremediation Technologies*, Singh, S.N. and Tripathi, R.D., Eds, Springer, Berlin, Heidelberg, 2007, pp. 331–351.

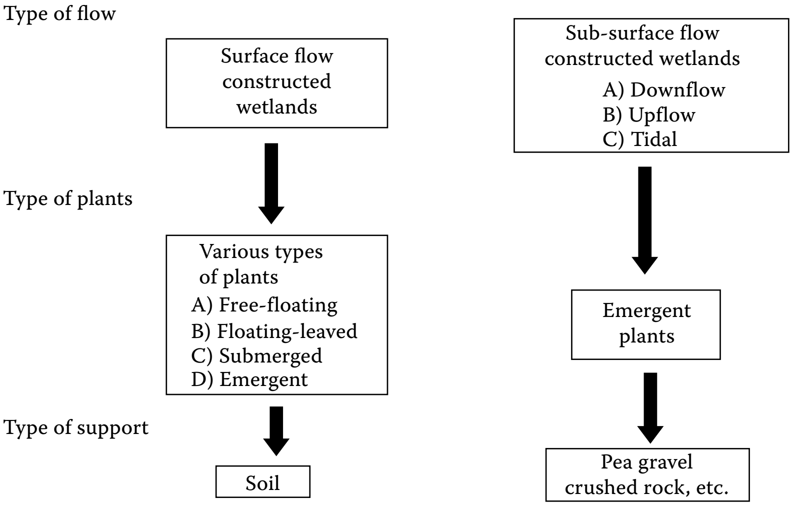

FIGURE 10.3 Types of CWs according to the type of flow, plant, and supporting media.

The basic classification of CWs is based on the type of flow regime and macrophytic growth. In general terms, two types can be described (Figure 10.3). The selection of the most appropriate option shall be according to various operational factors and to the plants available in the region of establishment of the system.[37,38,40,44]

10.3.1 LAGOONS WITH FREE-FLOATING PLANTS

Lagoons with free-floating macrophytes consist of one or more shallow ponds in which plants float on the surface. Several free-floating plants (FFP) have been tested to purify water by removing nutrients and metals (Table 10.2). They range from large plants with rosettes of aerial and/or floating leaves and well-developed submerged roots to minute surface-floating plants with few or no roots.[44]

The metal removal in this kind of systems is mainly due to plant uptake.[69,70] Adsorption to the roots or surface plant, translocation, and intracellular accumulation have been described as the main removal mechanisms.[71,72] The majority of works have been carried out in single-metal microcosms in batch-operated systems. The genus *Azolla* has been widely assessed for removing metals at low initial metal concentrations. Bennicelli and coworkers[73] reported that *A. californiana* was able to remove Hg(II) (75–93%) and Cr(III) (74–91%) from synthetic water solutions. The concentration of metals ranged from 71 to 964 mg/kg dry weight in the plant tissues. Similar results for Hg (90%, 94%, and 80%) and Cd(II) (>80%) removal were found using *A. pinnata*. The metal content in the biomass was directly related to that of the solution, being 667 and 740 mg/kg, for Hg(II) and Cd(II), respectively at an initial concentration of 3.0 mg/L. In all cases, the metal presence inhibited the plant growth at 20–30%.[74] Likewise, *A. filiculoides* is an excellent accumulator of Pb(II) (1.8% of dry weight). More in-depth studies carried out to characterize the mechanisms of such Pb(II) accumulation and storage showed that Pb(II) uptake in *Azolla* leaves takes place in the cell wall and vacuoles. In mature *Azolla* leaves, lead accumulated in larger aggregates than in young leaves. The tonoplasts may be involved in lead accumulation through secondary ion transporters in the vacuoles via H^+-ATPase activity.[75]

The phytofiltration of Pb(II) and Cd(II) has been also studied using species of *Salvinia*. *S. minima* Baker is a small free-floating aquatic fern native to Mexico, Central America and South America. It has been proved to be an excellent aquatic phytoremediator and hyperaccumulator of Cd(II) and Pb(II).[72,76] The relevance of using a compartmentalization analysis (CA) complementary to the use of BCFs and metal removal kinetics by plants has been demonstrated using *S. minima*

Table 10.2
Types of Plants Utilized in CWs and Lagoons

	Type of Plants	Reference
Free-floating	*Eichhornia crassipes*	48
	Pistia stratiotes	49
	Lemnaceae	50
	Azolla filiculoides	51
	Ipomoea aquatica	52
	Bacopa monnieri	53
	Salvinia minima	54
Floating-leaved	*Nymphaea spontanea*	55
	Nymphaea aurora	56
	Hydrocotyle umbellata	57
Submerged	*Nuphar variegatum*	58
	Elodea canadensis	59
	Potamogeton natans	59
	Hydrilla sp.	60
	Vallisneria spiralis	61
Emergent	*Phragmites australis*	62
	Bolboschoenus maritimus	62
	Zizania latifolia	63
	Typha latifolia	59
	Alisma plantago-aquatica	59
	Sagittaria sagittifolia L.	59
	Juncus effusus	64
	Typha domingensis	65
	Phragmites australis	66
	Phalaris arundinacea	66
	Spartina alterniflora	67
	Carex rostrata	68
	Eriophorum angustifolium	68

exposed to Pb(II) as a model system.[72] The CA is used to define the fate of the metal within four compartments in the microcosm (surface of the plant, intracellular space, water column, and sediments) by using a series of EDTA washings. Recently, based on the use of this methodological tool, a bioadsorption factor (BAF) and an intracellular accumulation factor (IAF) were proposed in order to gain a full insight into the hyperaccumulating lead capacity of *S. minima*. It was clear that such an ability was mainly due to a strong adsorption capacity (BAF in the range of 780–1980) compared to a weaker one for intracellular accumulation (IAF in the range of 57–1007). Surprisingly, the ability of *S. minima* to accumulate the metal into the cells was not inhibited at concentrations as high as 28.40 ± 0.22 mg Pb(II)/L.[77]

Phetsombat and coworkers[78] found significant Cd(II) and Pb(II) increases in the accumulation of these two metals by *S. cucullata*, when exposure time (2–8 d) and concentration were increased (from 0.5 to 4.0 and from 5 to 40 mg/L of Cd(II) and Pb(II), respectively). The roots of *S. cucullata* had higher metal contents than leaves suggesting that the metals were bound to the root cells and were partially transported to the leaves. At the same time, there were significant decreases in the relative growth, biomass productivity, and total chlorophyll content when the exposure time and concentration were increased. Other studies have demonstrated the potential of *S. minima* to remediate Cu(II) in concentrations 100 times above that currently found in freshwater environments.[79]

Reports on the evaluation of FFP for metal removal at mesocosms level are scarce. The following discussion provides some of the more relevant reports related to this topic. *Eichhornia crassipes*, *Pistia stratiotes*, *Lemna minor*, *A. pinnata*, and *S. polyrhiza* were tested for their heavy metal removal capacity from the secondary treated municipal wastewater (150 L). Such a wastewater contained metals in various concentrations (mg/L), such as Cr (1.2), Cd (0.09), Cu (0.11), Zn (0.92), Fe (1.8), and Ni (0.07). The aquatic plants showed metal tolerance and surprisingly the secondary treated municipal wastewater promoted their growth. *E. crassipes* was the most efficient accumulator removing up to 70% of Fe(II) and 59% of Ni(II). Metals were mostly accumulated in roots than in leaves, according to the translocation factors, which in general were <1. The highest translocation factor was obtained in *L. minor* for Fe (0.94) and the lowest for Zn in *A. pinnata* (0.48). The biomass produced may be used for biogas production, papermaking, and so on, while treated wastewater may be of possible use for irrigation. Maximum removal at 20 d hydraulic retention period and decreasing trend after that indicate that aquatic plants should be harvested every 20 d for wastewater treatment. This technology is highly recommendable for tropical wastewaters where sewage is mixed with industrial effluents.[80]

Aquatic floating plants have been also tested for the removal of heavy metals from the coal mining effluent in mesocosms. The high removal efficiency (>60% for Fe, Cr, Cu, Cd, and Zn) found when a combination of *E. crassipes* and *L. minor* was used may be due to preferential higher absorption capacities of each plant.[81] Experimental sets containing only *E. crassipes* removed the highest concentration of heavy metals. The translocation factor indicated lower transportation of heavy metals from roots to leaves. A lower accumulation of metals in leaves than in root can be associated with protection of photosynthesis from toxic levels of trace elements.[82] No symptom of metal toxicity was found; therefore this method can be applied to the large-scale treatment of wastewaters in which metal concentrations are low. The mining effluents treated by this method can be used for various purposes in industry and agriculture or can be safely discharged into surrounding water bodies.[81]

Jayaweera and coworkers[83] described the different mechanisms involved in the phytoremediation of Fe-rich industrial wastewaters by water hyacinth grown under different nutrient conditions in batch-type lagoons. Fe removal was largely due to an uptake process and chemical precipitation of Fe_2O_3 and $Fe(OH)_3$ followed by flocculation and sedimentation. Chemical precipitation was more significant especially during the first three weeks of the study. Plants grown without any nutrient addition, other than Fe as a heavy metal, showed the highest removal efficiency of 47% with the highest accumulation of 6707 Fe mg/kg dry weight. Active effluxing of Fe back to the wastewater at intermittent periods was a key mechanism to avoid Fe phytotoxicity in the plant cultivated in all nutrient conditions. It was concluded that water hyacinth grown under nutrient-poor conditions is ideal to remove Fe from wastewaters with a hydraulic retention time of approximately six weeks.

A discussion of the use of floating aquatic plants for metal removal at large scale in surface flow constructed wetlands (SFCWs) is provided below.

10.3.2 SURFACE FLOW CONSTRUCTED WETLANDS

This type of wetlands consists of a shallow sealed basin or sequence of basins, containing 20–30 cm of rooting soil, with a water depth <0.4 m. Dense emergent vegetation covers usually more than 50% of the surface. However, floating-leaved attached macrophytes, that is, plants with roots in the sediment and floating leaves, submerged macrophytes, and floating macrophytes are also found.[44,47] In tropical regions, treatment wetlands are often dominated by floating aquatic plants rather than emergent macrophytes that are more common in temperate regions.[84] The most commonly emergent species used for SFCWs are *Phragmites australis* (Common reed), *Typha* spp. (Cattail), *Scirpus* spp. (Bulrush), *Sagittaria latifolia* (Arrowhead), and so on.

The advantages of SFCWs are that their capital and operating costs are low and their construction, operation, and maintenance are not complicated. Their main disadvantage is that they generally require a larger land area than other systems.[38]

Not many reports on the simultaneous use of different plants in SFCWs are available. Maine and coworkers[85] reported the treatment of wastewater from a tool manufacturing plant at large scale (100 m^3/d). Three floating (*P. stratiotes*, *E. crassipes*, and *S. rotundifolia*) and eight emergent plants (*Cyperus alternifolius*, *P. elephantipes*, *Thalia geniculata*, *Polygonum punctatum*, *Pontederia cordata*, *Pontederia rotundifolia*, *Typha domingensis*, and *Aechmea distichantia*) were transplanted to the CW. Cr, Ni, and Fe concentrations were reduced by 86%, 67%, and 95%, respectively. However, soluble reactive phosphate removal was not efficient. The FeS precipitation probably caused the high retention of Fe (95%). Phosphate and ammonium were not retained within the wetland, while 70% and 60% of the nitrate and nitrite were removed. The assessment of the removal efficiency during the different macrophyte dominance stages was also carried out. During *E. crassipes* dominance, metals were retained in the macrophyte biomass. On the other hand, when *E. crassipes* together with *T. domingensis* were dominant, sedimentation was the main removal mechanism. Finally, during *T. domingensis* dominance stage, pollutants were retained in both sediment and macrophyte biomass. Removal efficiency did not show significant differences among the three vegetation stages even though removal mechanisms were different. Therefore, the choice of the most suitable species depends on the tolerance of the macrophytes to the conditions of the wastewater.[65]

10.3.3 Subsurface Flow Constructed Wetlands

Subsurface flow wetlands are gravel and/or soil/sand-filled trenches, channels, or basins with no standing water, which support emergent vegetation. They are also known as vegetated submerged bed systems or reed-bed or root-zone wastewater treatment systems.[47] There are two types of subsurface flow constructed wetlands (SSFCWs), the horizontal flow CW (HFCW) and the vertical flow CW (VFCW). In the HFCW, the wastewater flows slowly through the bed in a relatively horizontal path and comes into contact with a network of aerobic, anoxic, and anaerobic zones. The aerobic zones occur around roots and rhizomes that leak oxygen into the substrate. On the other hand, VFCWs are fed intermittently to flood the surface and wastewater, then gradually percolate down through the bed and are collected by a drainage network at the base. The bed drains freely and it allows air to refill the bed.[44]

The SSFCWs have several advantages over the SFCWs. They have greater cold tolerance, promote a minimization of pest and odor problems, and, possibly, have greater assimilation potential per unit of land area, which results in a smaller requirement of land for the same volume of wastewater. In tropical regions, one of their great advantages is that they do not promote mosquitos proliferation. On the other hand, SSFCWs are more expensive to construct and may be more difficult to regulate than SFCWs. Furthermore, maintenance and repair costs are generally higher. Clogging and unintended surface flows problems have been also reported for this kind of system.[38]

Metal removal in SSFCWs has been recently focused on metal elimination from synthetic water and different wastewaters,[66,86] on the evaluation of the effects of season, temperature, plant species, and chemical oxygen demand (COD) loading on metals removal,[87] and on the accumulation of metals in wetland plant species and sediments.[88,89] Recent reviews on heavy metal phytoremediation wetlands are also available.[48]

10.4 BIOADSORBENTS-BASED SYSTEMS

Current reviews on biosorption are related to general approaches[90–93] to diverse types of biomass such as microbial biomass, plant wastes, and agro-based waste materials, or to a specific metal.[4,94–98] However, a review on metal biosorption using macrophytes biomass is not available. In this chapter, a review on the current knowledge of biosorption using preferentially nonliving biomass from aquatic plants is presented.

Biosorption is a property of both living and dead organisms and may be simply defined as the removal of substances from solution by biological material. Such substances can be organic and inorganic, and in gaseous, soluble, or insoluble forms.[93] Biosorption has shown to be a very promising biotechnology for metal removal from effluents.[90] Its major advantages are its low cost, high metal-binding capacity, high efficiency for reducing quickly the pollutant concentration in an environmentally friendly manner, simplicity, and availability of biomass.[93,99,100]

Ahluwalia and Goyal[94] have pointed out some disadvantages of biosorption such as the early saturation of biomass, which can be a problem since metal desorption is necessary prior to further use, irrespective of the metal value. Furthermore, the potential for biological process improvement is limited because cells are not performing an active metabolism.

Biosorption is a rather complex process affected by several factors that include different binding mechanisms (Figure 10.4). Most of the functional groups responsible for metal binding are found in cell walls and include carboxyl, hydroxyl, sulfate, sulfhydryl, phosphate, amino, amide, imine, and imidazol moieties.[4,90] The cell wall of plant biomass has proteins, lipids, carbohydrate polymers (cellulose, xylane, mannan, etc.), and inorganic ions of Ca(II), Mg(II), and so on. The carboxylic and phosphate groups in the cell wall are the main acidic functional groups that affect directly the adsorption capacity of the biomass.[101]

Additionally, studies about chemical modification of the biomass surface to improve biosorption have been widely reported.[102,103] Equilibrium[91] and kinetics[104] biosorption have been described using different models.

Recent reports on biosorbents based on diverse types of macrophytes are found widely in the literature. Free-floating aquatic plants from the genera *Salvinia*, *Azolla*, *Eichhornia*, *Lemna*, and *Pistia* have been described the most. *S. natans* biomass was able to uptake As(V) at low initial concentrations from 0.25 to 2 mg/L (74.8% and 54%, respectively). The experimental data fitted well to both Langmuir and Freundlich isotherms. The effect of pH and biomass quantities on sorption rate has also been investigated along with some metabolic parameters.[105]

Recently, nonliving biomass of *S. cucullata* has been described as a low-cost absorbent of Cr(VI).[106] Optimum conditions for the Cr(VI) adsorption by acid-treated *S. cucullata* were found out using a full factorial design. The Cr(VI) removal efficiency of the adsorbent was found to increase with the increase in time, temperature, adsorbate concentration, and stirring speed, and to decrease with increase in pH and adsorbent dose. The Fourier transform infrared spectroscopy (FT-IR) analysis revealed that in addition to electrostatic force, the adsorption may be due to

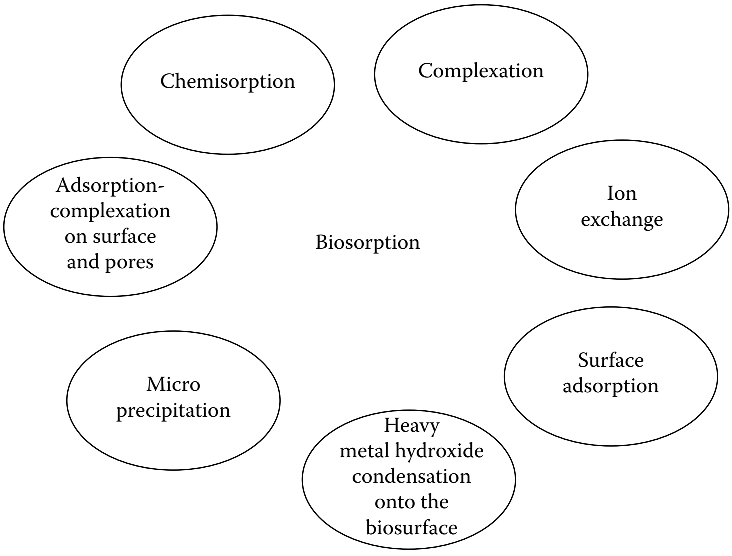

FIGURE 10.4 Binding mechanisms involved in metal biosorption.

formation of complex with the ligands (Lewis bases) available in the adsorbents. The vital role played by chelation was also shown. Authors suggest that the formation of chelates could have been favored at lower pHs and therefore the adsorption efficiency was higher. Column studies were carried out at the optimum operating conditions and the maximum uptake obtained was 98.75 mg/g. Adsorption data from the column studies fitted well to the Bohart–Adams model. Furthermore, Cr(VI) removal studies were carried out by using activated carbon obtained from *S. cucullata*. Results showed that the initial part of the adsorption process confined only to surface adsorption and the slower kinetics could be due to intraparticle diffusion. The FT-IR showed the anionic binding with the chelate forming part of the adsorbent. Column studies were also carried out to evaluate the suitability of the adsorbent in treating Cr(VI)-contaminated water and the maximum uptake of Cr(VI) observed was 156 mg/g at an initial concentration of 100 mg/L.[107]

A. filiculoides biomass has been evaluated for Pb(II), Cd(II), Ni(II), and Zn(II) adsorption in different stages. Nonliving biomass of *A. filiculoides* was activated by NaOH and then $CaCl_2$/$MgCl_2$/NaCl. This process can occur due to the increase of ion-exchange agents such as $(–COO)_2Ca$ and $(–COO)_2Mg$ bindings and/or $–COONa_2OOC–$ groups. These binding sites can be formed from demethylation of cell wall pectin in the alkali solution and then contacting with ternary chloride salts solution. Such an activation resulted in a higher q_{max} obtained for the alkali-treated biomass, especially for Pb(II) and Cd(II) at the highest temperature (313°K) (1.272 versus 0.977 and 1.35 versus 0.931 for Pb(II) and Cd(II), respectively). This biomass had also faster adsorption kinetics in comparison to the nonactivated *Azolla* biomass.[108]

Removal of Hg(II) from aqueous solutions has been also possible using *A. filiculoides* nonliving biomass. Diverse techniques such as scanning electron microscopy (SEM), determination of nitrogen and amino acid content, BET (Brunauer, Emmett, Teller) surface area by N_2 adsorption at 77 K, acid/base titration, ion-exchange capacity, and electrophoretic measurements were used in an attempt to elucidate the mechanisms involved in mercury sequestration. Samples were also characterized by energy dispersive spectroscopy and x-ray diffraction after contact and equilibration with mercury solution. The reduction of Hg(II) to Hg(I), that is, soluble mercuric to insoluble mercurous chloride (Hg_2Cl_2) on the adsorbent surface, was found to be a controlling reaction mechanism. Although mercury sorption was studied at elevated concentrations similar to those encountered in industrial effluents, it is suggested that the findings would also apply to final stage water treatment.[109]

Less complex techniques have been reported to be useful to study the acidic and alkaline treatment processes of biosorbents and the role of carboxyl and carboxylate groups in metal adsorption. Rakhshaee and coworkers[101] used potentiometric titration curves to assess the content of such groups in *L. minor* biomass treated with NaOH and HCl. The results showed an increase (up to 25%) in the adsorption of Hg(II), Cr(III), Cr(VI), and Cu(II) with NaOH-treated biomass as a consequence of an increase of –COO– groups (0.92–2.42 mmol/g). On the contrary, the –COOH groups increase observed (1.50–2.41 mmol/g) due to the acidic treatment led to a decrease in the metal ions uptake (up to 33%) despite activation by the chloride salts.

Recent reports pointed out that water hyacinth (*E. crassipes*) nonliving biomass is suitable for development of an efficient biosorbent for the removal of chromium from wastewater of chemical and allied process industries. Gude and Das[110] found that the adsorption rate of Cr(VI) from aqueous solutions was rapid following the first-order kinetic model and the equilibrium exhibited a Langmuir-type behavior. The maximum Cr(VI) adsorption was found to be 7.5 mg/g of dry weight, whereas the calculated activation energy was around 54.6 kJ/mol. Based on these results, the authors mentioned that about 500 mg of dry biomass could remove Cr(VI) successfully from 100 mL of chromite mine water containing 2.8 mg/L Cr(VI). On the contrary, it has been reported[111] that although the Largreen first-order model was applicable to some of the data of Cr(VI) adsorption by water hyacinth biomass, the pseudo-second-order reaction model was applicable to all data. Furthermore, the Freundlich isotherm was found to represent the measured sorption data well. The FT-IR showed that the hydroxyl group was the chromium-binding site within a pH range from 1 to 5, where chromium did not precipitate.

Spirodela intermedia, *L. minor*, and *P. stratiotes* were able to remove Pb(II), Cd(II), Ni(II), Cu(II), and Zn(II), although the two former ions were removed more efficiently. Data fitted the Langmuir model only for Ni and Cd, but the Freundlich isotherm for all metals tested. The adsorption capacity values (K_F) showed that Pb was the metal more efficiently removed from water solution (166.49 and 447.95 mg/g for *S. intermedia* and *L. minor*, respectively). The adsorption process for the three species studied followed first-order kinetics. The mechanism involved in biosorption resulted in an ion-exchange process between monovalent metals as counterions present in the macrophytes biomass and heavy metal ions and protons taken up from water.[112]

The effect of activation treatments has been also evaluated in multimetal (Cu(II), Cd(II), and Ni(II)) systems using untreated, acid pretreated (H_2SO_4), and alkali pretreated (NaOH) biomass of *L. minor*. The results revealed that the adsorption capacities of the biomass in multimetal systems were lower than those obtained in a single-metal system, that is, Cd(II) adsorption decreased by almost 60% in the untreated biomass. The ionic charge, ionic radii, and electrode potential affect metal ions adsorption in the multimetal systems. On the other hand, the maximum adsorption capacities were higher with alkali pretreated biomass (83, 69, and 59 mg/g for the Cd(II), Cu(II), and Ni(II) ions, respectively). The FT-IR results showed that dried biomass have different functional groups for heavy metal ions binding, such as carboxyl, phosphate, amide, thiol, and hydroxide groups.[113]

Nonliving biomass of *E. crassipes*, *Valisneria spiralis*, and *P. stratiotes* were examined in terms of their heavy metal (Cd(II), Ni(II), Zn(II), Cu(II), Cr(II), and Pb(II)) sorption capacity, from individual-metal and multimetal aqueous solutions. Surprisingly, *V. spiralis* was the most efficient plant and *E. crassipes* was the least efficient one for removal of all the metals. Cd(II) was removed up to 98% by *V. spiralis*. Sorption data for Cr(II), Ni(II), and Cd(II) fitted better to the Langmuir isotherm equation, while the sorption data for Pb(II), Zn(II), and Cu(II) fitted better to the Freundlich isotherm equation. In general, the presence of other metal ions did not influence significantly the targeted metal sorption capacity of the test plant biomass. Ion exchange was proven to be the main mechanism involved in biosorption and there was a strong ionic balance between adsorbed (H^+ and M^{2+}) and the released ions (Na^+ and K^+) to and from the biomass.[114]

Regarding submerged plants, sorption of Cu(II) by *Myriophyllum spicatum* L. (Eurasian water milfoil) has been shown to be fast and fits isotherm models such as Langmuir, Temkin, and Redlich–Peterson. The maximum sorption capacity (q_{max}) of copper onto *M. spicatum* L. was 10.80 mg/g, while the overall sorption process was best described by the pseudo-second-order equation.[115] Likewise, *Hydrilla verticillata* has been described as an excellent biosorbent for Cd(II). In batch conditions, the q_{max} calculated was 15.0 mg/g. Additionally, *H. verticillata* biomass was capable of decreasing Cd(II) concentration from 10 to a value below the detection limit of 0.02 mg/L in continuous flow studies (fixed-bed column). It was also found that the Zn ions affected Cd(II) biosorption.[116]

Sorption mechanisms of Hg(II) by the nonliving biomass of *Potamogeton natans* was also elucidated using chemical and instrumental analyses including atomic absorption, electron microscopy, and x-ray energy dispersion analyses. The results showed a high maximum adsorption of Hg(II) (180 mg/g), which took place over the entire biomass surface. Nevertheless, there were spots on the surface where apparent multilayer sorption of Hg(II) occurred. The minimum concentration of Hg(II) in solution that can be removed appears to be about 4–5 mg/L.[117]

Other aquatic weeds such as reed mat, mangrove (leaves), and water lily (Nymphaceae family plants) have been found to be promising biosorbents for chromium removal. The highest Cr(III) adsorption capacity was exhibited by reed mat (7.18 mg/g), whereas for Cr(VI), mangrove leaves showed maximum removal capacity (8.87 mg/g) followed by water lily (8.44 mg/g). It is interesting to mention that Cr(VI) was reduced to Cr(III), with the help of tannin, phenolic compounds, and other functional groups on the biosorbent, and subsequently adsorbed. Unlike the results discussed previously for the use of acidic treatments, in this case, such treatments significantly increased the Cr(VI) removal capacity of the biosorbents, whereas the alkali treatment reduced it.[118]

Lichen biomass from *Parmelina* and *Cladonia* genera have resulted good biosorbents of Pb(II), Cr(III), and Ni(II) ions. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of Pb(II) and Cr(III) ions by *Parmelina tiliaceae* biomass. The monolayer biosorption capacity of the lichen found for Pb(II) and Cr(III) ions was 75.8 and 52.1 mg/g, respectively. The D–R isotherm model indicated that the biosorption was carried out by a chemical ion-exchange mechanism, since the mean free energy calculated was 12.7 and 10.5 kJ/mol for Pb(II) and Cr(III) biosorption, respectively. The calculated thermodynamic parameters such as the change of free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) showed that the biosorption of Pb(II) and Cr(III) ions onto *P. tiliaceae* biomass was feasible, spontaneous, and exothermic under the examined conditions.[119] The equilibrium, thermodynamic, and kinetic models mentioned before were also used to describe the biosorption of Pb(II) and Ni(II) ions from aqueous solution using *Cladonia furcata* biomass. The monolayer biosorption capacity of the biomass was found to be 12.3 and 7.9 mg/g for Pb(II) and Ni(II) ions, respectively. From the D–R model, the mean free energy calculated was 9.1 kJ/mol for Pb(II) biosorption and 9.8 kJ/mol for Ni(II) biosorption, indicating that the biosorption of both metal ions was carried out by a chemical ion-exchange mechanism. Thermodynamic parameters related to the biosorption capacity indicated the occurrence of a feasible, spontaneous, and exothermic process. Experimental data were also tested in terms of kinetic characteristics and it was found that biosorption processes of both metal ions followed well pseudo-second-order kinetics.[120]

Finally, Chojnacka[121] investigated the biosorption characteristics of *Riccia fluitans* and its potential to adsorb Cr(III) from aqueous solutions. The results showed that the biomass was rich in protein (27–31%) and possessed a high cation-exchange capacity (14.5 mequiv/g). The carboxyl groups were found in a higher quantity (6.08 mequiv/g). Additionally, it was found that in multi-ion systems (Cu, Mn, and Zn), the Cr(III) biosorption capacity was significantly affected (3.91 versus 6.10 mequiv/g) since metal ions competed for metal-binding sites. The results also showed that bound metal ions were exchanged with alkaline earth metals, confirming that the dominating mechanism of metal binding by *R. fluitans* was ion exchange.

As was mentioned earlier in this chapter, most of the biosorption reviews deal with nonliving biomass. However, it is also relevant to understand the presence of various biosorption mechanisms when metabolism is active, using living biomass. *S. minima* has proven to be an excellent Pb biosorbent. The biosorption process was found to follow a pseudo-second-order kinetics and to be dependent on the initial metal concentration (from 0.8 to 28.40 mg Pb/L). Data fitted well both the Langmuir and the Freundlich models . Very high $q_{\max}$ were obtained for both, synthetic wastewater and deionized water (58 and 44 mg/g, respectively). Such a high capacity to adsorb Pb was most likely due to its exceptional physicochemical characteristics such as a very high surface area (264 m^2/g) and a good content of carboxylic groups (0.95 mmol H^+/g dry weight).[77]

In natural conditions, *Ceratophyllum demersum* and *Potamogeton pectinatus L.* have been found to be effective adsorbents of Cd(II), Cu(II), and Pb(II). The adsorption percentage of the metals onto plant surfaces followed the pattern: Pb(II) > Cu(II) > Cd(II). *P. pectinatus* biomass adsorbed a higher content of heavy metals than *C. demersum*. According to the results, both species are of interest in the phytoremediation and biomonitoring studies of polluted waters.[122]

In controlled conditions, Lesage and collaborators[123] assessed the sorption/desorption properties of Co, Cu, Ni, and Zn by living *Myriophyllum spicatum biomass*. The sorption process was well described by the Langmuir model for Co, Ni, and Zn, whereas sorption of Cu was better described by the Freundlich isotherm. The biomass showed the highest affinity for Cu being the maximum sorption capacity (113 mg/g), 49-, 38-, and 17-fold that of Co, Ni, and Zn (2.3, 3.0, and 6.8 mg/g, respectively). At the highest initial concentration of 100 mg/L, a maximum of 29 mg/g of Cu was sorbed onto the surface of the biomass. The potential regeneration of the biomass and the recovery of heavy metals were also evaluated using HCl (0.1 M). However, the acid wash did not fully recover the metals sorbed onto the surface and evidence of leaching within the biomass was observed. Therefore, this procedure was not suggested as a viable strategy. On the other hand, Keskinkan and collaborators[124] found a lower $q_{\max}$ for Cu(II) (10.37 mg/g) and Zn(II) (15.59 mg/g) removal using the living biomass of *M. spicatum*. On the contrary, both *M. spicatum* and *C. demersum* showed to be excellent Pb(II) adsorbents ($q_{max} = 46.49$ and 44.8 mg/g, respectively). The thermodynamic parameters, specifically, the Gibbs free energy with negative values, indicated the spontaneity of the adsorption process between metals and plants. The lowest value was obtained for copper and the *C. demersum* system (−0.45), while the highest value of this parameter was achieved for lead and the *M. spicatum* system (−10.83).

10.5 CONCLUSIONS

Phytofiltration, defined as the use of plants to remove pollutants from wastewaters, has proven to be an efficient and environmentally friendly biotechnology. All phytofiltration systems, such as rhizofiltration, CWs and lagoons, and biosorbents-based systems, are very efficient in metal removal. However, the selection of the appropriate plant species and/or a specific system of phytofiltration is critical for a successful application at field scale. Aquatic plants, especially the free-floating and submerged plants, have shown a great potential in this area. Finally, even though most of the removal mechanisms of such pollutants have been studied, a better understanding of them within a particular system will be necessary for increasing the cases of successful applications of phytofiltration.

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11 Effects of Metals on Microorganisms in the Environment

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CONTENTS

11.1 BIOLOGICAL FUNCTIONS OF HEAVY METALS

Life depends on interactions between organic and inorganic components. The organic building blocks of life consist of nucleic acids, proteins, carbohydrates, and lipids; however, many of these organic compounds require inorganic metals to function properly. Metals that have a biological function, such as copper, nickel, magnesium, manganese, and zinc, are deemed essential metals.[1] These metals commonly serve as cofactors for proteinaceous enzymes, but they may also be used to stabilize proteins and bacterial cell walls.[1–3] Enzymatic function is reliant on a specific three-dimensional structure. A change in a single amino acid may alter the shape of an active site, leading to inactivation of the enzyme. Metal cofactors also act by affecting the folding patterns of enzymes. A positively charged metal ion may have specific interactions with negatively charged amino acids, such as aspartic and glutamic acid residues. The interaction between metal ions and amino acids is sufficient to alter the entire structure, and therefore function, of an enzyme.

Heavy metals with no known biological function, such as aluminum, arsenic, lead, and mercury, are nonessential metals.[4,5] These metals are toxic because they can irreversibly bind to enzymes that require metal cofactors. Toxic metals readily bind to sulfhydryl groups of proteins.[6,7] In fact, toxic metals interact so strongly with sulfhydryl groups that the structure may be permanently distorted. These metals can have an even broader effect when they inhibit chaperone-assisted refolding of denatured proteins.[8] The nonessential metals are also involved in the formation of reactive oxygen species that impose oxidative stress on microorganisms.[9] The results of heavy metal exposure have also been shown to result in single-strand breakage in DNA.[10] Single-stranded DNA is often observed during stressful conditions, specifically during the mismatch repair process; however, metals have been shown to inhibit mismatch repair.[11] Therefore, nonessential metals can inactivate enzymes directly (by binding to active sites in place of the necessary cofactors) or indirectly (by maintaining mutations in the DNA sequence that are not repaired).

Cadmium is an example of a heavy metal that can produce toxic effects both directly and indirectly. Cadmium was once thought to be a nonessential toxic metal, but it was rather recently discovered that it could serve as an enzyme cofactor in the marine diatom *Thalassiosira weissflogii*.[12] The diatom uses cadmium as a cofactor for carbonic anhydrase, an enzyme that catalyzes the reversible hydration of carbon dioxide to form bicarbonate and is used in acquiring inorganic carbon. Zinc is used in place of cadmium in other organisms, but *T. weissflogii* evolved under the zinc-limiting conditions of the ocean. Cadmium is not toxic to the diatom because the metal-binding site of the enzyme is stable even in the absence of the metal, a unique adaptation to this carbonic anhydrase. Carbonic anhydrase in *T. weissflogii* can easily use cadmium or zinc at the active site.[13]

All metals, regardless of whether they are essential or nonessential, can exhibit toxic effects at high concentrations.[14–16] Excess concentrations of essential metals can lead to nonspecific binding, which can affect the enzyme structure and function. Because controlling metal concentrations is vital for maintaining homeostatic conditions within bacterial cells, evolution has bestowed upon organisms a number of ways to regulate concentrations of essential metals and to resist the toxicity of nonessential metals.[17–20]

11.2 MICROBIAL RESPONSE TO METALS

There are a number of different mechanisms by which microorganisms resist metal toxicity (Table 11.1). Five mechanisms that microbes use to mediate metal toxicity have been proposed and they include (1) formation of a permeability barrier,[21–24] (2) active transport,[25–29] (3) sequestration,[30–32] (4) enzymatic detoxification,[33,34] and (5) reduction in sensitivity.[35,36] Microbes may use one or more of these mechanisms to exclude nonessential metals and regulate internal concentrations of essential metals.

Some microbes are able to decrease the permeability of their membranes to prevent toxic metals from entering. If the toxic metals are not able to physically enter the cell, they will not be able to affect vital metal-sensitive structures, such as proteins. One way to prevent heavy metals from entering is by decreasing the production of membrane channel proteins.[18] It is also possible for the metal-binding sites in the membrane and periplasm to be saturated with nontoxic metals.[37] A third possibility is the formation of an extracellular polysaccharide coat, which binds and prevents metals from reaching the surface of the cell.[24,38]

In microbes without a permeability barrier, or when the barrier fails, a mechanism must be in place to export metals from the cytoplasm. These active transport systems involve energy-dependent, membrane-bound efflux pumps that can be encoded by either chromosomal- or plasmid-borne genes. Active transport is the most well-studied metal resistance mechanism. Some of these include the *ars* operon for exporting arsenic from *E. coli*, the *cad* system for exporting cadmium from *Staphylococcus aureus*, and the *cop* operon for removing excess copper from *Enterococcus hirae*.[33,39,40]

Microbes that lack a specific active transport system for removing toxic metals may be able to sequester heavy metals either inside or outside of the cell. Intracellular sequestration occurs when cytoplasmic metal-binding molecules are produced in response to metal stress, preventing the metals from interacting with vital cell structures. The two most common molecules used for intracellular

TABLE 11.1
Microbial Responses to Metals in the Environment

Mechanism	Metal	Resistance Conferred	Reported in Species	Reference
Permeability barrier	Cd^{2+}	8.90 μM	*Arthrobacter viscosus*	22
	Cd^{2+}	178 μM	*Pseudomonas* sp. strain I1a	24
	Cd^{2+}	445 μM	*Arthrobacter* sp. strain D9	24
	Cd^{2+}	89.0 μM	*Klebsiella aerogenes*	21
	Cd^{2+}	Not reported	*Pseudomonas fluorescens*	23
	Cu^{2+}	89.0 μM	*Klebsiella aerogenes*	21
	Cu^{2+}	Not reported	*Pseudomonas fluorescens*	23
	Ni^{2+}	Not reported	*Pseudomonas fluorescens*	23
	Zn^{2+}	Not reported	*Pseudomonas fluorescens*	23
Active transport	Ag^{+}	5.0 μM	*Enterococcus hirae*	27
	As^{3+}	500 μM	*Bacillus subtilis*	33
	Cd^{2+}	0.445 μM	*Escherichia coli*	25
	Cd^{2+}	1500 μM	*Escherichia coli*	28
	Cu^{+}	8000 μM	*Enterococcus hirae*	27
	Zn^{2+}	7.65 μM	*Escherichia coli*	25
Sequestration	Cd^{2+}	2000 μM	*Pseudomonas* sp. strain H1	24
	Cd^{2+}	2450 μM	*Bacillus* sp. strain H9	24
	Cd^{2+}	2500 μM	*Alcaligenes* sp.	42
	Cu^{2+}	3000 μM	*Escherichia coli*	32
	Ni^{2+}	1700 μM	*Staphylococcus aureus*	30
Enzymatic detoxification	As^{5+}	4000 μM	*Bacillus subtilis*	33
	Hg^{2+}	2.5 μM	*Staphylococcus aureus*	43
	Hg^{2+}	125 μM	*Bacillus* sp.	44
	Hg^{2+}	5.0 μM	*Streptomyces lividans*	46
	Hg^{2+}	19.9 μM	Mercury-contaminated soil community	52
	Hg^{2+}	1.0 μM	*Thiobacillus ferrooxidans*	47
Reduction in sensitivity	Cd^{2+}	3000 μM	*Pseudomonas putida*	36
	Cd^{2+}	136 μM	*Escherichia coli*	58
	Zn^{2+}	2.09 mg/g soil	Agricultural soil community	53
	Zn^{2+}	200 μM	*Escherichia coli*	54

sequestration are metallothioneins and cysteine-rich proteins.[18,40] Examples of molecules used for extracellular sequestration are glutathione and ionic phosphate, which can cause metals to form insoluble complexes.[41,42]

Some metals can be converted to a less toxic form through enzyme detoxification. The most well-described example of this mechanism is the mercury resistance system, which occurs in *S. aureus*,[43] *Bacillus* sp.,[44] *E. coli*,[45] *Streptomyces lividans*,[46] and *Thiobacillus ferrooxidans*.[47] The *mer* operon in these bacteria includes two different metal resistance mechanisms.[48] MerA employs an enzyme detoxification approach as it encodes a mercury reductase, which converts the divalent mercury cation into elemental mercury.[49] Elemental mercury is more stable and less toxic than the divalent cation. Other genes in the operon encode membrane proteins that are involved in the active transport of elemental mercury out of the cell.[50–52]

Moving from single microorganisms to microbial communities, metals create selection pressure for microbes with cell structures that are less sensitive to metals. For example, mutations may occur that alter metal-binding sites of proteins without rendering the enzyme inactive. Another method for preventing metal toxicity is to produce excess amounts of the target so that there is an insufficient amount of metal to bind to all of the cellular molecules.[4,35,53]

11.2.1 GENOME-BASED APPROACHES TO INVESTIGATE MICROBIAL METAL RESISTANCE MECHANISMS

Results of recent microarray studies examining microbial global gene expression patterns in response to metals suggest that additional metal resistance mechanisms exist. Studies have examined genome-wide responses of *E. coli* to zinc,[54] cadmium,[55,56] cobalt, and nickel.[57] The results of these studies have indicated that metals tend to suppress genes involved in protein synthesis and increase the expression of genes involved in various stress responses and efflux systems. Periplasmic metal-binding proteins, such as ZraP for zinc,[54] YodA for cadmium,[58] and CusF for copper and silver,[59] have also been produced in response to metals.

Gene expression can be a useful indicator for characterizing mechanisms by which organisms adapt to changes in their environment (i.e., exposure to metals). Gene expression patterns provide clues as to how environmental conditions affect transcription of the genome, alter protein synthesis, and guide external responses of the organism. Also, experiments investigating stressor-specific expression patterns might lead to development of rapid methods of screening potential toxicants in the environment.[60]

11.3 EFFECT OF METALS ON MICROBIAL PROCESSES

Even with all of these mechanisms in place for metal resistance, microbes remain susceptible to heavy metals at high concentrations. In the environment, heavy metal toxicity affects many important processes mediated by microorganisms, including litter decomposition,[61–63] methanogenesis,[64–66] acidogenesis,[67,68] nitrogen transformation,[69–71] enzymatic activity,[72–74] and biodegradation of organics[75,76] (Table 11.2).

11.3.1 METALS AND GENERAL SOIL MICROBIOLOGICAL PROCESSES

Many studies have reported the effects of metals on general soil microbiological processes. Metals including cadmium, chromium, copper, lead, mercury, nickel, and zinc have been reported to inhibit many of the microbial processes listed above. Metal toxicity in the environment ultimately decreases litter decomposition, which can be measured by the rate of mass loss. Both copper (0.5 mg Cu g^{-1} soil) and zinc (1.0 mg Zn g^{-1} soil) were shown to decrease the rate of decomposition of unpolluted Scots pine needle litter near a brass mill in Sweden.[61] Duarte et al.[63] also determined that copper and zinc toxicity reduced leaf decomposition rates and fungal reproduction. Other metals, such as cadmium, nickel, and lead, have also been reported to decrease litter decomposition.[77]

Acidogenesis and methanogenesis, which are involved in the anaerobic decomposition of biomass, have also been reported to be inhibited by a variety of metals.[67,78] Interestingly, methanogenesis has been reported to be stimulated by mercury, lead, nickel, cadmium, and copper in anaerobic sediments[64] and by cobalt and nickel in wastewater containing methanol.[66] The specific mechanisms of such stimulation have not been investigated thoroughly.

Metals have been shown to negatively affect nitrogen transformation and urea hydrolysis. For example, Antil et al.[69] discovered that the microbial biomass in a soil receiving sewer water or industrial wastewater decreased with increasing concentrations of cadmium and nickel. The rate of urea hydrolysis was 1.6 times greater in an uncontaminated soil than in a soil containing 0.026 mg Ni g^{-1}. Ammonium concentrations increased for up to 14 days in a soil containing over

TABLE 11.2
Reported Metal Concentrations That Cause Inhibition of Microbial Processes in the Environment

Process	Metal	Inhibitory Concentration	Microbe Studied	Environment	Reference
Litter decomposition	Cu^{2+}	0.50 mg/g soil	Indigenous community	Scots pine needle litter	61
	Cu^{2+}	20 μM	Indigenous community	Leaf litter immersed in stream	63
	Cu^{2+}	0.482 mg/g soil	Indigenous community	Scots pine fine root and needle litter	62
	Ni^{2+}	0.190 mg/g soil	Indigenous community	Scots pine fine root and needle litter	62
	Zn^{2+}	1.00 mg/g soil	Indigenous community	Scots pine needle litter	61
	Zn^{2+}	20 μM	Indigenous community	Leaf litter immersed in stream	63
Methanogenesis	Co^{2+}	40 μM	*Methanosarcina* sp.	Mineral salts medium containing bicarbonate buffer and 1 mM sulfur	66
	Cu^{2+}	78.7 μM	Methanogenic bacteria	Fermented cow dung slurry	78
	Hg^{2+}	1 mg/g soil	Indigenous community	Soil microcosm	64
	Ni^{2+}	40 μM	*Methanosarcina* sp.	Mineral salts medium containing bicarbonate buffer and 1 mM sulfur	66
	Ni^{2+}	0.25 mg/g soil	Indigenous community	Sewage sludge	65
	Pb^{2+}	1 mg/g soil	Indigenous community	Soil microcosm	64
	Pb^{2+}	0.125 mg/g soil	Indigenous community	Sewage sludge	65
	Pb^{2+}	24.1 μM	Methanogenic bacteria	Fermented cow dung slurry	78
	Zn^{2+}	153 μM	Methanogenic bacteria	Fermented cow dung slurry	78
Acidogenesis	Cd^{2+}	258 μM	Indigenous community	Glucose-acclimated seed sludge	67
	Cr^{6+}	327 μM	Indigenous community	Glucose-acclimated seed sludge	67
	Cu^{2+}	78.7 μM	Indigenous community	Dairy wastewater	68
	Zn^{2+}	53.5 μM	Indigenous community	Glucose-acclimated seed sludge	67
	Zn^{2+}	306 μM	Indigenous community	Dairy wastewater	68
Nitrogen transformation	Cd^{2+}	0.040 mg/g soil	Indigenous community	Soils receiving sewer/industrial wastewater	69
	Cu^{2+}	3.0 mg/g soil	Indigenous community	Soil microcosm	70

continued

TABLE 11.2 (continued)

Process	Metal	Inhibitory Concentration	Microbe Studied	Environment	Reference
	Ni^{2+}	2.29 mg/g soil	Indigenous community	Soils receiving sewer/industrial wastewater	69
	Pb^{2+}	0.590 mg/g soil	Indigenous community	Soil microcosm	71
Enzymatic activity (acid phosphatase, endocellulase, and β-glucosidase)	Cd^{2+}	0.0002 mg/g soil	Indigenous community	Soil microcosm	72
Enzymatic activity (acid phosphatase, dehydrogenase, and β-glucosidase)	Cd^{2+}	0.0010 mg/g soil	Indigenous community	Soil microcosm	73
Enzymatic activity (catalase, invertase, and phosphatase)	Cd^{2+}	0.001 mg/g soil	Indigenous community	Soil microcosm	74
Enzymatic activity (acid phosphatase, endocellulase, and β-glucosidase)	Cu^{2+}	0.011 mg/g soil	Indigenous community	Soil microcosm	72
Enzymatic activity (acid phosphatase, dehydrogenase, and β-glucosidase)	Cu^{2+}	0.161 mg/g soil	Indigenous community	Soil microcosm	73
Enzymatic activity (acid phosphatase, endocellulase, and β-glucosidase)	Ni^{2+}	0.0114 mg/g soil	Indigenous community	Soil microcosm	72
Enzymatic activity (urease)	Pb^{2+}	0.590 mg/g soil	Indigenous community	Soil microcosm	71
Enzymatic activity (acid phosphatase, endocellulase, and β-glucosidase)	Pb^{2+}	0.0194 mg/g soil	Indigenous community	Soil microcosm	72
Enzymatic activity (acid phosphatase, dehydrogenase, and β-glucosidase)	Pb^{2+}	0.100 mg/g soil	Indigenous community	Soil microcosm	73
Enzymatic activity (acid phosphatase, endocellulase, and β-glucosidase)	Zn^{2+}	0.0508 mg/g soil	Indigenous community	Soil microcosm	72
Enzymatic activity (acid phosphatase, dehydrogenase, and β-glucosidase)	Zn^{2+}	0.218 mg/g soil	Indigenous community	Soil microcosm	73
Enzymatic activity (catalase and urease)	Zn^{2+}	0.100 mg/g soil	Indigenous community	Soil microcosm	74
Biodegradation (toluene)	Cd^{2+}	448 μM	*Bacillus* sp.	Mineral salts medium containing 36 mM phosphate	89
Biodegradation (2- and 3-chlorophenol)	Cd^{2+}	178 μM	Indigenous community	Sediment slurry	88
Biodegradation (2,3,4-trichloroaniline)	Cd^{2+}	1.6 μM	Indigenous community	Soil microcosm	87
Biodegradation (2,4-D)	Cd^{2+}	26.7 μM	*Ralstonia eutropha* JMP134	Mineral salts medium	24
Biodegradation (2,4-DME)	Cd^{2+}	100 μM	Indigenous community	Sediment microcosm	75

continued

TABLE 11.2 (continued)

Process	Metal	Inhibitory Concentration	Microbe Studied	Environment	Reference
Biodegradation (naphthalene)	Cd^{2+}	334 μM	*Burkholderia* sp.	Mineral salts medium containing 1.05 mM phosphate	85
Biodegradation (various polychlorinated biphenyl isomers)	Cd^{2+}	100–1000 μM	*Alcaligenes* spp. and *Pseudomonas* spp.	Tris-buffered minimal medium	84
Biodegradation (various polychlorinated biphenyl isomers)	Co^{2+}	100–10,000 μM	*Alcaligenes* spp. and *Pseudomonas* spp.	Tris-buffered minimal medium	84
Biodegradation (2- and 3-chlorophenol)	Cr^{6+}	385 μM	Indigenous community	Sediment slurry	88
Biodegradation (2,4-DME)	Cr^{3+}	25.0 μM	Indigenous community	Sediment microcosm	75
Biodegradation (2- and 3-chlorophenol)	Cu^{2+}	315 μM	Indigenous community	Sediment slurry	88
Biodegradation (various polychlorinated biphenyl isomers)	Cu^{2+}	100–1000 μM	*Alcaligenes* spp. and *Pseudomonas* spp.	Tris-buffered minimal medium	84
Biodegradation (toluene)	Ni^{2+}	606 μM	*Bacillus* sp.	Mineral salts medium containing 36 mM phosphate	89
Biodegradation (various polychlorinated biphenyl isomers)	Ni^{2+}	100–2000 μM	*Alcaligenes* spp. and *Pseudomonas* spp.	Tris-buffered minimal medium	84
Biodegradation (toluene)	Zn^{2+}	403 μM	*Bacillus* sp.	Mineral salts medium containing 36 mM phosphate	89
Biodegradation (2,4-DME)	Zn^{2+}	7.0 μM	Indigenous community	Sediment microcosm	75
Biodegradation (various polychlorinated biphenyl isomers)	Zn^{2+}	200–5000 μM	*Alcaligenes* spp. and *Pseudomonas* spp.	Tris-buffered minimal medium	84

1 mg Ni g^{-1} but decreased over time in uncontaminated soil samples. Nitrate concentrations increased over time regardless of the nickel concentration. Decreases in cell biomass and urea hydrolysis were also observed in response to lead toxicity.[71]

11.3.2 METALS AND BIOREMEDIATION

Many different heavy metal and organic pollutants, located at hazardous waste sites throughout the world, pose threats to wildlife and human health.[79,80] Excavation and incineration are two methods for eliminating organic wastes from these sites, but these methods can be inefficient and costly.[81] Bioremediation, which involves using microorganisms to break down organic pollutants, has been considered an attractive alternative.[82] One potential drawback to using bioremediation is that 40% of the sites on the U.S. Environmental Protection Agency's (EPA) National Priorities List (NPL) are cocontaminated with both organics and heavy metals.[83] Metals have the potential to affect organic pollutant degradation at these sites; however, the effects of metals on biodegradation are not completely understood.[76]

Numerous studies have investigated the effects of heavy metals on biodegradation. Studies examining biodegradation[84,85] often utilize bacteria that can use organic contaminants as sole carbon sources. Growth (an indicator of biodegradation in these studies) is often measured by optical density, protein content, oxygen consumption, or the amount of target organic compound that is removed over time.[76,86] Most studies have shown that metals inhibit biodegradation of various aromatic and aliphatic hydrocarbons.[87–90] One issue with these studies is that the metal may bind to the organic compound, preventing entry of the carbon source into the cell.[91] It is not clear whether reductions in biodegradation in these studies were due to direct toxicity or an inhibition of uptake of the target organic pollutant.

Not all studies have shown a connection between metal toxicity and inhibition of biodegradation. Some studies have shown that heavy metals do not affect the degradation of organic compounds.[92,93] For example, Baldrian et al.[94] showed that cadmium and mercury did not inhibit the ability of the fungus *Pleurotus ostreatus* to degrade polycyclic aromatic hydrocarbons. It is possible that the metals were being sequestered by a component of the soil medium used in these studies. In addition, both physiological (e.g., the use of a different enzyme system by the fungus in comparison with bacteria) and anatomical (e.g., the compartmentalized nature of eukaryotic cells of the fungus) features unique to fungi may account for the lack of an effect.

Interestingly, some studies[75,95] have shown increased biodegradation by bacteria in response to metals. In most cases, there is a dose-dependent relationship between metal concentration and biodegradation. Said and Lewis,[75] however, observed that an aerobic consortium of microbes degraded 2,4-dichlorophenoxyacetic acid methyl ester (2,4-DME) at a faster rate when exposed to 100 μM cadmium per liter than when exposed to 10 μM cadmium. These results could be due to selective pressures faced by the microbial consortium at higher metal concentrations. Perhaps, only the most resistant microbes survived when exposed to higher metal concentrations. These microbes no longer had to compete with other microbes for the carbon source. Another possible explanation is that metal resistance mechanisms may be more rapidly induced in response to higher metal concentrations.

A wide range of inhibitory metal concentrations has been reported in the literature. For example, reported concentrations of zinc that reduce biodegradation range from 9.18×10^{-2} [75] to 1.13×10^{4} μM.[84] This is likely due to a lack of standardized experimental conditions. Varying carbon sources, environmental conditions (e.g., medium composition and pH), and organisms of interest among studies likely account for the wide range of inhibitory concentrations reported in the literature. Some studies were performed using a single strain of bacteria, while others used an indigenous community of microbes. Some organisms were grown in soil or sediment microcosms, whereas others were grown in minimal salts media. Environmental conditions can affect metal toxicity by altering metal speciation and bioavailability.

11.4 METAL SPECIATION

The total metal concentration in a system has been the most commonly employed indicator of metal inhibition of microorganisms in the environment. Clearly, other parameters are important, considering the large disparities between reported minimum inhibitory concentrations (MICs) among studies. A better indicator of metal toxicity in the environment is the concentration of the most bioavailable form, or species, of the metal.[96] The most bioavailable species are those that will presumably associate most readily with enzymes and other active sites to initiate biological responses. Under most conditions, the most bioavailable form of a metal is considered to be the free, ionic, solution-phase species.[97,98] Despite the free cation usually being the most abundant species, many other species are present, such as metal phosphates, carbonates, hydroxides, and sulfides, depending on the physiochemical conditions (e.g., pH, redox potential, and ionic strength) of the medium. Metals can also form hydroxo-complexes or complexes with various other organic ligands.[99] It is also possible for most of the metal to speciate into insoluble precipitates, such as metal phosphates, which is likely to occur in microbiological studies employing phosphate buffers.[85,89,100]

Different metal species vary in their biological reactivity.[98,99] For example, the free ionic form of a metal may act by substituting a cofactor for a vital enzyme. Hydroxylated metal ions have been suggested to bind to the cell surface and alter the net charge of the cell to reduce its viability.[101] Because different species may have different effects on biological processes, some species may be more toxic than others. There is a paucity of information in the literature regarding the relative toxicity of different metal species.

11.4.1 MEASUREMENT OF BIOAVAILABLE METAL SPECIES

The total metal concentration in a solution can be easily determined using methods such as atomic absorption spectroscopy (AAS); however, the bioavailability of different metal species likely varies. In addition, much of the original concentration may have speciated into insoluble precipitates. Therefore, the concentration of some bioavailable species may be extremely low, perhaps even within or below the nanomolar range.[99] Ion-selective electrodes are useful for measuring the bioavailable concentration of a metal because they measure only the free, ionic species, which is often most prevalent.[102]

Immunoassays represent another approach to detect solution-phase metal concentrations. Immunoassays utilize antibodies that recognize metal-bound chelating agents, such as ethylenediamine-tetraacetic acid (EDTA).[103] Bioreporters have also been used to determine solution-phase metal concentrations.[104,105] These are cells that contain a reporter gene, such as *lacZ*, that is attached to a promoter region capable of being regulated by a heavy metal. Bioreporters for detecting mercury have been created using the *lacZ* system[35] and the *lux* system, which emitted light in response to mercury exposure.[106] Both immunoassays and bioreporters are advantageous because they can be used to accurately measure the bioavailable metal concentration in complex media and soil systems; however, the total concentration of bioavailable metal reported by biosensors varies depending on the metal resistance mechanisms of the specific bioreporter cell.[105] Specifically, the rates of uptake, efflux, and complexation can affect the amount of metal that is detected by the biosensor.

Additional methods for separating or determining different metal species in solution exist, although they may not be as accurate as the techniques that measure total solution-phase concentrations. Ligand-field (d–d) spectroscopy facilitates determination of which ligands are involved in forming metal species. Electrons from the d-orbitals of metals are excited at different wavelengths in different metal–ligand complexes.[2] Ion chromatography can also be utilized to separate species based on charge. Recently, dynamic speciation sensors that consider the kinetic properties of different species have been employed. These sensors take into account diffusion and speciation reactions of species such as metal hydroxides, carbonates, and sulfates, as well as metal complexes with organic ligands to determine the bioavailability of these species.[107]

It is extremely difficult to directly measure the concentration of various metal species in solution, except for the free, ionic species. Therefore, several investigators have employed geochemical modeling software, such as MINEQL+ (Environmental Research Software, Hallowell, Maine) or MINTEQA2[108] to predict metal speciation patterns as a function of ionic strength and pH.[87,109,110] These computer programs take into account equilibrium constants for each ion in solution and calculate the concentration of all metal species under specified conditions. The accuracy of programs such as MINEQL+ has been verified experimentally. For example, Sandrin and Maier[85] used a cadmium ion-selective electrode to determine the concentration of divalent cadmium ion in a minimal salts medium over a pH range of 4–7. The experimental concentrations were comparable with those predicted by the modeling software. These programs do not take into account all organic ligands present in complex media, so they tend to be most useful in experiments employing minimal, chemically defined media.

11.4.2 EFFECT OF MEDIUM COMPOSITION ON METAL SPECIATION AND TOXICITY

Many different chemical components in a microbiological medium may interact with metals. Results of many studies of metal toxicity are often not directly comparable due to the wide range of media used. Some varieties of complex biological media contain metal-binding components, such as yeast and beef extract, peptone, and amino acids.[99] These complex ingredients may differ slightly in their exact chemical composition among batches, so it is difficult to accurately and consistently determine metal speciation patterns in these types of media. Assessing the role of metal speciation on toxicity in these systems is complicated because much of the total metal can bind to components of the yeast or beef extract instead of vital cellular components.[111]

Other studies use soil or sediment samples for a more accurate indication of microbial activity in natural environments. In these samples, organic matter and clay particles play a role in metal toxicity.[76,112,113] Both organic material and clay particles in soil can bind metals and reduce their bioavailability. For example, Pardue et al.[87] demonstrated that much less solution-phase cadmium was required to inhibit trichloroaniline (TCA) dechlorination in a mineral-based soil than in a soil containing a higher concentration of organic matter. Other studies have shown that adding clay minerals to a medium mitigates toxicity. Clay minerals, such as kaolinite, montmorillonite, bentonite, and vermiculite, can bind to metals to decrease the amount that is bioavailable.[112–115]

Because metals can bind with components of complex media and soil to form species that are less bioavailable than the free, ionic species, it is important to use a chemically defined medium to accurately describe metal speciation.[2,116] The most straightforward determination of metal speciation can be accomplished using a minimal medium. Minimal media usually include a variety of mineral salts (e.g., NaCl, NH_4Cl, $MgSO_4$, and $CaCl_2$) and a single carbon source (e.g., glucose, succinate, and acetate). In experiments investigating effects of metal toxicity on biodegradation, the carbon source in the minimal medium is the organic pollutant to be degraded.[84,85,89] To obtain a better representation of the natural environment, a defined amount of soil has been mixed into a minimal medium that contained a pollutant as a carbon source.[75,117] Even in relatively simple types of media, such as minimal media, buffers are present at concentrations that can affect metal speciation.[99]

Many different buffers have been used to study metal toxicity. Phosphate buffers are commonly used in minimal media.[89,118–120] Phosphate ions readily form insoluble precipitates with many metals, decreasing the bioavailability of the metal in the process. Some metals are less sensitive to phosphate precipitation than others. For example, concentrations of the free cobalt ion (Co^{2+}) show no significant decrease with up to 15 mM (mmol per liter) phosphate. In contrast, when only 3 mM phosphate is present, both nickel- and cadmium-free ion concentrations decline to 78% and 34%, respectively, of the concentration when no phosphate is present.[121] Phosphate is so efficient at sequestering metals that it has been used in some studies to decrease concentrations of free metal ions in solution. For example, White and Knowles[91] added phosphate to their minimal medium to decrease the concentration of free cobalt and zinc ions that formed recalcitrant complexes with nitrilotriacetic acid, a model compound for studying the effects of metal binding on the bioavailability and biodegradation of organics.

Phosphate buffers that form precipitates with metals can confound data obtained in metal toxicity studies. For example, precipitates may be mistaken for cell biomass if the turbidity of the culture is being used as an indicator of growth.[99] One potential solution to this problem is decreasing the pH of the solution to dissolve metal-phosphate precipitates;[91] however, most metal phosphates remain insoluble at neutral to moderately acidic pH values. Another method for circumventing this problem is using glycerophosphate instead of inorganic phosphate.[122] Glycerophosphate will not form insoluble precipitates with metals, but some metal ions may still bind to the compound. In addition, use of glycerophosphate creates a confounding variable in biodegradation studies by acting as an additional carbon source. A final way of addressing the problem of phosphate precipitation of metals is to decrease the total phosphate concentration, although this alternative may compromise the efficacy of the buffering system.[121] Changing the phosphate concentration can affect metal toxicity. Korkeala and Pekkanen[123] observed that lowering the phosphate buffer concentration from 0.2 to 0.05 M increased the MIC of cadmium for *Micrococcus luteus* and *Bacillus subtilis* grown on Plate Count Agar. Curiously, the same decrease in phosphate concentration showed the opposite effect for *Streptococcus bovis* throughout the pH range from 6 to 8. The authors speculated that the variation in sensitivity to phosphates among these organisms could be explained by differences in the composition and structure of the cell walls. Since phosphate buffers lead to precipitation issues when examining metal speciation and toxicity, it is important to consider the use of buffers that lack such a strong affinity for metals.

Metals react less strongly with zwitterionic buffers than with phosphate buffers.[124] Zwitterions are ions that have both a positive and a negative charge. Some examples of zwitterionic buffers are HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), MES (morpholinoethanesulfonic acid), MOPS (3-(*N*-morpholino)propanesulfonic acid), PIPES (1,4-piperazinebis(ethanesulfonic acid)), and TES (*N*-Tris(hydroxymethyl)methyl-2-aminoethanesulfonic acid). These buffers have limited interactions with metals, so they do not confound interpretation of the results of metal toxicity studies as do phosphate buffers. A limitation regarding the use of these buffers, though, is that the studies should be conducted under the optimal pH range from 6 to 7.5,[125] as determined by the pK_a of each buffer. Tris-base (2-amino-2-(hydroxymethyl)-1,3-propanediol) is another buffer that has been used in many studies, but studies have shown that Tris buffer is capable of interacting strongly with some metals, including Hg^{2+} and Cu^{2+}.[126]

Although buffer components are often present at the highest concentration in a medium, metals can also bind to inorganic ligands in solution. Ligands such as Cl^-, OH^-, and SO_4^{2-} can form soluble complexes with many metals.[127] These complexes remain in solution, but are considered to be less bioavailable than the free, ionic species under most conditions.[97] Even though other soluble metal species are considered less bioavailable, they may play roles in metal toxicity.

11.4.3 EFFECT OF pH ON METAL SPECIATION AND TOXICITY

Free, ionic species of metals are at their highest concentrations at lower pH, so metals tend to be more bioavailable under these conditions.[121,128] At acidic pH, more protons are available to saturate metal-binding sites.[99] For example, metals are less likely to form insoluble precipitates with phosphates when the pH of the system is lowered because much of the phosphate has been protonated. Under basic conditions, metal ions can replace protons to form other species, such as hydroxo-metal complexes. Some of the hydroxo-metal complexes are soluble, such as those formed with cadmium, nickel, and zinc, whereas those formed with chromium and iron are insoluble.

Many studies[123,129–131] have shown that pH mediates metal toxicity. In some cases, increasing pH has been reported to reduce metal toxicity. Babich and Stotzky[132,133] found that increasing pH reduced the toxicity of nickel to a variety of different microorganisms, including bacteria (*Serratia marcescens*), filamentous fungi (*Arthrobotrys conoides*, *Penicillium vermiculatum*, and *Rhizopus stolonifer*), and a type of yeast (*Cryptococcus terreus*). Under moderately basic conditions (pH 8.5), much of the nickel may not have been bioavailable because it complexed with various ligands (e.g., Cl^-, OH^-, and SO_4^{2-}). It is also possible that the nickel was less toxic at a higher pH because some organisms may prefer basic environments to neutral or acidic environments. Aluminum has also been shown to be more toxic to *E. coli* at pH 5.4 than at pH 6.8.[134]

More commonly, metal toxicity has been reported to increase with pH. Increasing pH has been shown to increase the toxicity of zinc, copper, and uranium to certain algal species[130,135] and of cadmium to various bacteria (*B. subtilis*, *E. coli*, *M. luteus*, and *Streptococcus. bovis*), actinomycetes (*Micromonospora chalcea*, *Nocardia corallina*, and *Streptomyces flavovirens*), and fungi (*Saccharomyces cerevisiae* and *Schizosaccharomyces octosporus*).[123,136] Metal toxicity may increase at higher pH values because cells may be able to take up or adsorb more of the metal ions under these conditions.[85,137] Under more acidic conditions, metals compete with protons for binding sites on the cell surface.[130] Also, functional groups associated with the membrane are protonated under acidic conditions, potentially reducing the electrostatic attraction between the metal cations and the membrane. A third possibility is that metals are removed from the cell more efficiently under acidic conditions by efflux pumps that are driven by the proton motive force.[26]

Another possible explanation for the observation that increased toxicity of metals occurs as pH increases is the formation of species that are more toxic, such as the hydroxo-metal species.[101,138,139]

Because most studies that have implicated hydroxo-metal species were carried out in complex media, the concentration of these species was not accurately determined. Sandrin and Maier[85] used a minimal salts medium that allowed the use of geochemical modeling software (MINEQL+) to predict the concentration of monovalent hydroxylated cadmium ($CdOH^+$) from pH 4 to 7. In this system, cadmium toxicity decreased with pH. The predicted concentration of monovalent hydroxylated cadmium increased with pH until reaching a peak at pH 5.9, and then the concentration slowly decreased until pH 7. Although the concentration of the divalent cadmium ion simultaneously decreased at higher pH values, those concentrations (1.00×10^1 μM at pH 7) remained at least three orders of magnitude higher than monovalent hydroxylated cadmium concentrations (7.26×10^{-3} μM at pH 7). This suggests that, if $CdOH^+$ plays a role in mediating cadmium toxicity, it is more than three orders more toxic than Cd^{2+}.

pH-dependent metal speciation patterns differ among metals. For example, concentrations of the free, ionic species of copper and zinc in minimal media rapidly decline at pH values >5, while the free, ionic form of cobalt remains prevalent until the pH value is >8.[121] The effect of pH on hydroxo-metal species also varies among metals. In a study that investigated pH-dependent chemical speciation in seawater, Zirino and Yamamoto[140] found that monovalent hydroxylated zinc levels peaked at pH 8, whereas monovalent hydroxylated cadmium levels increased from pH 8 to 9.

The pH of a medium also impacts the formation of metal-phosphate precipitates. For example, divalent ionic cadmium (Cd^{2+}) concentrations rapidly decline as both phosphate concentration and pH increase. Sandrin and Hoffman[121] determined that when no phosphate is present in a commonly used mineral salts medium, the concentration of divalent ionic cadmium remains relatively constant until an abrupt decline above pH 8. When 15 mM inorganic phosphate is added to the medium, divalent cadmium ion concentrations rapidly decline at pH values above only 6.

Maintaining a constant pH during an experiment is crucial because of the dependency of metal speciation on pH. Buffers are required to prevent large deviations in pH throughout an experiment. Studies examining the effect of metal toxicity on biodegradation usually use a buffer that has a neutral to moderately acidic operational pH range.[75,76,89] The operational pH range is determined by the pK_a of the buffer, which is the pH at which half of the weak acid used for buffering is protonated. When the pH is beyond the operational range of a buffer, even small additions of acid, such as the excretion of acidic metabolic end products, may drastically change the pH and alter metal speciation patterns and resulting effects on microorganisms.

Microbial gene expression in response to metals is affected by pH. For example, DNA microarray experiments in our laboratory revealed that 151 genes in *E. coli* were differentially expressed between pH 5 and pH 7 treatments only in the presence of cadmium (5 μM total)[56] (Figure 11.1a). For example, a variety of stress response genes (e.g., *yciM*, *hdeA*, *blr*, *otsA*, and *yjbJ*), transport-related genes (e.g., *ycfU* and *nupG*), genes encoding oxidoreductases (e.g., *yjeS*, *ydgJ*, *ydiS*, *ygfT*, and *ybjN*), and hypothetical genes were expressed under acidic conditions only in the presence of cadmium. Cadmium has been shown to be less toxic under these conditions.[85,123,136] The mechanism by which pH affects transcriptional responses to metals is unclear, but metal speciation may play a role. Geochemical modeling software that was used in the same study[56] predicted that concentrations of toxic cadmium species, such as $CdOH^+$, were greater at pH 7 than at pH 5 (Figures 11.1b and c). Some of the hypothetical genes that were upregulated at pH 7 only in the presence of cadmium may have been involved in transport or protection from these toxic species.

11.5 STRATEGIES TO MITIGATE DELETERIOUS EFFECTS OF METALS ON MICROORGANISMS

Several techniques have been proposed for mitigating the toxicity of metals in the environment. These strategies for enhancing microbial processes, such as litter decomposition, methanogenesis, acidogenesis, nitrogen transformation, and biodegradation of organics, include using metal-resistant bacteria,[84] treatment additives,[141] clay minerals,[112] and chelating agents.[122] The manipulation of

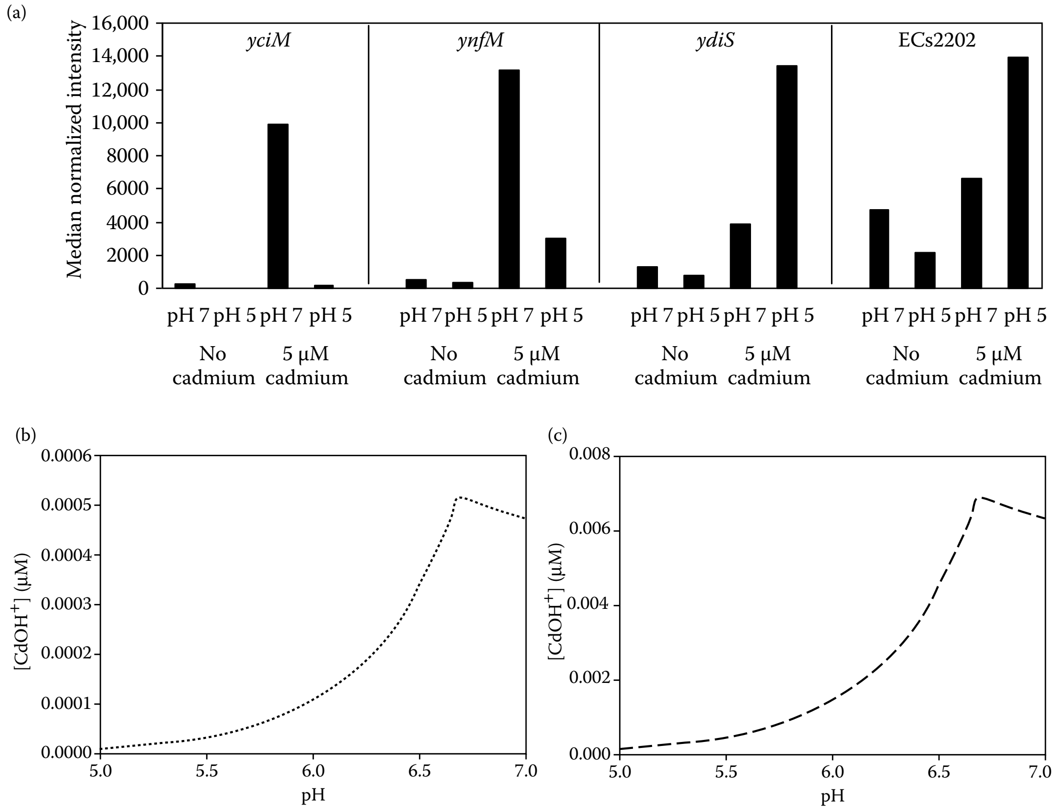

FIGURE 11.1 Effect of pH on microbial gene expression responses to cadmium. Examples of a stress response gene (*yciM*), a transport-related gene (*ynfM*), an oxidoreductase gene (*ydiS*), and a hypothetical gene (ECs2202) are provided (a). Effect of pH on (CdOH$^+$) (b) and (CdOHCl) (c) in M9 medium containing cadmium (5.4 μM) as predicted by MINEQL+ geochemical modeling software. (Parts (b) and (c) from Worden, C. et al., *FEMS Microbiol Lett*, 293, 58–64, 2009. With permission.)

physiochemical factors (i.e., divalent cation concentrations and pH) has also been explored as an approach to diminish metal toxicity.[99] The effect of pH on metal toxicity has been perhaps the most well studied of these physiochemical factors.

Few studies have investigated the use of metal-resistant bacteria in enhancing microbial processes, such as organic contaminant biodegradation in cocontaminated environments.[142] In soil microcosms contaminated with both 2,4-dichlorophenoxyacetic acid (2,4-D) (0.5 mg/g) and cadmium (0.06 mg/g), cadmium-sensitive *Alcaligenes eutrophus* JMP134 was only able to degrade 2,4-D in the presence of cadmium-resistant isolates, such as *Pseudomonas* sp., *Bacillus* sp., and *Arthrobacter* sp.[24] Cadmium was accumulated by metal-resistant microorganisms, thereby reducing cadmium bioavailability and toxicity in the environment. More recently, a strain of *Pseudomonas chlororaphis* exhibited the ability to degrade naphthalene in the presence of 100 μM nickel and cobalt.[142] This strain contained a *cnr*-like operon that provided resistance through the efflux of metal from the cell. Many other microbes appear capable of removing heavy metals from cocontaminated systems prior to bioremediation efforts. For example, *Stenotrophomonas* sp. CD02 was able to grow in complex media containing 4 mM cadmium and removed up to 80% of the dissolved metal ions after reaching stationary growth.[143]

Treatment additives, chelating agents, and clay minerals can be added to a system to bind to metals and reduce metal mobility. Treatment additives, such as carbonates, phosphates, and hydroxides, form insoluble precipitates with metals, thus decreasing their bioavailability. Jonioh et al.[141]

examined the effect of adding calcium carbonate on lead toxicity to microorganisms isolated from a contaminated environment. Additional carbonate (ranging from 1% to 10%) was found to reduce lead toxicity. The additive increased the soil pH and formed an insoluble precipitate with the lead, decreasing the overall lead bioavailability. White and Knowles[91] added excess phosphate in order to bind and remove cobalt and zinc, thus preventing metal complexation with the carbon source, nitrilotriacetic acid.

Chelating agents have been employed to reduce metal toxicity toward microorganisms used for biodegradation. EDTA has been involved in reducing the toxicity of nickel to an actinomycete[144] and of copper to bacteria and algae;[145] however, EDTA also has a strong affinity for essential metals, it is toxic to some microorganisms, and therefore may have limited applications for bioremediation.[146] Malakul et al.[122] used a less toxic, commercially available chelating resin (Chelex 100) to reduce cadmium toxicity during naphthalene biodegradation. Additional carbon sources could also be considered as metal chelators.[147] The addition of succinate (0.5% wt/vol) reduced nickel uptake in *Pseudomonas aeruginosa* (0.5-fold). Adding other carbon sources could become problematic in biodegradation studies because the microorganism could preferentially utilize the additional carbon source over the organic pollutant.

Clay minerals have been shown to reduce metal bioavailability and toxicity to a variety of organisms (112–115). Babich and Stotzky[112] reduced the toxicity of cadmium to a fungus (*Aspergillus niger*), a bacterium (*Bacillus megaterium*), and an actinomycete (*N. corallina*) by adding kaolinite (1–20%) or montmorillonite (1–5%) to an agar medium containing cadmium. Bentonite and vermiculite (3%) reduced the toxicity of cadmium to *Streptomyces bottropensis*.[114] Similarly, in solution studies, Kamel[114] reported that 3% bentonite and vermiculite reduced the toxicity of 1.33 mM cadmium to *Streptomyces bottropensis.* Increased clay concentrations resulted in greater protection.

Metal toxicity is also affected by physiochemical factors, such as pH and the concentration of divalent cations. Adding divalent cations, such as zinc, has been reported to mitigate toxicity produced by other metals. For example, the addition of 60 μM zinc reduced toxicity in *Pseudomonas putida* caused by 3 mM cadmium.[148] Zinc had no effect on cells grown in the absence of cadmium. Little is understood surrounding the mechanism of protection; however, cadmium uptake was observed to be dependent on zinc concentration.[149] Zinc was found to be a competitive inhibitor of cadmium uptake.

pH is perhaps the most well studied of the physiochemical factors affecting metal toxicity (as indicated by the numerous studies mentioned in the previous section). Although it has been widely reported that lowering pH decreases metal toxicity,[123,135,136,140] there are only a few studies that have applied this observation to biodegradation. Sandrin and Maier[85] observed the effect of pH on cadmium toxicity (334 μM) during naphthalene biodegradation by a *Burkholderia* sp. At pH 4 and 5, similar growth on naphthalene was observed in the presence and absence of cadmium; however, at pH 6 and 7, little growth occurred. A similar effect of pH on nickel toxicity was observed for *Burkholderia cepacia* PR1301.[131] Growth was not affected at pH 5 when nickel (3.41 mM) was present, but was completely inhibited at pH 7 in the presence of the same concentration of nickel.

A more detailed understanding of the effects of additives and physiochemical factors on metal toxicity should provide insight into efficient strategies for mitigating metal toxicity in the environment. These approaches are important both for reducing the inhibition of general microbial processes in soil, including litter decomposition, methanogenesis, acidogenesis, and nitrogen transformation, and for enhancing biodegradation at waste sites cocontaminated with metal and organic pollutants.

11.6 SUMMARY AND FUTURE DIRECTIONS FOR RESEARCH

Divergent reports of effects of metals on microorganisms in the environment underscore a lack of understanding about the interactions between organic and inorganic components of life. Despite all of the mechanisms that microbes employ for protection from metal toxicity, metals remain capable of producing toxic effects at high concentrations, regardless of whether or not they have biological functions. In the environment, metals inhibit many important microbial processes, ranging from decomposition of biomass or organic pollutants to nitrogen transformation and enzymatic activities. Metal toxicity in these systems is influenced by environmental conditions, including different metal speciation patterns that are based on environmental pH and ionic strength. These various levels of complexity must be taken into account in metal-contaminated systems in order to effectively mitigate metal toxicity in the environment. A number of strategies already exist, including using metal-resistant bacteria, incorporating treatment additives, and altering physiochemical factors, such as pH. It will be necessary to use a standardized set of experimental conditions to further investigate and evaluate these strategies.

The interpretation of previous attempts at measuring the impact of metals on microbially mediated processes has been hindered by the use of a wide range of experimental conditions and measurements. Already, a shift from studies based on total metal concentration to those based on bioavailable metal concentrations has occurred. The next step will entail accurately predicting and measuring metal speciation patterns in order to identify microbial responses to metal speciation. Only then will it be possible to develop more effective methods to quantify and mitigate deleterious effects of metals on the myriad processes that microbes mediate in the environment.

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12 Legislation and Regulations for Hazardous Waste

Nazih K. Shammas

CONTENTS

12.1 INTRODUCTION

Once, the amount of waste produced in the United States was small and its impact on the environment was viewed as relatively minor. Times have changed. With the industrial revolution in the late 1800s, the country began to experience unparalleled growth. New products were developed, and the consumer was offered an ever-expanding array of material goods.

This growth continued through the early twentieth century and accelerated after World War II when the nation's industrial base, strengthened by war, turned its energy toward domestic production. The results of growth, however, were not all positive. While the country produced more goods and prospered economically, it also generated more waste, both hazardous and nonhazardous. For example, at the end of World War II, U.S. industry was generating roughly 500,000 metric tons of hazardous waste per year. This amount continued to increase over the next 50 years. A national survey conducted by the United States Environmental Protection Agency (U.S. EPA) in 1996 estimated that 279 million metric tons of hazardous waste were generated nationwide in 1995, more than 500-fold.

This phenomenal growth in waste production was not mirrored by advancements in the field of waste management. Much of the waste produced entered the environment, where it often posed a serious threat to ecological systems and public health. Some of the threats posed by the mismanagement of hazardous waste are obvious. Reports of chemical accidents or spills of hazardous waste that close highways, or illegal midnight dumping that contaminates property, are familiar. Yet, even when hazardous waste is managed or disposed of in a careful manner, it may still pose a serious threat to human health and the environment. For example, toxic hazardous wastes can leak from a poorly constructed or improperly maintained hazardous waste landfill. Such waste contamination can severely, and sometimes irreversibly, pollute groundwater, the primary source of drinking water for half the nation.

Ground water pollution is not the only problem posed by hazardous waste mismanagement. The improper disposal of hazardous waste has polluted streams, rivers, lakes, and other surface waters, killing aquatic life, destroying wildlife, and stripping areas of vegetation. In other cases, careless waste disposal has been linked to respiratory illnesses, skin diseases (including skin cancer), and elevated levels of toxic materials in the blood and tissue of humans and domestic livestock. In still other cases, the mismanagement of hazardous waste has resulted in fires, explosions, or the generation of toxic gases that have killed or seriously injured workers and firefighters.

Hazardous waste is generated from many sources, ranging from industrial manufacturing process wastes, to batteries, to fluorescent light bulbs. Hazardous waste may come in many forms, including liquids, solids, gases, and sludges. To cover this wide range, U.S. EPA has developed a system to identify specific substances known to be hazardous and provide objective criteria for including other materials in this universe. The regulations contain guidelines for determining what exactly is a waste (called a solid waste) and what is excluded from the hazardous waste regulations, even though it otherwise is a solid and hazardous waste. Finally, to promote recycling and the reduction of the amount of waste entering the system, U.S. EPA provides exemptions for certain wastes when they are recycled in certain ways.

In the mid-1970s, it became clear to Congress and the American people that action had to be taken to ensure that the huge volumes of municipal and industrial solid waste, including hazardous waste generated nationwide, were managed properly. This realization began the process that resulted in the passage of the Resource Conservation and Recovery Act (RCRA) as an amendment to the Solid Waste Disposal Act (SWDA) in 1976. The goals set by RCRA[1] are

1. To protect human health and the environment from the hazards posed by waste disposal.
2. To conserve energy and natural resources through waste recycling and recovery.
3. To reduce as expeditiously as possible the amount of waste generated, including hazardous waste.

Since 1980, under RCRA Subtitle C, U.S. EPA has developed a comprehensive program to ensure that hazardous waste is managed safely: from the moment it is generated; while it is transported, treated, or stored; until the moment it is finally disposed (Figure 12.1). This cradle-to-grave management system establishes requirements for each of the following:

1. *Hazardous waste identification*: To facilitate the proper identification and classification of hazardous waste, RCRA begins with hazardous waste identification procedures.

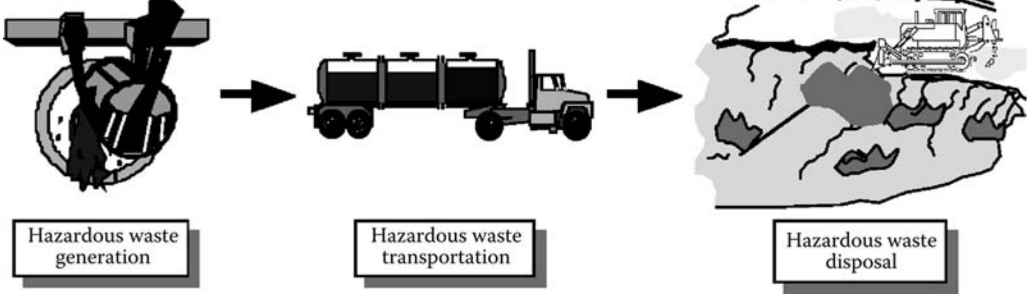

FIGURE 12.1 RCRA's cradle-to-grave hazardous waste management system. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

2. *Hazardous waste recycling and universal wastes*: To provide for the safe recycling of hazardous wastes and facilitate the management of commonly recycled materials, RCRA includes provisions for hazardous waste recycling and universal wastes.
3. *Hazardous waste generators*: To ensure proper and safe waste management, the RCRA regulations provide management standards for those facilities that produce hazardous waste and provide reduced regulations for facilities that produce less waste.
4. *Hazardous waste transporters*: To govern the transport of hazardous waste between management facilities, RCRA regulates hazardous waste transporters.
5. *Treatment, storage, and disposal facilities (TSDFs)*: To fully protect human health and the environment from hazardous waste treatment, storage, and disposal, the TSDF requirements establish generic facility management standards, specific provisions governing hazardous waste management units, and additional precautions designed to protect soil, ground water, and air resources.
6. *Land disposal restrictions (LDR)*: To reduce the hazards posed by permanently land-disposed waste, this program requires effective and expeditious hazardous waste treatment.
7. *Combustion*: To minimize the hazards posed by the burning of hazardous waste, RCRA imposes strict standards on units conducting such combustion.
8. *Permitting*: To ensure that only facilities meeting the TSDF standards are treating, storing, and disposing of hazardous waste and to provide each TSDF with a record of the specific requirements applicable to each part of its operation, RCRA requires owners and operators of these facilities to obtain a permit.
9. *Corrective action*: Since hazardous waste management may result in spills or releases into the environment, the corrective action program is designed to guide the cleanup of any contaminated air, groundwater, or soil resulting from such management.
10. *Enforcement*: To ensure that RCRA-regulated facilities, from generators to TSDFs, comply with these regulations, RCRA provides U.S. EPA with the authority to enforce provisions of the Act.
11. *State authorization*: To empower states and make enforcement more efficient, RCRA also allows U.S. EPA to authorize state governments to administer various parts of the RCRA program.

Although RCRA creates the framework for the proper management of hazardous and nonhazardous solid waste, it does not address the problems of hazardous waste found at inactive or abandoned sites or those resulting from spills that require emergency response. These problems are addressed by a different act, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly called Superfund, which was enacted in 1980.

12.2 ACTS, REGULATIONS, AND POLICY

Although RCRA is the acronym for the Resource Conservation and Recovery Act, it is often used interchangeably to refer to the law, the regulations, and the U.S. EPA policy and guidance. To avoid confusion, the term "the Act" refers to the public law and statutory requirements passed by Congress. The term "regulations" is used interchangeably with standards or regulatory requirements and means the rules developed by U.S. EPA to implement the statute.

12.2.1 The Act

The Act provides, in broad terms, general guidelines for the waste management program envisioned by Congress (e.g., U.S. EPA is directed to develop and promulgate criteria for identifying hazardous waste). The Act also provides the U.S. EPA Administrator (or his or her representative) with the necessary authority to develop these broad standards into specific requirements for the regulated community.

What is commonly known as RCRA, or the Act, is actually a combination of the first federal solid waste statutes and all subsequent amendments (Figure 12.2). In 1965, Congress enacted the SWDA, the first statute that specifically focused on improving solid waste disposal methods. The SWDA established economic incentives for states to develop planning, training, research, and demonstration projects for the management of solid waste. The Act was amended in 1976 by RCRA, which substantially remodeled the nation's solid waste management system and laid out the basic framework of the current hazardous waste management program.

The Act, which has been amended several times since 1976, continues to evolve as Congress alters it to reflect changing waste management needs. The Act was amended significantly on November 8, 1984, by the Hazardous and Solid Waste Amendments (HSWA), which expanded the scope and requirements of RCRA. HSWA was created largely in response to citizens, concerns that existing methods of hazardous waste disposal, particularly land disposal, were not safe. Because of their significance and differences in their implementation, HSWA provisions are emphasized throughout this chapter. Congress also revised RCRA in 1992 by passing the Federal Facility Compliance Act, which strengthened the authority to enforce RCRA at federal facilities. In addition, the Land Disposal Program Flexibility Act of 1996 amended RCRA to provide regulatory flexibility for the land disposal of certain wastes.

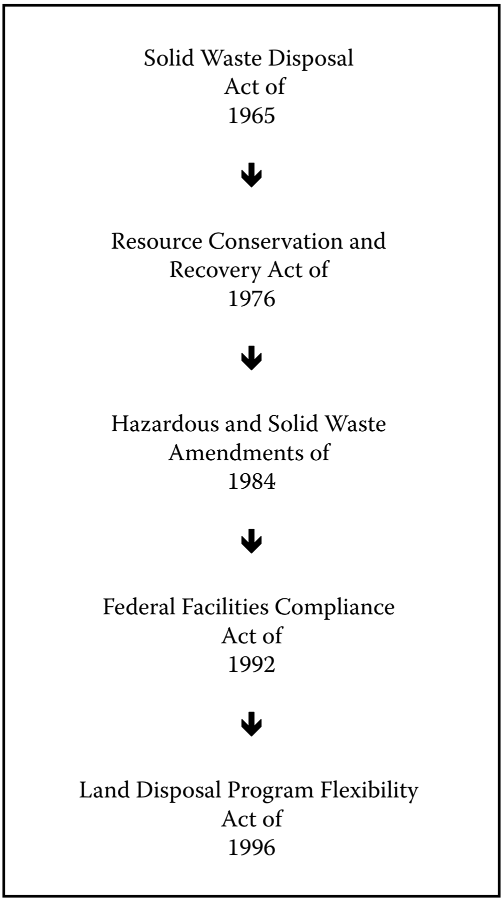

FIGURE 12.2 Evolution of significant RCRA legislation. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

TABLE 12.1
Outline of the RCRA Act

Subtitle	Provisions
A	General provisions
B	OSW; authorities of the Administrator and Interagency Coordinating Committee
C	Hazardous waste management
D	State or regional solid waste plans
E	Duties of the Secretary of Commerce in resource and recovery
F	Federal responsibilities
G	Miscellaneous provisions
H	Research, development, demonstration, and information
I	Regulation of USTs
J	Standards for the tracking and management of medical waste

Source: Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.

Today, the Act consists of 10 subtitles (Table 12.1). Subtitles A, B, E, F, G, H, and J outline general provisions; authorities of the Administrator; duties of the Secretary of Commerce; federal responsibilities; miscellaneous provisions; research, development, demonstration, and information requirements; and medical waste tracking. Other subtitles lay out the framework for the three major programs that comprise RCRA Subtitle C (the hazardous waste management program), Subtitle D (the solid waste program), and Subtitle I [the underground storage tank (UST) program].

12.2.2 REGULATIONS

The Act includes a Congressional mandate directing U.S. EPA to develop a comprehensive set of regulations. Regulations, or rulemakings, are issued by an agency, such as U.S. EPA, that translate the general mandate of a statute into a set of requirements for the Agency and the regulated community.

Regulations are developed by U.S. EPA in an open and public manner according to an established process. When a regulation is formally proposed, it is published in an official government document called the *Federal Register* to notify the public of U.S. EPA's intent to create new regulations or modify existing ones. U.S. EPA provides the public, which includes the potentially regulated community, with an opportunity to submit comments.

The final regulation is published, or promulgated, in the *Federal Register*.[1] Included with the regulation is a discussion of the Agency's rationale for the regulatory approach, known as preamble language. Final regulations are compiled annually and incorporated into the Code of Federal Regulations (CFR) according to a highly structured format based on the topic of the regulation. This latter process is called codification, and each CFR title corresponds to a different regulatory authority. For example, U.S. EPA's regulations are in Title 40 of the CFR. The codified RCRA regulations can be found in Title 40 of the CFR, Parts 240–282. These regulations are often cited as 40 CFR, with the part listed afterward (e.g., 40 CFR Part 264), or the part and section (e.g., 40 CFR §264.10).

Although this relationship between an Act and the regulations is the norm, the relationship between HSWA and its regulations differs slightly. Congress, through HSWA, not only provided U.S. EPA with a general mandate to promulgate regulations but also placed explicit instructions in the statute to develop certain regulations. Many of these requirements are so specific that U.S.

EPA incorporated them directly into the regulations. HSWA is all the more significant because of the ambitious schedules that Congress established for implementation of the Act's provisions. Another unique aspect of HSWA is that it established statutory requirements that would go into effect automatically (with the force of regulations) if U.S. EPA failed to issue regulations by certain dates.

The interpretation of statutory language does not end with the codification of regulations. U.S. EPA further clarifies the requirements of the Act and its regulations through guidance documents and policy. It published the *RCRA Orientation Manual*[2] in order to educate and inform the public about the broad requirements of RCRA's regulatory program. Two other U.S. EPA documents provide an informative look back at the past and a speculative look forward to the future of the RCRA program. For a look back, the report *25 Years of RCRA: Building on Our Past to Protect Our Future*[3] commemorates RCRA's 25th Anniversary in October 2001 and highlights the accomplishments of RCRA's protective framework to date. For a look ahead, the draft white paper *Beyond RCRA: Prospects for Waste and Materials Management in the Year 2020*[4] identifies trends that could affect the future of waste management and resource conservation and also suggests general strategies that might be used to build a new vision for the future of the program.

12.2.3 Guidance and Policy

Guidance documents are issued by U.S. EPA primarily to provide direction for implementing and complying with regulations. They are essentially "how to" documents. For example, the regulations in 40 CFR Part 270 detail what is required in a permit application for a hazardous waste management facility, while the guidance for this Part suggests how to evaluate a permit application to ensure that all information has been included. Guidance documents also elaborate on the U.S. EPA's interpretation of the requirements of the Act.

Policy statements, on the other hand, specify operating procedures that should generally be followed. They are mechanisms used by U.S. EPA program offices to outline the manner in which the RCRA programs are implemented. For example, U.S. EPA's Office of Solid Waste (OSW) may issue a policy outlining what actions should generally be taken to achieve RCRA corrective action cleanup goals. In many cases, policy statements are addressed to the staff working on implementation, but they may also be addressed to the regulated community.

12.3 OVERVIEW OF RCRA PROGRAMS

To provide an overall perspective on how RCRA works, each of its programs—solid waste, hazardous waste, and USTs—and their interrelationships are briefly summarized here. The Subtitle D (solid waste) program is discussed prior to the Subtitle C (hazardous waste) program. Although this is alphabetically out of order, the structure is designed for better understanding by the reader.

12.3.1 RCRA Subtitle D: Solid Waste

RCRA's solid waste management program encourages environmentally sound solid waste management practices that maximize the reuse of recoverable material and foster resource recovery. The term "solid waste" is very broad, including not only the traditional nonhazardous solid wastes, such as municipal garbage, but also some hazardous wastes. RCRA Subtitle D addresses solid wastes, including those hazardous wastes that are excluded from the Subtitle C regulations (e.g., household hazardous waste) and hazardous waste generated by conditionally exempt small quantity generators (CESQGs).

The U.S. EPA recommends an integrated, hierarchical approach for managing municipal solid waste that includes[1,2]

1. Source reduction
2. Recycling
3. Combustion
4. Landfilling.

Here, source reduction and recycling are the preferred elements of the system.

Subtitle D focuses on state and local governments as the primary planning, regulating, and implementing entities for the management of nonhazardous solid waste, such as household garbage and nonhazardous industrial solid waste. U.S. EPA provides these state and local agencies with information, guidance, and policy and regulations through workshops and publications to help states and the regulated community make better decisions in dealing with waste issues, to reap the environmental and economic benefits of source reduction and recycling of solid wastes, and to require upgrading or closure of all environmentally unsound disposal units. In order to promote the use of safer units for solid waste disposal, U.S. EPA developed federal criteria for the proper design and operation of landfills and other solid waste disposal facilities. Many states have adopted these criteria into their state solid waste programs.

12.3.2 RCRA SUBTITLE C: HAZARDOUS WASTE

RCRA Subtitle C establishes a federal program to manage hazardous wastes from the moment it is generated to the moment it is finally disposed—that is, from cradle to grave.[2] The objective of the Subtitle C program is to ensure that hazardous waste is handled in a manner that protects human health and the environment. To this end, there are Subtitle C regulations for the generation, transportation and treatment, storage, or disposal of hazardous wastes. In practical terms, this means regulating a large number of hazardous waste handlers. As of 1999, U.S. EPA had on record 1575 TSDFs; 17,000 transporters; and about 20,000 large quantity generators (LQGs).[2]

The Subtitle C program has resulted in perhaps the most comprehensive regulations U.S. EPA has ever developed. The regulations first identify the criteria to determine which solid wastes are hazardous, and then establish various requirements for the three categories of hazardous waste handlers: generators, transporters, and TSDFs. In addition, the Subtitle C regulations set technical standards for the design and safe operation of TSDFs. These standards are designed to minimize the release of hazardous waste into the environment. Furthermore, the regulations for TSDFs serve as the basis for developing and issuing the permits required by the Act for each facility. Permits are essential to making the Subtitle C regulatory program work, since it is through the permitting process that U.S. EPA or a state applies the technical standards to TSDFs.

The hazardous waste management program includes safeguards to protect human health and the environment from hazardous waste that is disposed of on the land. These safeguards are known as the LDR. RCRA also minimizes the hazards of burning hazardous waste by imposing strict standards on combustion units. Because hazardous waste management may result in spills or releases into the environment, RCRA also contains provisions governing corrective action, or the cleanup of contaminated air, groundwater, and soil.

Since waste recycling and recovery are the major components of RCRA's goals, they must be implemented consistently with proper hazardous waste management. As a result, RCRA contains provisions to ensure safe hazardous waste recycling and to facilitate the management of commonly recycled wastestreams.

The RCRA statute additionally grants U.S. EPA broad enforcement authority to require all hazardous waste management facilities to comply with the regulations. The program also contains provisions that allow U.S. EPA to authorize state governments to implement and enforce the hazardous waste regulatory program. State programs must be at least as stringent as the federal program.

12.3.3 RCRA Subtitle I: USTs

RCRA Subtitle I regulates USTs that contain petroleum or hazardous substances. A major objective of Subtitle I is to prevent and clean up releases from tanks. Under Subtitle I, U.S. EPA has developed performance standards for new tanks, upgrading requirements for existing tanks, and regulations to prevent, detect, and clean up releases at all UST sites. State UST programs may be approved to operate in lieu of the federal program.

Many UST owners and operators must secure loans from financial and other institutions to comply with environmental regulations, such as UST upgrading and maintenance requirements. The program contains specific provisions to protect lending institutions from liability that they might incur from extending these loans. Similar to RCRA Subtitle C, Subtitle I contains provisions that allow U.S. EPA to approve state government implementation and enforcement of the UST regulatory program.

The expense and threats of contamination from leaking USTs necessitate efficient, effective, and thorough cleanups. To guarantee that such cleanups will be conducted in an efficient and protective manner, Subtitle I also established a Leaking Underground Storage Tank (LUST) Trust Fund. The Fund facilitates cleanup oversight and guarantees cleanups when the responsible owner and operator cannot take action, or when the situation requires emergency response.

12.3.4 Miscellaneous Statutory Provisions

Consistent with RCRA's focus on recycling, the statute contains provisions for U.S. EPA to encourage recycling and promote the development of markets for items with recovered materials content. To help achieve this goal, U.S. EPA publishes federal procurement guidelines that set minimum recovered materials content standards for certain designated items. RCRA requires federal procuring agencies to purchase items composed of the highest percentage of recovered materials practicable. These requirements are specified in Comprehensive Procurement Guidelines (CPGs) and Recovered Materials Advisory Notices (RMANs).

RCRA's focus is not limited to solid waste, hazardous waste, or USTs. Medical waste can pose similar threats to human health and the environment. As a result, RCRA established a medical waste tracking program to ensure that such waste is properly handled from the moment it is generated to the moment it is disposed. This program was a demonstration program that began on June 22, 1989 and ended on June 22, 1991. At this time, the program has expired and no federal U.S. EPA tracking requirements are currently in effect, although some states have medical waste requirements.

12.3.5 RCRA and Its Relationship to Other Environmental Statutes

RCRA is only one of several regulatory programs in place to protect the environment. The RCRA regulations work closely with other environmental statutes such as the Clean Air Act (CAA); Clean Water Act (CWA); the Emergency Planning and Community Right-to-Know Act (EPCRA); the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA); the Marine Protection, Research, and Sanctuaries Act (MPRSA); the Occupational Safety and Health Act (OSHA); the Safe Drinking Water Act (SDWA); and the Toxic Substances Control Act (TSCA).

One statute in particular, the CERCLA, or Superfund, is closely tied to RCRA: both are designed to protect human health and the environment from the dangers of hazardous waste. While these programs are similar, they do have different regulatory focuses: RCRA regulates how wastes should be managed to avoid potential threats to human health and the environment; CERCLA focuses on actual releases, or substantial threats of a release in the environment of a hazardous substance, pollutant, or contaminant that present an imminent and substantial threat to human health.

12.3.6 PUBLIC INVOLVEMENT IN RCRA

The regulated community that must understand and comply with RCRA and its regulations is a large, diverse group. It includes not only facilities typically thought of as hazardous waste generators, such as industrial manufacturers, but also government agencies and small businesses, such as a local dry cleaner generating small amounts of hazardous solvents, or a gas station with underground petroleum tanks.

RCRA contains extensive public participation and involvement provisions to facilitate public participation in the permitting, corrective action, and state authorization processes. U.S. EPA, consistent with the requirements of the Administrative Procedures Act (APA), proactively involves the public every time the Agency issues a rulemaking that establishes or changes regulatory provisions. The RCRA program seeks to ensure that all segments of the population have an equal opportunity to participate in the regulatory process and equal access to regulatory information.

12.4 RCRA TODAY

When RCRA was first enacted in 1976, U.S. EPA was faced with a huge implementation task. The bulk of the activity during the first few years focused on developing basic regulations for the management of both hazardous and nonhazardous solid waste in order to provide adequate protection of human health and the environment. Although most of these elementary standards are now in place, the RCRA program has not remained stagnant. U.S. EPA continues to measure and analyze the program's results to help identify ways to make the RCRA program more efficient and achieve better, more cost-effective protection of public health and the environment.

12.4.1 WASTE MINIMIZATION

U.S. EPA has devoted much of its efforts in the past to the treatment and cleanup of pollutants after they are generated. In fact, great strides have been made in environmental protection over the past 20 years. U.S. EPA realizes, however, that there are environmental and economic incentives to reducing or eliminating waste before it is even generated. Consequently, both the RCRA solid and hazardous waste programs have adopted waste minimization elements. U.S. EPA uses the term "waste minimization" to mean the reduction, to the extent feasible, of solid and hazardous waste. Both programs emphasize source reduction (reducing waste at its source, before it is even generated) and environmentally sound recycling.

In the text of HSWA, Congress specifically declared that the reduction or elimination of hazardous waste generation at the source should be a priority of the RCRA hazardous waste program. To encourage hazardous waste minimization nationwide, U.S. EPA developed the Waste Minimization National Plan. This initiative promotes a long-term national effort to minimize the generation of hazardous chemicals in wastes. The goals of the National Plan include the following[2]

1. Reducing the presence of the most persistent, bioaccumulative, and toxic (PBT) chemicals in hazardous wastes by 50% by the year 2005.
2. Emphasizing source reduction and environmental source recycling over treatment and disposal.
3. Preventing transfers of chemical releases from one medium (air, water, and land) to another.

U.S. EPA has also developed strategies and priorities for encouraging source reduction and recycling of nonhazardous solid wastestreams regulated by RCRA Subtitle D. It envisions a flexible integrated waste management hierarchy where source reduction, recycling, waste combustion, and landfilling all play a part in the successful management of solid waste at the local level. Source reduction and recycling are preferred approaches and are at the top of the management hierarchy. Waste combustion and landfilling are less emphasized. In addition, to expand the use of recovered materials, U.S. EPA has developed the procurement program, which establishes guidelines recommending that federal agencies purchase products containing recycled materials.

12.4.2 Streamlining the RCRA Regulation

U.S. EPA is currently identifying options to reinvent the RCRA program by streamlining compliance requirements. It reinvention philosophy includes providing flexibility in how results are achieved, sharing information and decision making with all stakeholders, creating incentives for compliance with environmental requirements, lessening the burden of complying with environmental requirements, and seeking a better interface with other environmental regulations.

U.S. EPA is also placing an increasing emphasis on making the RCRA hazardous waste program more risk based and results based (i.e., ensuring that the regulations correspond to the level of risk posed by the hazardous waste being regulated and that technicalities will not interfere with the ultimate goals for a site). This approach is particularly valuable for the cleanup of contaminated sites. Placing excessive regulation on sites whose contamination poses low risks to human health and the environment may create disincentives for cleanup. Focusing regulations on risk and results would allow states greater flexibility in determining the appropriate way to clean up sites contaminated with relatively small quantities of hazardous waste.

12.4.3 Subtitle C Federal/State Partnership

RCRA, like most federal environmental legislation, encourages states to develop their own hazardous waste programs as an alternative to direct implementation of the federal program. At the inception of RCRA, Congress envisioned that a successful national program would be put in place through joint action of the federal and state governments—U.S. EPA would set national goals and standards based on the Agency's technical expertise, and the states would be responsible for implementing those policies.

Because its hazardous waste regulations are developed in stages, over time, U.S. EPA has a phased approach for approving state programs. Each state must either adopt the new regulations or upgrade those elements of its program that do not meet federal standards. The authorization process is often long and cumbersome. U.S. EPA has developed streamlined procedures for these state revisions to make the process quicker and more efficient. These procedures help reduce the amount of resources needed for preparing and processing authorization applications and speed up state implementation of additional parts of the RCRA program.

12.4.4 Demonstrating Results

It is important for the U.S. EPA to develop protective environmental goals, and it is equally important for it to determine if these goals are actually being achieved. Recognizing this, Congress enacted the Government Performance and Results Act (GPRA) of 1993 to provide for the establishment of strategic planning and performance measurements throughout the federal government. The intent of GPRA is to improve public confidence in federal agencies by holding agencies accountable for achieving program results.

U.S. EPA adopted the GPRA framework by developing an Agency-wide strategic plan that encompasses all U.S. EPA offices and program areas. The strategic plan contains several goals specific to RCRA, such as preventing pollution, reducing risk to humans and the environment, better waste management, and restoration of contaminated waste sites. As part of the requirements of GPRA, U.S. EPA has also developed specific and quantifiable objectives for each of these goals. Progress toward these target objectives is measured and evaluated annually. This framework ensures that U.S. EPA can evaluate the success of its different programs and can demonstrate tangible results to the general public.

12.5 HAZARDOUS WASTE RECYCLING, USED OIL, AND UNIVERSAL WASTES

RCRA hazardous wastes do not cease to be dangerous simply because they are being reused, recycled, or reclaimed. Many hazardous waste recycling operations may pose serious health and environmental hazards and should be subject to regulation. Reuse, recycling, and reclamation should be viewed instead as ways of managing hazardous wastes, which, if properly conducted, can avoid environmental hazards, protect scarce natural resources, and reduce the nation's reliance on raw materials and energy. Promoting reuse and recovery is certainly one of the goals of RCRA; however, this goal does not take precedence over assuring the proper management of hazardous waste.

U.S. EPA has tried, to the extent possible, to develop regulations for hazardous waste management that foster environmentally sound recycling and conservation of resources, but at the same time provide adequate protection of human health and the environment. This chapter outlines the regulations governing recycling of hazardous wastes, and describes special management standards for two commonly recycled wastestreams: used oil and universal wastes.

12.5.1 HAZARDOUS WASTE RECYCLING

The hazardous waste identification process (as discussed in Chapter 1) describes how to determine whether a material is a solid and hazardous waste. How a material is regulated under RCRA (i.e., whether or not it is a solid and potentially a hazardous waste) when it is recycled depends on what type of material it is and what type of recycling is occurring. If the recycled material is not a solid waste, then it is not a hazardous waste and is not subject to RCRA Subtitle C requirements. However, if the material qualifies as a solid and hazardous waste, it is subject to RCRA Subtitle C jurisdiction.

Many hazardous wastes can be recycled safely and effectively. To address the goal of encouraging recycling while protecting human health and the environment, U.S. EPA has tried to tailor the level of regulation to reflect the actual hazard of the recycling activity. In this approach to regulation, recycling standards range from full regulation to specialized standards to exemptions from regulation. Handlers of hazardous waste slated for recycling must determine what type of regulation they fall under based on the recycling activity being conducted and the type of material being managed.

12.5.1.1 Full Regulation

Most recycled hazardous wastes are subject to full hazardous waste regulation. This means that handlers of these recyclable materials (i.e., persons who generate, transport, or store these prior to recycling) are subject to the same regulations as handlers who are managing hazardous wastes prior to disposal.

While management of the hazardous wastes prior to recycling is subject to regulation, the recycling process itself is exempt from RCRA (except for some air emission standards). For example, if a facility receives hazardous spent solvents from another facility for redistillation (heating a mixture to separate it into several pure components), the recycling units themselves are not subject to RCRA design and operating standards for hazardous waste units. However, the owners and operators of the recycling facility must follow all applicable RCRA Subtitle C requirements (including the requirement to obtain a permit) for container or tank storage areas used to store such wastes prior to recycling.

12.5.1.2 Exemptions

Not all hazardous wastes pose the same degree of hazard when recycled. U.S. EPA believes that wastes that may be recycled in a protective manner, or that are addressed under other environmental regulations, warrant exemptions from RCRA Subtitle C. Consequently, handlers of these materials are not subject to any hazardous waste regulations. These exempt recyclable hazardous wastes are[2]

1. *Industrial ethyl alcohol*: Industrial ethyl alcohol that is reclaimed is exempt from RCRA Subtitle C because the U.S. Bureau of Alcohol, Tobacco, and Firearms (BATF) already regulates it from the point of generation to redistillation.
2. *Scrap metal*: Scrap metal that is disposed of or recycled is a solid waste; however, it is exempt from Subtitle C regulation when it is reclaimed (i.e., recycled to recover metal content). This does not apply to processed scrap metal that is excluded from hazardous waste regulation entirely.
3. *Waste-derived fuels from refining processes*: Fuels produced by refining oil-bearing hazardous wastes with normal process streams at petroleum refining facilities are exempt if such wastes resulted from normal petroleum refining, production, and transportation practices. For these wastes to be considered as refined, they must be inserted into a part of the process designed to remove contaminants. This would typically mean insertion prior to distillation.
4. *Unrefined waste-derived fuels and oils*: Fuels produced at a petroleum refinery from oil-bearing hazardous wastes that are introduced into the refining process after the distillation step or that are reintroduced in a process that does not include distillation are exempt if the resulting fuel meets the specifications under the federal recycled used oil standards. Oil that is recovered from hazardous waste at a petroleum refinery and burned as a fuel is also exempt provided it meets the used oil specifications.

12.5.1.3 Special Standards

While RCRA specifically exempts some wastes when recycled, some recycling processes may still pose enough of a hazard to warrant some degree of regulation. However, due to the nature of the recycling process itself or the nature of the materials being recycled, these processes may require a specialized set of standards. These processes are as follows[2]:

1. *Use constituting disposal*: Use constituting disposal refers to the practice of recycling hazardous wastes by placing them on the land or using them as ingredients in a product that will be placed on the land. To be placed on the land, waste-derived products must (1) be made for the general public's use; (2) have undergone a chemical reaction so as to be inseparable by physical means; and (3) meet applicable LDR treatment standards. Once these waste-derived products meet these standards, they are no longer restricted from placement on the land. Materials that do not meet these criteria remain regulated. There are also special standards for hazardous wastes used to make zinc micronutrient fertilizers.
2. *Precious metals reclamation*: Precious metals reclamation is the recycling and recovery of precious metals (i.e., gold, silver, platinum, palladium, iridium, osmium, rhodium, and ruthenium) from hazardous waste. Because U.S. EPA found that these materials will be handled protectively as valuable commodities with significant economic value, generators, transporters, and storers of such recyclable materials are subject to reduced requirements.
3. *Spent lead–acid battery reclamation*: Persons who generate, transport, regenerate, collect, and store spent lead–acid batteries prior to reclamation, but do not perform the actual reclamation, are not subject to hazardous waste regulation. U.S. EPA established those provisions to encourage the recycling of these batteries. However, owners and

operators of facilities that store spent batteries before reclamation, other than spent batteries that are regenerated (processed to remove contaminants and restore the product to a useable condition), are subject to regulation in a manner similar to hazardous waste TSDFs. Handlers of lead–acid batteries may also choose to manage them under the universal waste provisions.

4. *Burning for energy recovery*: The process of recycling hazardous waste by burning it for energy recovery may pose significant air emission hazards. Therefore, U.S. EPA established specific operating standards for units burning hazardous wastes for energy recovery. These units are known as boilers and industrial furnaces (BIFs).

12.5.2 USED OIL

In developing a hazardous waste regulatory program to facilitate and encourage recycling, Congress felt that certain commonly recycled materials warranted a regulatory program of their own. As a result, Congress and U.S. EPA created special management standards for used oil. Under these standards, recycled used oil is not subject to the hazardous waste regulatory program applicable to other recycled materials, but rather to its own management provisions.

Used oil has certain unique properties that make it distinct from most hazardous wastestreams. First of all, used oil is generated by a wide range of entities, including, but not limited to, large manufacturing facilities, industrial operations, service stations, quick-lube shops, and even households. Every year privately owned automobile and light trucks generate over 300 million gallons of used crank case oil. Second, used oil is an easily recyclable material. For example, just 1 gallon of used oil provides the same 2.5 quarts of lubricating oil as 42 gallons of crude oil. However, even used oil that does not exhibit any characteristics of hazardous waste can have harmful effects if spilled or released into the environment.

12.5.2.1 Used Oil Regulation

In an effort to encourage the recycling of used oil, and in recognition of the unique properties and potential hazards posed by used oil, Congress passed the Used Oil Recycling Act in 1980. This Act amended RCRA by requiring U.S. EPA to study the hazards posed by used oil and to develop used oil management standards to protect human health and the environment. As a result, U.S. EPA developed special recycling regulations for used oil that are completely separate from hazardous waste recycling standards. First, in November 1985, U.S. EPA promulgated restrictions on the burning of used oil for energy recovery. Second, in September 1992, U.S. EPA developed a more comprehensive used oil recycling program[5] that incorporated the existing burning restrictions, and added used oil management standards for all facilities that handle used oil.

Since U.S. EPA's used oil program is designed to encourage used oil recycling, the regulations include a recycling presumption, namely, an assumption that all used oil that is generated will be recycled. The recycling presumption simplifies the used oil management system by enabling handlers to only comply with the used oil regulations, instead of the hazardous waste regulations. Only when the used oil is actually disposed of or sent for disposal must handlers determine whether or not the used oil exhibits a characteristic of hazardous waste and manage it in accordance with hazardous waste regulations. For additional information about used oil management, refer to Ref. 6.

12.5.2.2 Used Oil Characteristics

Used oil is any oil that has been refined from crude oil or any synthetic oil that has been used and, as a result of such use, is contaminated by physical or chemical impurities. In other words, used oil must meet each of the following three criteria: origin, use, and contamination. First, the used oil must be derived from crude oil or synthetic oil (i.e., derived from coal, shale, or polymers). Second, the oil must have been used as a lubricant, hydraulic fluid, heat transfer fluid, or other similar uses. Unused oil such as cleanout tank bottoms from virgin product fuel oil storage is not used oil because it has not been used. Finally, the used oil must be contaminated by physical or chemical impurities as a result of such use. Physical impurities could include contamination by metal shavings, sawdust, or dirt. Chemical impurities could include contamination by water or benzene, or degradation of lubricating additives.

12.5.2.3 Used Oil Handlers

Persons who handle used oil are subject to specific management requirements depending on the extent of their used oil recycling activities. The following handlers are subject to used oil management standards:[2]

1. *Generators*: Used oil generators are persons whose actions or processes produce used oil, or first causes used oil to be subject to regulation. Examples of common generators include car repair shops, service stations, and metalworking industries. Individuals who generate used oil through the maintenance of their own personal vehicles and equipment, known as used oil do-it-ourselfers, are not considered used oil generators.
2. *Collection centers and aggregation points*: Used oil collection centers and aggregation points are facilities that accept small amounts (<55 gallons) of used oil and store it until enough is collected to ship it elsewhere for recycling. Used oil collection centers typically accept used oil from multiple sources that include both businesses and private citizens. Used oil aggregation points collect oil from places run by the same owner and operator as the aggregation point, and also from private citizens.
3. *Transporters*: Used oil transporters are persons who haul used oil in quantities >55 gallons and deliver it to transfer facilities, rerefiners, processors, or burners.
4. *Transfer facilities*: Used oil transfer facilities are any structures or areas (such as loading docks or parking areas) where used oil is held for longer than 24 hours, but not longer than 35 days, during the normal course of transportation.
5. *Processors and rerefiners*: Used oil processors and rerefiners are facilities that process used oil so that it can be burned for energy recovery or reused.
6. *Burners*: Used oil burners are handlers who burn used oil for energy recovery in boilers, industrial furnaces, or hazardous waste incinerators.
7. *Marketers*: Used oil marketers are handlers who either (1) direct shipments of used oil to be burned as fuel in regulated devices (i.e., boilers, industrial furnaces, and incinerators) or (2) claim that used oil to be burned for energy recovery is on-specification. A marketer must already be a used oil generator, transporter, processor, rerefiner, or burner.

12.5.2.4 Used Oil Management Standards

The used oil management standards apply to a wide variety of facilities with very different business practices. These standards are designed to establish minimum regulations for all facilities, addressing such practices as proper storage, transportation, recordkeeping, and burning. These standards vary by facility type. The most stringent requirements apply to facilities that process or rerefine used oil. Used oil transporters, transfer facilities, and used oil burners are subject to a reduced set of standards. Generators have the fewest requirements.

12.5.2.4.1 Used Oil as a Hazardous Waste

Because used oil mixed with hazardous wastes increases risks to human health and the environment, all handlers are encouraged to keep used oil from becoming contaminated with hazardous wastes. To prevent intentional mixing, U.S. EPA subjects mixtures of used oil and listed hazardous waste to all applicable hazardous waste standards.

From an enforcement point of view, however, the Agency cannot always determine whether used oil has been mixed with a listed hazardous waste. As a result, U.S. EPA decided to use an objective test that focused on the halogen level in used oil (listed spent halogenated solvents were often found to be mixed with used oil). This objective test is known as the rebuttable presumption. According to this test, used oil that contains more than 1000 mg/L of total halogens is presumed to have been mixed with a listed hazardous waste, and is therefore subject to applicable hazardous waste regulations. A person may rebut this presumption by demonstrating through analysis or other documentation that the used oil has not been mixed with listed hazardous waste. Nevertheless, used oil that is known to have been mixed with a listed hazardous waste is considered a listed hazardous waste, regardless of the halogen level.

The principle for mixtures of used oil and characteristic hazardous waste is somewhat different. First, if used oil is mixed with a waste that only exhibits the characteristic of ignitability, or is listed solely for ignitability, and the resultant mixture is no longer ignitable, then the mixture can be managed as used oil, despite the inherent characteristics that the used oil may bring to the mixture. U.S. EPA believes that materials that are ignitable-only should not affect the chemical constituent or other properties of used oil when mixed, and therefore, should not add additional risks to human health and the environment when burned. However, used oil mixed with a waste that is hazardous because it exhibits one or more characteristics of hazardous waste (other than just ignitability) must no longer exhibit any characteristics if it is going to be managed as used oil.

12.5.2.4.2 Used Oil Contaminated with Polychlorinated Biphenyls

The use and disposal of polychlorinated biphenyls (PCBs) are regulated by the TSCA. In addition to the RCRA used oil management standards, marketers and burners of used oil contaminated with any quantifiable level of PCBs are subject to the current TSCA requirements, which provide comprehensive management standards for such used oils.

12.5.2.4.3 Storage

Although different used oil handlers may have specific management requirements for their oil, all handlers must

1. Store used oil in tanks and containers. Storage of used oil in lagoons, pits, or surface impoundments is prohibited, unless these units are subject to hazardous waste TSDF standards.
2. Clearly mark containers and tanks with the words “used oil.”
3. Keep containers and tanks in good condition and free of leaks.
4. Respond to releases of used oil from their storage units.

Transfer facilities, processors and rerefiners, and burners must also have secondary containment systems to prevent oil from reaching the environment in the event of a spill or leak. Secondary containment consists of an oil-impervious dike, berm, or retaining wall to contain releases, as well as an oil-impervious floor to prevent migration.

12.5.2.4.4 Burning Restrictions

Levels of contamination in used oils may vary widely, depending on different types of uses or length of use. Recognizing this fact, U.S. EPA has established a set of criteria, called used oil specifications (Table 12.2), to evaluate the potential hazards posed by used oil when burned for energy recovery. Used oil that is tested and is not within these set of parameters is termed “off-specification used oil.”

Off-specification used oil may be burned for energy recovery, but it is strictly regulated. Such used oil may only be burned in

1. Boilers
2. Industrial furnaces

TABLE 12.2
U.S. EPA Used Oil Specifications

Parameter	Allowable Level
Arsenic	5 mg/L maximum
Cadmium	2 mg/L maximum
Chromium	10 mg/L maximum
Flash point	100°F minimum
Lead	100 mg/L maximum
Total halogens	4000 mg/L maximum

Source: Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.

3. Hazardous waste incinerators
4. Generator space heaters that meet certain operating conditions

Conversely, used oil that meets all specification levels, which is known as on-specification used oil, is not subject to any restrictions when burned for energy recovery. In fact, on-specification used oil is comparable to product fuel in terms of regulation. Once the specification determination is made, and certain recordkeeping requirements are complied with, the on-specification used oil is no longer subject to used oil management standards.

12.5.3 UNIVERSAL WASTE

The special management provisions for used oil clearly eased the management burden and facilitated the recycling of such material. U.S. EPA also discovered that subjecting other commonly recycled materials to hazardous waste regulation was burdensome for many handlers of these wastes. This burden has the potential of discouraging waste recycling by facilities that are otherwise willing to engage in such activity. In response to these concerns, U.S. EPA promulgated the universal waste program in May 1995.[7]

The universal waste program promotes the collection and recycling of certain widely generated hazardous wastes, known as universal wastes. Three types of waste were originally covered under the universal waste regulations and a fourth was added in July 1999:

1. Hazardous waste batteries.
2. Hazardous waste pesticides that are either recalled or collected in waste pesticide collection programs.
3. Hazardous waste thermostats.
4. Hazardous waste lamps.

In June 2002, U.S. EPA proposed to add mercury-containing equipment. Other similar wastes may be added to the universal waste regulations in the future. The regulated community may also petition U.S. EPA to include additional wastes in the universal waste program.

There are four types of regulated participants in the universal waste system:

1. Small quantity handlers of universal waste (SQHUW).
2. Large quantity handlers of universal waste (LQHUW).
3. Universal waste transporters.
4. Universal waste destination facilities.

A complete overview of the universal waste regulations can be found in Ref. 8.

12.5.3.1 Universal Waste Handlers

There are two types of handlers of universal waste. The first type of handler is a person who generates, or creates, universal waste. For example, this may include a person who uses batteries, pesticides, thermostats, or lamps and who eventually decides that they are no longer usable. The second type of handler is a person who receives universal waste from other handlers, accumulates the waste, and then sends it on to other handlers, recyclers, or treatment or disposal facilities without performing the actual treatment, recycling, or disposal. This may include a person who collects batteries, pesticides, or thermostats from small businesses and sends the wastes to a recycling facility. The universal waste handler requirements depend on how much universal waste a handler accumulates at any one time.

12.5.3.1.1 Small Quantity Handlers of Universal Waste

SQHUW accumulate <5000 kg (approximately 11,000 lb) of all universal waste categories combined at their location at any time. Accumulation time for universal wastes at any location is limited to one year. SQHUW are required to manage universal waste in a way that prevents releases to the environment. They must also immediately respond to releases of universal waste. They must distribute basic waste handling and emergency information to their employees to ensure that their staff are aware of proper handling and emergency procedures.

12.5.3.1.2 Large Quantity Handlers of Universal Waste

LQHUW accumulate a total of 5000 kg or more of universal waste at any time. The designation as an LQHUW is retained for the remainder of the calendar year in which the 5000-kg threshold was exceeded, and may be re-evaluated in the following calendar year. LQHUW must comply with the same requirements as SQHUW, as well as a few additional ones. They must also maintain basic records documenting shipments received at the facility and shipments sent from the facility, must obtain an U.S. EPA identification (ID) number, and must comply with stricter employee training requirements.

12.5.3.2 Universal Waste Transporters

Universal waste transporters are persons who transport universal waste from handlers of universal waste to other handlers, destination facilities, or foreign destinations. These wastes do not need to be accompanied by an RCRA hazardous waste manifest during transport, but transporters must comply with applicable Department of Transportation (DOT) requirements.

Transporters may store universal waste for up to 10 days at a transfer facility during the course of transportation. Transfer facilities are transportation-related facilities such as loading docks, parking areas, and storage areas. If a transporter keeps universal waste for more than 10 days at one location, the transporter is subject to all applicable SQHUW or LQHUW regulations.

12.5.3.3 Universal Waste Destination Facilities

Universal waste destination facilities are facilities that treat, dispose of, or recycle a particular category of universal waste. These facilities are subject to the same requirements as fully regulated hazardous waste TSDFs. Full regulation includes permit requirements, general facility standards, and unit-specific standards. The universal waste program includes only two additional specific universal waste requirements for destination facilities. These requirements are procedures for rejecting shipments of universal waste and the documentation of the receipt of universal waste.

12.6 HAZARDOUS WASTES REGULATIONS GOVERNING GENERATORS, TRANSPORTERS, AND TSDFs

12.6.1 HAZARDOUS WASTES GENERATORS

Under RCRA, hazardous waste generators are the first link in the cradle-to-grave hazardous waste management system. All generators must determine whether their waste is hazardous and must oversee the ultimate fate of the waste. RCRA requires generators to ensure and fully document that the hazardous waste they produce is properly identified, managed, and treated prior to recycling or disposal. The degree of regulation to which each generator is subject depends to a large extent on how much waste each generator produces every calendar month. The regulations applicable to generators of hazardous waste can be found in Ref. 9.

12.6.1.1 Regulated Generators

The RCRA regulations broadly define the term "generator" to include any person, by site, who first creates or produces a hazardous waste (e.g., from an industrial process) or first brings a hazardous waste into the RCRA system (e.g., imports a hazardous waste into the United States).

Because generators are the first step in the RCRA system, it is important that they properly classify and identify their waste to ensure proper handling later in the hazardous waste management process.

Hazardous waste generators may include various types of facilities and businesses ranging from large manufacturing operations, universities, and hospitals to small businesses and laboratories. Because these different types of facilities generate different volumes of wastes resulting in varying degrees of environmental risk, RCRA regulates generators based on the amount of waste that they generate in a calendar month. As a result, there are three categories of hazardous waste generators:[2,9]

1. LQGs
2. Small quantity generators (SQGs)
3. CESQGs

12.6.1.2 Regulatory Requirements

LQGs and SQGs are subject to regulations that require each generator to

1. Identify and count waste.
2. Obtain a U.S. EPA ID number.
3. Comply with accumulation and storage requirements (including requirements for training, contingency planning, and emergency arrangements).
4. Prepare the waste for transportation.
5. Track the shipment and receipt of such waste.
6. Meet recordkeeping and reporting requirements.

CESQGs are not subject to most of the generator requirements applicable to LQGs and SQGs, but they must identify their hazardous waste, comply with storage limit requirements, and ensure waste treatment or disposal in an on-site or off-site

1. Permitted or interim status hazardous waste TSDF
2. State hazardous waste facility
3. State permitted, licensed, or registered solid waste disposal facility
4. State municipal solid waste landfill (MSWLF)
5. Recycling facility
6. Universal waste facility.

Any person importing hazardous waste into the United States from a foreign country is subject to hazardous waste generator standards. RCRA also contains specific requirements for hazardous waste exports. Importers and exporters must also comply with the provisions of international trade treaties, such as the Basel Convention and the Organization for Economic Cooperation and Development (OECD) Council Decision.

Because farmers disposing of certain pesticide wastes on their own land are subject to regulation under both RCRA and FIFRA, RCRA specifically excludes such farmers from the generator requirements.

12.6.2 HAZARDOUS WASTE TRANSPORTERS

Hazardous waste transporters play an integral role in the cradle-to-grave hazardous waste management system by delivering hazardous waste from its point of generation to its ultimate destination. Since such transporters are moving regulated wastes on public roads and highways, rails, and waterways, they are regulated not only by RCRA, but by DOT standards as well. To avoid regulatory discrepancies and redundant regulations, hazardous waste transporter regulations were developed jointly by U.S. EPA and DOT.

12.6.2.1 Regulated Transporters

A hazardous waste transporter is any person engaged in the off-site transportation of hazardous waste within the United States, if such transportation requires a manifest. Off-site transportation of hazardous waste includes shipments from a hazardous waste generator's facility property to another facility for treatment, storage, or disposal. Regulated off-site transportation includes shipments of hazardous waste by air, rail, highway, or water.

Transporter regulations apply only to the off-site transport of hazardous waste. They do not apply to the on-site transportation of hazardous waste within a facility's property or boundary. "On-site" refers to geographically contiguous properties, even if the properties are separated by a public road. Consequently, a facility may ship wastes between two properties without becoming subject to the hazardous waste transporter regulations, provided that the properties are contiguous.

Transporter requirements do apply to shipments between noncontiguous properties that require travel on public roads. Examples of such on-site transportation include generators and TSDFs transporting waste within their facilities, or on their own property.

12.6.2.2 Regulatory Requirements

Transporters of hazardous waste must comply with both U.S. EPA and DOT regulations. The RCRA regulations require a transporter to[2]

1. Obtain a U.S. EPA ID number
2. Comply with the manifest system
3. Properly handle hazardous waste discharges.

During the normal course of transportation, transporters may hold waste temporarily (for up to 10 days) at a transfer facility.

Transporters of hazardous waste may also be subject to RCRA generator or storage facility requirements (e.g., if the transporter stores waste at a transfer facility for more than 10 days or imports hazardous waste into the United States).

12.6.3 TREATMENT, STORAGE, AND DISPOSAL FACILITIES

TSDFs are the last link in the cradle-to-grave hazardous waste management system. The requirements for TSDFs are more extensive than the standards for generators and transporters. They include general facility operating standards, as well as standards for the various types of units in which hazardous waste is managed. General facility standards address good management practices for any facility engaged in hazardous waste management. The technical standards go beyond these requirements to ensure that all elements of the TSDF are constructed and operated to prevent leaks of hazardous waste into the environment. The technical standards also address the diversity of hazardous waste operations being conducted around the country by guiding facilities in the proper design, construction, operation, maintenance, and closure of a variety of hazardous waste treatment, storage, and disposal units. These unit standards include requirements for a wide range of hazardous waste management units, from containers to landfills, in order to ensure that these units handle waste safely and effectively.

12.6.3.1 Regulated TSDFs

With some exceptions, a TSDF is a facility engaged in one or more of the following activities:

1. *Treatment*: Any method, technique, or process designed to physically, chemically, or biologically change the nature of a hazardous waste.
2. *Storage*: Holding hazardous waste for a temporary period, after which the hazardous waste is treated, disposed of, or stored elsewhere.
3. *Disposal*: The discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid or hazardous waste on or in the land or water. A disposal facility is any site where hazardous waste is intentionally placed and where the waste will remain after a TSDF stops operation.

12.6.3.2 Regulatory Standards

The standards include full operation and management requirements for permitted facilities (new) and less stringent provisions for interim status facilities (existing). The TSDF standards require facilities to comply with

1. General facility standards
2. Preparedness and prevention requirements
3. Contingency plans and emergency procedure provisions
4. Manifest, recordkeeping, and reporting requirements.

TSDFs owners and operators can treat, store, or dispose of waste in a variety of units. Each unit has its own specific standards governing unit design, construction, operation, and maintenance. Owners and operators can manage their waste in any of the following units[2]:

1. Containers
2. Containment buildings
3. Drip pads (Figure 12.3)
4. Land treatment units
5. Landfills (Figure 12.4)
6. Surface impoundments (Figure 12.5)
7. Tanks
8. Waste piles (Figure 12.6)
9. Miscellaneous units.

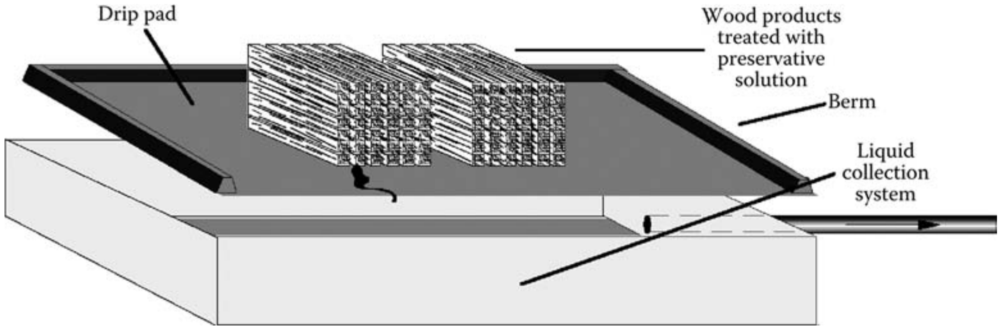

FIGURE 12.3 Cross section of a drip pad. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

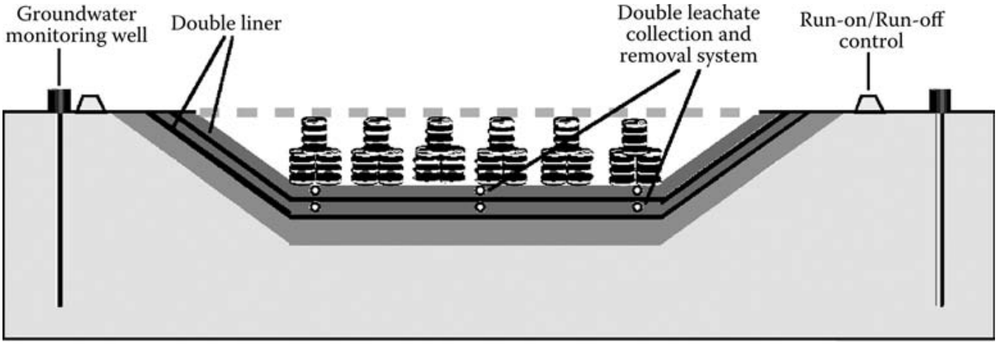

FIGURE 12.4 Cross section of a landfill. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

LQGs accumulating waste in containers, containment buildings, drips pads, and tanks are subject to the interim status TSDF standards for these units. SQGs accumulating waste in containers and tanks are subject to the interim status standards for these units.

The TSDF standards also establish requirements to ensure that hazardous waste management units are closed in a manner that protects human health and the environment. The closure provisions require the facility to stop accepting waste; remove all waste from management units; and decontaminate all soils, structures, and equipment. Some units (i.e., land treatment units, landfills, and surface impoundments) serve as places for the final disposal of hazardous waste. These land disposal units must comply with additional postclosure requirements to ensure proper long-term unit maintenance.

Because closure and postclosure activities can be very expensive, the TSDF standards require owners and operators to demonstrate financial assurance. These provisions also require all TSDFs to set aside funds in order to compensate third parties for bodily injury and property damage that might result from hazardous waste management operations.

RCRA's TSDF standards also include provisions to protect groundwater and air resources from hazardous waste contamination. RCRA requires owners and operators of land-based units (i.e., land treatment units, landfills, surface impoundments, and waste piles) to monitor the groundwater below their TSDF for possible contamination, and clean up any discovered contamination.

In order to protect air resources, TSDFs are required to install unit controls to prevent organic emissions from escaping into the air. The air emission controls apply to process vents, equipment leaks, containers, surface impoundments, and tanks.

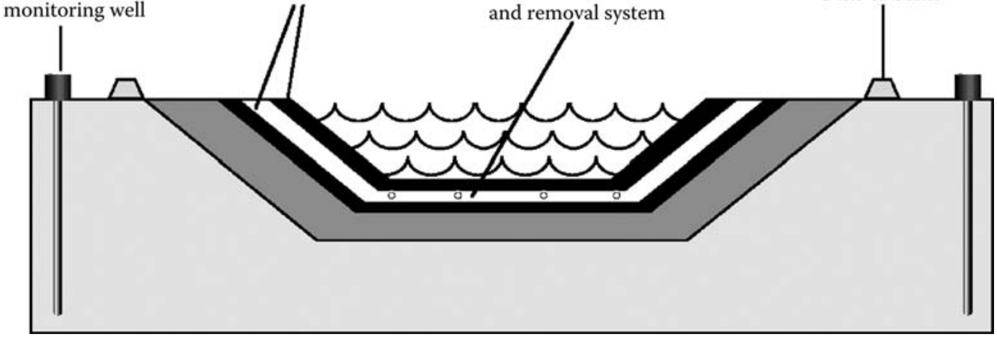

FIGURE 12.5 Cross section of a surface impoundment. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

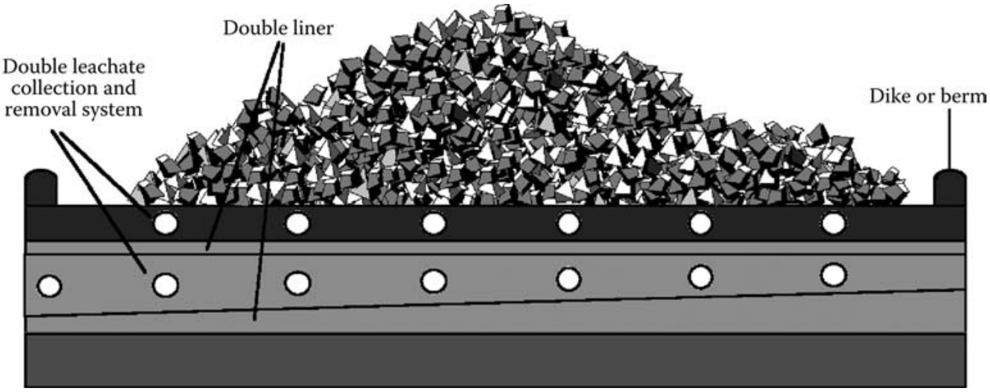

FIGURE 12.6 Cross section of a waste pile. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

12.7 LAND DISPOSAL RESTRICTIONS

A common hazardous waste management practice is to place hazardous waste in land-based units (i.e., land treatment units, landfills, surface impoundments, or waste piles). In 1999, approximately 69% of hazardous nonwastewaters generated under RCRA were permanently disposed of on the land. The permanent disposal of hazardous waste in land-based units has the potential to threaten human health and the environment through groundwater contamination. As a result, the RCRA program contains extensive technical requirements to ensure that land-based units prevent hazardous leachate from escaping into the environment. To complement the unit-specific standards, which alone do not fully protect human health and the environment from the potential risks of land-based hazardous waste management, RCRA includes the LDR program.

The LDR program approaches groundwater protection differently from unit-specific technical standards. This program does not mandate physical barriers to protect groundwater, but instead requires that hazardous wastes undergo fundamental physical or chemical changes so that they pose less of a threat to groundwater, surface water, and air when disposed. The obvious advantage of such a hazardous waste treatment is that it provides a longer-lasting form of protection than simple hazardous waste containment. While synthetic barriers designed to prevent the migration of leachate can break down and fail over time, physical and chemical changes to the waste itself provide a more permanent type of protection.

When directing U.S. EPA to establish the LDR program, Congress called for regulations that specified concentrations of hazardous constituents or methods of treatment that would substantially decrease the toxicity of hazardous waste or decrease the likelihood that contaminants in such wastes would leach. U.S. EPA responded to these requirements by establishing waste-specific treatment standards that dictate to what extent waste must be treated. All hazardous wastes, except under certain circumstances, must meet a specific treatment standard before they can be disposed of.

12.7.1 APPLICABILITY

Wastes must be an RCRA hazardous waste in order to be subject to the LDR program. In other words, unless a waste meets the definition of a solid and hazardous waste, its disposal is not regulated under the LDR program. Once a generator identifies its waste as hazardous (either listed, characteristic, or both), the waste is assigned a waste code. When U.S. EPA establishes a treatment standard for the waste code, the waste will then become restricted (i.e., subject to the LDR requirements). RCRA requires that U.S. EPA establish treatment standards for hazardous wastes within six months of promulgating a new listing or characteristic. Until U.S. EPA establishes a treatment standard for a waste, this newly identified or newly listed waste (i.e., waste for which U.S. EPA is yet to establish a treatment standard) can continue to be land disposed without treatment. When U.S. EPA promulgates a final treatment standard for a waste, handlers of the waste must manage it in accordance with all the LDR requirements and cannot dispose of it on the land until it meets all applicable treatment standards.

While the LDR program generally applies to all persons who generate, transport, treat, store, or dispose of restricted hazardous wastes, there are exclusions from the LDR requirements. The following wastes are not subject to the LDR program[2]:

1. Waste generated by CESQGs.
2. Waste pesticides and container residues disposed of by farmers on their own land.
3. Newly identified or newly listed hazardous wastes for which U.S. EPA is yet to promulgate treatment standards.
4. Certain waste releases that are mixed with a facility's wastewater and discharged pursuant to CWA.

Wastes meeting any of these descriptions may continue to be land disposed without being subject to the LDR program.

The LDR requirements attach to a hazardous waste at its point of generation. In other words, once a waste has been generated, identified, and assigned a waste code, it must be treated in accordance with LDR requirements before being disposed of. As a general principle, a hazardous waste must meet all applicable treatment standards to be eligible for land disposal. For the purposes of the LDR program, a generator of a listed hazardous waste must determine whether the waste also exhibits any hazardous waste characteristics. If it does, then the treatment standard for all waste codes must be met before land disposal.

12.7.2 LDR PROHIBITIONS

The LDR program consists of prohibitions on[1,2]

1. Disposal
2. Dilution
3. Storage.

This series of prohibitions restricts how wastes subject to LDR requirements are handled. The most visible aspect of the LDR program is the disposal prohibition, which includes treatment standards, variances, alternative treatment standards (ATSs), and notification requirements. Land disposal means placement in or on the land, except in a corrective action unit, and includes, but is not limited to, placement in a landfill, surface impoundment, waste pile, injection well, land treatment facility, salt dome formation, salt bed formation, underground mine or cave, or placement in a concrete vault, or bunker intended for disposal purposes. The other two components work in tandem with the disposal prohibition to guide the regulated community in proper hazardous waste management. The dilution prohibition ensures that wastes are properly treated, and the storage prohibition ensures that waste will not be stored indefinitely to avoid treatment.

12.7.2.1 Disposal Prohibition

The first component of the LDR program, the disposal prohibition, prohibits the land disposal of hazardous waste that has not been adequately treated to reduce the threat posed by such waste. The criteria that hazardous wastes must meet before being disposed of are known as treatment standards. These treatment standards can be either

1. Concentration levels for hazardous constituents that the waste must meet or
2. Treatment technologies that must be performed on the waste before it can be disposed of.

U.S. EPA bases the LDR treatment standards on the performance of available technologies. It conducts extensive research into available treatment technologies to determine which proven, available technology is the best at treating the waste in question. The technology that best minimizes the mobility or toxicity (or both) of the hazardous constituents is designated as the best demonstrated available technology (BDAT) for that waste. The treatment standards are based on the performance of this BDAT.

When treatment standards are set as concentration levels, the regulated community may use any method or technology (except dilution, as discussed later in this chapter) to meet that concentration level. The concentration level is based on the performance of the BDAT, but the regulated community does not need to use this technology to meet the treatment standard. U.S. EPA prefers to use concentration-based standards because they stimulate innovation and the development of alternative treatment technologies. However, when U.S. EPA feels that the waste will only be effectively treated by the BDAT or when there is no way to measure hazardous constituent levels, U.S. EPA will designate the BDAT as the treatment standard. This means that the regulated community must treat the waste with that specific technology in order to meet the treatment standard.

The treatment standards are found in the regulations in a table arranged by hazardous waste codes.[10] The treatment standards that require the use of a specific technology are expressed as a five-letter code representing the technology. There are 30 such codes representing specific technology-based standards. A selection from these codes and the technologies that they require are found in Table 12.3.

12.7.2.1.1 Characteristic Hazardous Wastes

Both listed and characteristic hazardous wastes must meet the LDR treatment standards before they are eligible for land disposal. There are, however, some unique situations that arise when dealing with characteristic wastes under the LDR program.

TABLE 12.3
Examples from LDR Technology-Based Standards

Code	Technology	Description
BIODG	Biodegradation	Biodegradation uses microorganisms to break down organic compounds to make a waste less toxic
CHRED	Chemical reduction	Chemical reduction converts metal and inorganic constituents in wastewater into insoluble precipitates that are later settled out of the wastewater, leaving a lower concentration of metals and inorganics in the wastewater
CMBST	Combustion	Combustion destroys organic wastes or makes them less hazardous through burning in boilers, industrial furnaces, or incinerators
DEACT	Deactivation	Deactivation is treatment of a waste to remove the characteristic of ignitability, corrosivity, or reactivity
MACRO	Macroencapsulation	Macroencapsulation is the application of a surface coating material to seal hazardous constituents in place and prevent them from leaching or escaping
NEUTR	Neutralization	Neutralization makes certain wastes less acidic or certain substances less alkaline
PRECP	Precipitation	Precipitation removes metal and inorganic solids from liquid wastes to allow the safe disposal of the hazardous solid portion
REMTL	Recovery of metals	Recovery of organics uses direct physical removal methods to extract metal or inorganic constituents from a waste
RORGS	Recovery of organics	Recovery of organics uses direct physical removal methods (e.g., distillation and steam stripping) to extract organic constituents from a waste
STABL	Stabilization	Stabilization (also referred to as solidification) involves the addition of stabilizing agents (e.g., Portland cement) to a waste to reduce the leachability of metal constituents

Source: Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.

The treatment standards for most characteristic hazardous wastes entail rendering the waste nonhazardous (i.e., decharacterizing the waste or removing the characteristic). However, some characteristic waste treatment standards have additional requirements. The regulated community must examine these wastes for underlying hazardous constituents. These constituents are not what cause the waste to exhibit a characteristic, but they can pose hazards nonetheless. The underlying hazardous constituents must be treated in order to meet contaminant-specific levels. These levels are referred to as the universal treatment standards (UTS), which are listed in the Appendix of this chapter.[11] This is why some characteristic wastes that no longer exhibit a characteristic must still be treated to meet additional LDR requirements. Once such characteristic hazardous wastes have been decharacterized and treated for underlying constituents, they can be disposed of in a nonhazardous waste landfill.

12.7.2.1.2 Variances, Extensions, and Exemptions

If a restricted waste does not meet its applicable treatment standard, it is prohibited from land disposal. Although most wastes become eligible for disposal by meeting the treatment standards, in some instances this may not be possible. For example, there may not be enough treatment capacity to treat a waste, or the concentration level may not be achievable. To address these situations, U.S. EPA established procedures that allow wastes to be disposed of under special circumstances. The following exemptions, variances, and extensions allow wastes to be disposed of without meeting their respective treatment standards or to be treated to a different standard[1,2]:

1. National capacity variances
2. Case-by-case extensions
3. No-migration variances
4. Variances from a treatment standard
5. Equivalent treatment method variances
6. Surface impoundment treatment exemptions.

While national capacity variances, when needed, are automatically granted to all affected hazardous waste management facilities, the other five exemptions, variances, and extensions require a facility to specifically petition U.S. EPA.

National capacity variance: When developing a treatment standard, U.S. EPA examines the available treatment capacity to determine whether it is sufficient to handle current and future waste management needs. If U.S. EPA determines that nationally there is not enough capacity to treat a waste, it can automatically extend the effective date of the waste's treatment standard. Such an extension to the effective date is intended to give the waste treatment industry more time to develop the capacity to handle the waste. Wastes under a national capacity variance can be disposed of, without meeting the treatment standards, in landfills and surface impoundments that meet minimum technical requirements (e.g., liners, leachate collection and removal systems, and leak detection systems).

Case-by-case extensions: A facility may petition U.S. EPA for a case-by-case extension to delay the effective date of a waste's treatment standard: upon showing that capacity does not exist for that particular waste. Similar to national capacity variances, wastes granted case-by-case extensions can be disposed of without meeting the treatment standards in landfills and surface impoundments that meet minimum technical requirements.

No-migration variances: No-migration variances differ from capacity variances in that they apply to the disposal unit instead of to the waste, and allow wastes to be disposed of in the unit without meeting the treatment standards. To obtain a no-migration variance for a disposal unit, a facility must petition U.S. EPA and demonstrate that there will be no migration of hazardous constituents from the unit (i.e., the waste will not leak or escape from the unit) for as long as the wastes remain hazardous.

Variances from a treatment standard: Variances from a treatment standard allow the regulated community to petition U.S. EPA and show that the required LDR treatment standard is not appropriate for their waste, or that the treatment standard is not achievable. If a variance is granted, U.S. EPA will specify an alternative standard to meet.

Equivalent treatment method variances: Equivalent treatment method variances allow the regulated community to petition U.S. EPA and demonstrate that a technology different from the required LDR treatment technology can achieve the same results. If approved, the applicant can use the alternative technology in place of the required technology.

Surface impoundment treatment exemptions: Surface impoundment treatment exemptions allow the regulated community to petition U.S. EPA for permission to treat hazardous waste in surface impoundments. Under normal circumstances, owners and operators cannot place untreated hazardous waste on the land, even if it is in a land-based unit for treatment. Since many facilities use surface impoundments as a means of treating waste, the surface impoundment treatment exemption allows owners and operators to conduct such treatment under certain conditions. Surface impoundments treating waste under this exemption must comply with double liner and minimum technical requirements, and provisions for the removal of sludges and treatment residues.

12.7.2.1.3 Alternative Treatment Standards

In establishing treatment standards, U.S. EPA applied the BDAT methodology to the typical forms of waste generated by industry. Some forms of hazardous waste are unique and were not taken into account by the BDAT process when treatment standards were established. As a result, U.S. EPA created a number of broad ATSs for special types of waste.[2]

Lab packs: Laboratories commonly generate small volumes of many different listed hazardous wastes. Rather than manage all these wastes separately, labs often consolidate these small containers into lab packs. Trying to meet the individual treatment standards for every waste contained in a lab pack would be impractical. To ease the compliance burden, U.S. EPA established an ATS for lab packs that allows the whole lab pack to be incinerated, followed by treatment for any metal in the residues. Treatment using this alternative standard satisfies the LDR requirements for all individual wastes in the lab pack.

Debris: Debris can become contaminated with hazardous waste accidental releases or spills. While such contaminated debris is typically regulated under the contained-in policy, it may also be subject to LDR treatment standards. The physical characteristics of such debris may make it difficult to meet the LDR treatment standard for the waste that is contaminating it. For example, incinerating a solvent-saturated brick wall is not necessarily going to destroy the solvent constituents that are safely nestled in between the pieces of brick. Instead of requiring debris to meet these sometimes inappropriate and difficult standards, U.S. EPA established a set of alternative standards that can be used to treat hazardous debris (40 CFR §268.45, Table 1). The alternative standards range from removing all contaminants with high-pressure washing to encapsulating the debris in order to prevent hazardous constituents from leaching. Debris treated with these ATSs meets the LDR requirements, and in many cases, can be disposed of as nonhazardous waste.

Soil: Cleanup, or remediation, of hazardous waste sites will often produce contaminated soil. Contaminated soil must be handled as hazardous waste if it contains a listed hazardous waste or if it exhibits a characteristic of hazardous waste. As with hazardous waste, land disposal of hazardous soil is prohibited until the soil has been treated to meet LDR standards. These contaminated soils, due to either their large volume or unique properties, are not always amenable to the waste code-specific treatment standards. Because of this, U.S. EPA promulgated alternative soil treatment standards in §268.49 in May 1998. The alternative soil treatment standards mandate reduction of hazardous constituents in the soil by 90% or 10 times UTS, whichever is higher. Removal of the characteristic is also required if the soil is ignitable, corrosive, or reactive.

12.7.2.1.4 Notification, Certification, and Recordkeeping

In order to properly track the hazardous waste that is generated, transported, treated, stored, and disposed of, U.S. EPA imposes certain LDR notification, certification, and recordkeeping requirements on generators and TSDFs. LDR notifications inform the next waste handler how the waste must be treated to meet the treatment standard or whether it can be disposed of without treatment. When wastes do not need to meet a treatment standard, or already meet the standard, U.S. EPA requires the handler to sign a statement certifying such a claim.

Generators must send a notification with the initial shipment of every waste. If the waste, process, or receiving facility changes, another notification is required. The information that the notification must include varies according to the status of the waste. For example, the notification requirements will differ slightly if the waste meets its treatment standard or is subject to a national capacity variance.

Treatment facilities have to send similar notifications along with the shipment of treated wastes to disposal facilities. A certification normally accompanies this notification stating that the waste meets its treatment standards and may be land disposed. Disposal facilities are the final link in the waste management chain. As a result, they have to test the waste residue that they receive to ensure that it meets the treatment standards.

Each hazardous waste handler must comply with certain recordkeeping requirements for LDR notifications and paperwork. Generators, treatment facilities, and disposal facilities must keep copies of all LDR paperwork associated with the waste they ship or receive in their facility files for three years.

Characteristic wastes that are decharacterized subsequent to the point of generation (i.e., they become nonhazardous) are handled differently. Once a waste is decharacterized and has met its full LDR treatment standards, it can go to an RCRA nonhazardous waste facility. These LDR notifications and certifications are sent to the U.S. EPA Region or authorized state rather than to the receiving facility. This is intended to protect facilities from the burden of hazardous waste paperwork.

12.7.2.2 Dilution Prohibition

The second component of the LDR program is the dilution prohibition. When a waste's treatment standard is expressed as a numeric concentration level, it is often easier and less expensive to dilute the waste in water or soil in order to reduce the concentration of the hazardous constituents. This type of activity does not reduce the overall or mass load of toxic chemicals that could be released to the environment, and is inconsistent with the goals of the LDR program. To prevent this activity from being practiced, U.S. EPA established the dilution prohibition. The dilution prohibition states that it is impermissible to dilute hazardous waste to circumvent proper treatment. Adding water or soil to a waste to dilute it, combining wastes not amenable to the same type of treatment, and incinerating metal wastes are all examples of impermissible dilution.

12.7.2.3 Storage Prohibition

The final component of the LDR program is the storage prohibition. Before a waste can be treated, it is usually stored in units, such as containers and tanks. These storage units are not intended for the long-term management of waste, and therefore, are not required to provide the same level of protective measures as disposal units. To prevent indefinite storage, U.S. EPA regulations state that if waste storage exceeds one year, the facility has the burden of proving that such storage is being maintained in order to accumulate quantities necessary for effective treatment or disposal. For storage less than one year, U.S. EPA has the burden of proving that such storage is not for the purpose of accumulating quantities necessary for effective treatment or disposal. Generators accumulating waste on sites within their respective accumulation time limits, and transfer facilities temporarily storing manifested shipments of hazardous waste for <10 days, are not subject to this burden of proof requirement.

12.7.3 HISTORY OF LDR

The LDR program has a complicated history. The progression of the LDR program is important in understanding how and why the LDR program operates the way it does today. Since 1986, when the

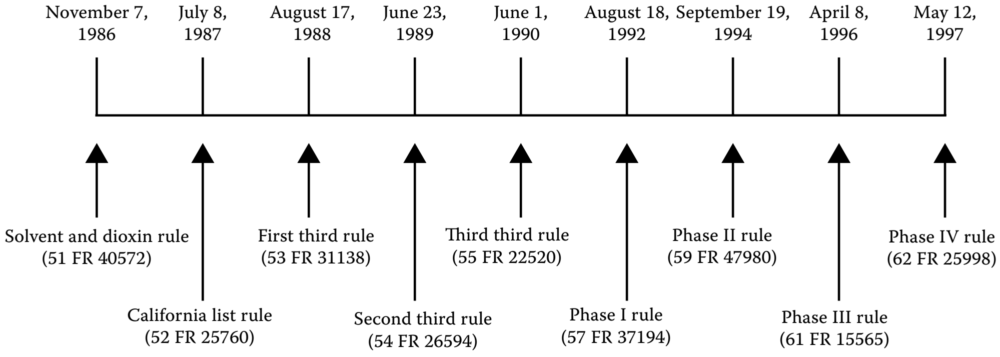

FIGURE 12.7 Significant LDR rulemakings. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

first treatment standards were promulgated, the LDR program has continually evolved. U.S. EPA has finished establishing treatment standards for all existing, newly identified, and newly listed wastes based on two rulemaking schedules (Thirds and Phases) in May 26, 1998 (Figure 12.7). It now promulgates the LDR treatment standards for a waste whenever a waste is initially identified or listed. Additional information can be found in Ref. 12.

12.8 HAZARDOUS WASTE COMBUSTION

A large number of TSDFs use combustion, the controlled burning of substances in an enclosed area, as a means of treating and disposing of hazardous waste. Approximately 11% of the hazardous nonwastewater generated in the United States in 1999 was treated using combustion. As a hazardous waste management practice, combustion has several unique attributes. First, if properly conducted, it permanently destroys toxic organic compounds contained in hazardous waste by breaking their chemical bonds and reverting them to their constituent elements, thereby reducing or removing their toxicity. Second, combustion reduces the volume of hazardous waste to be disposed of on land by converting solids and liquids to ash. Land disposal of ash, as opposed to disposal of untreated hazardous waste, is in many instances both safer and more efficient.

Combustion is an intricate treatment process. During burning, organic wastes are converted from solids and liquids into gases. These gases pass through the flame, are heated further, and eventually become so hot that their organic compounds break down into the constituent atoms. These atoms combine with oxygen and form stable gases that are released to the atmosphere after passing through air pollution control devices.

The stable gases produced by combustion of organics are primarily carbon dioxide and water vapor. Depending on waste composition, however, small quantities of carbon monoxide, nitrogen oxides, hydrogen chloride, and other gases may form. These gases have the potential to cause harm to human health and the environment. The regulation of these emissions is the primary focus of the RCRA combustion unit standards.

The management or disposal of metals and ash, other by-products of the combustion process, also causes concern. Ash is an inert solid material composed primarily of carbon, salts, and metals. During combustion, most ash collects at the bottom of the combustion chamber (bottom ash). When this ash is removed from the combustion chamber, it may be considered hazardous waste via the derived-from rule or because it exhibits a characteristic. Small particles of ash (particulate matter that may also have metals attached), however, may be carried up the stack with the gases (fly ash). These particles and associated metals are also regulated by the combustion regulations, as they may carry hazardous constituents out of the unit and into the atmosphere. Since combustion will not destroy inorganic compounds present in hazardous waste, such as metals, it is possible that such

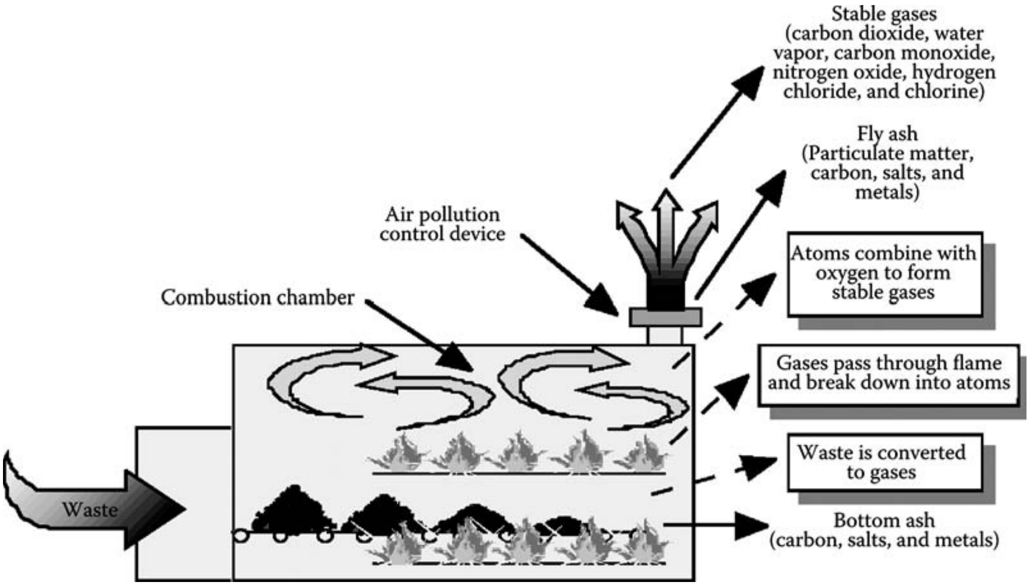

FIGURE 12.8 Combustion process. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

compounds may also end up in bottom ash and fly ash at harmful concentrations. Ash residue is subject to applicable RCRA standards and may need to be treated for metals or other inorganic constituents prior to land disposal (Figure 12.8).

In the early years of RCRA, U.S. EPA's idea was to combust as much hazardous waste as possible and landfill the resultant ash. This process destroyed the majority of the waste, thus reducing the volume requiring disposal. However, it was determined that incomplete or improperly conducted combustion had the potential to present a major public health risk and therefore, became the topic of much public outcry. This public concern, coupled with U.S. EPA's advancements in assessing potential risks arising from combustion, caused a shift in U.S. EPA's strategy on combustion. This shift in thinking resulted in the increasing stringency of combustion requirements over time.

In September 1999, U.S. EPA issued a joint CAA/RCRA rule that upgraded the emission standards for hazardous waste combustors, based on the maximum achievable control technology (MACT) approach commonly employed under the CAA. This process develops technology-based, emission limits for individual hazardous air pollutants. Much like the BDAT concept for LDR, the MACT emission standards are based on the performance of a technology. U.S. EPA researches available pollution control technologies to determine which available technology is the best at controlling each pollutant to determine allowable emission limits. The regulated community may then use any technology to meet the numeric emission standards set by U.S. EPA.

Consistent with U.S. EPA's trend of gradually increasing the stringency of standards over time, this joint rule promulgated more stringent emission standards for dioxins, furans, mercury, cadmium, lead, particulate matter, hydrogen chloride, chlorine gas, hydrocarbons, carbon monoxide, and several low-volatile metals. After the promulgation of this rule, a number of parties representing the interests of both industrial sources and the environmental community requested a judicial review of this rule.

In July 2001, the U.S. Court of Appeals for the District of Columbia Circuit vacated the challenged portions of the rule. When it made its decision, the Court invited any of the parties to request either that the current standards remain intact or that U.S. EPA be allowed time to publish interim standards. Acting on this initiative, U.S. EPA and the other parties jointly asked the Court for additional time to develop interim standards, and the Court granted this request. On February 13, 2002, U.S. EPA published these interim standards that temporarily replace the vacated standards. The interim standards will remain in place until U.S. EPA issues final "replacement" standards that comply with the Court's opinion. U.S. EPA has also completed other actions agreed to in the joint motion, such as extending the compliance date by one year to September 30, 2003, and finalizing several amendments to the compliance and implementation provisions by February 14, 2002.

12.8.1 REGULATED UNITS

Hazardous wastes are combusted for various purposes. The purpose of combustion is directly related to the type of unit used. There are two classes of combustion units, those that burn waste for energy recovery and those that burn waste for destruction.

12.8.1.1 Incinerators

The first class of combustion units is hazardous waste incinerators. Incineration is the combustion of hazardous waste primarily for destruction (i.e., disposal). It is a method of thermal destruction of primarily organic hazardous waste using controlled flame combustion (Figure 12.9). This process can reduce large volumes of waste materials to ash and lessen toxic gaseous emissions. An incinerator is an enclosed device that uses controlled flame combustion and does not meet the more specific criteria for classification as a boiler, industrial furnace, sludge dryer (a unit that dehydrates hazardous sludge), or carbon regeneration unit (a unit that regenerates spent activated carbon). Incinerators also include infrared incinerators (a unit that uses electric heat followed by a controlled flame afterburner) and plasma arc incinerators (a unit that uses electrical discharge followed by a controlled flame afterburner).

12.8.1.2 Boilers and Industrial Furnaces

The second class of combustion units is BIFs. Boilers are used to recover energy from hazardous waste, whereas industrial furnaces are used primarily to recover material values.

U.S. EPA defines boilers as enclosed devices that use controlled flame combustion to recover and export energy in the form of steam, heated fluid, or heated gases. A boiler comprises two main parts, the combustion chamber used to heat the hazardous waste and the tubes or pipes that hold the

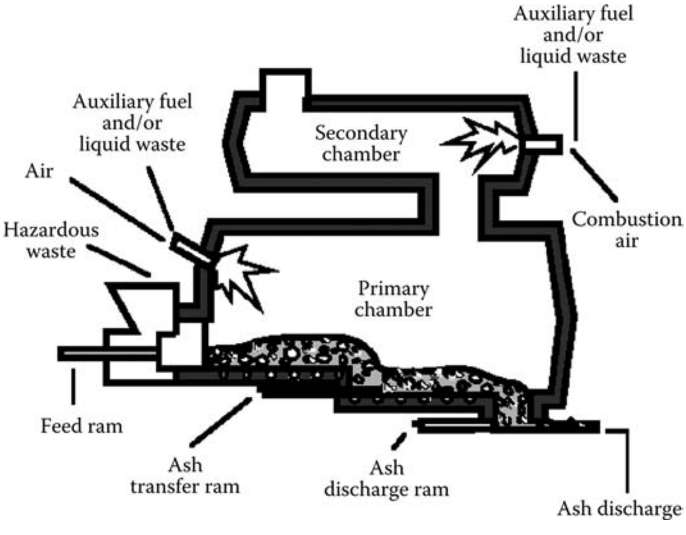

FIGURE 12.9 Cross section of an incinerator. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

fluid used to produce energy. The regulatory definition of a boiler requires that these two parts be in close proximity to one another to ensure the effectiveness of the unit's energy recovery system and to maintain high thermal energy recovery efficiency. In addition, the unit must export or use the majority of the recovered energy for a beneficial purpose.

Industrial furnaces are enclosed units that are integral parts of a manufacturing process and use thermal treatment to recover materials or energy from hazardous waste. These units may use hazardous waste as a fuel to heat raw materials to make a commodity (e.g., a cement kiln making cement) or the unit may recover materials from the actual hazardous waste (e.g., a lead smelter recovering lead values). The following 12 devices meet the definition of an industrial furnace[1,2]:

1. Cement kiln
2. Aggregate kiln
3. Coke oven
4. Smelting, melting, and refining furnace
5. Methane reforming furnace
6. Pulping liquor recovery furnace
7. Lime kiln
8. Phosphate kiln
9. Blast furnace
10. Titanium dioxide chloride process oxidation reactor
11. Halogen acid furnace
12. Combustion device used in the recovery of sulfur values from spent sulfuric acid.

After notice and comment, U.S. EPA may add other devices to this list of industrial furnaces upon consideration of factors related to the design and use of the unit.

Not all units that meet the definition of a boiler or industrial furnace are subject to the RCRA BIF standards. Each individual unit must first be evaluated against a number of exemptions from the BIF requirements. For a variety of reasons (e.g., to avoid duplicative regulation), U.S. EPA exempted the following units from the BIF regulations[1,2]:

1. Units burning used oil for energy recovery.
2. Units burning gas recovered from hazardous or solid waste landfills for energy recovery.
3. Units burning hazardous wastes that are exempt from RCRA regulation, such as household hazardous wastes.
4. Units burning hazardous waste produced by CESQGs.
5. Coke ovens burning decanter tank tar sludge from coking operations.
6. Certain units engaged in precious metals recovery.
7. Certain smelting, melting, and refining furnaces processing hazardous waste solely for metals recovery.
8. Certain other industrial metal recovery furnaces.

12.8.2 REGULATORY REQUIREMENTS

Emissions from hazardous waste combustors are regulated under two statutory authorities: RCRA and the CAA. The MACT standards set emission limitations for dioxins, furans, metals, particulate matter, total chlorine, hydrocarbons/carbon monoxide, and destruction and removal efficiency (DRE) for organics. Once a facility has demonstrated compliance with the MACT standards by conducting its comprehensive performance test (CPT) and submitting its notification of compliance (NOC), it is no longer subject to the RCRA emission requirements with a few exceptions. RCRA-permitted facilities, however, must continue to comply with their permitted emissions requirements until they obtain modifications to remove any duplicative emissions conditions from their RCRA permits. The combustion standards under RCRA, as well as the MACT standards under the CAA, are discussed below.

12.8.2.1 Combustion Standards under RCRA

Emissions from combustion units may comprise a variety of hazardous pollutants. To minimize potential harmful effects of these pollutants, U.S. EPA developed performance standards to regulate four pollutant categories:

1. Organics
2. Hydrogen chloride and chlorine gas
3. Particulate matter
4. Metals.

Boilers and most industrial furnaces have performance standards that they must meet. For each category or type of emission, the regulations establish compliance methods and alternatives.

12.8.2.1.1 Organics

Because the primary purpose of a combustion unit is to destroy the organic components found in hazardous waste, it is essential to verify that the unit is efficiently destroying organics in the waste. This is determined based on the unit's organic DRE as demonstrated in a trial burn. Since it would be nearly impossible to determine the DRE results for every organic constituent in the waste, certain principal organic hazardous constituents (POHCs) are selected for this demonstration. These POHCs are selected for each facility based on their high concentration in the wastestream and their greater difficulty to burn. If the unit achieves the required DRE for the POHCs, then it is presumed that it will achieve the same (or better) DRE for all other easier-to-burn organics in the wastestream. At least one POHC will be selected from each wastestream that the facility manages. The facility designates the selected POHCs in their permit application.

The combustion unit must demonstrate a DRE of 99.99% for each POHC in the hazardous wastestream. This means that for every 10,000 molecules of the POHC entering the unit, only one molecule can be released to the atmosphere. In addition, due to an increased threat to human health and the environment posed by certain dioxin-containing wastes, the required DRE for POHCs in these units has been established at 99.9999%, or one released molecule for every one million burned. These DRE standards must be met by both incinerators and BIFs.

12.8.2.1.2 Hydrogen Chloride and Chlorine Gas

Hydrogen chloride and chlorine gases form when chlorinated organic compounds in hazardous wastes are burned. If uncontrolled, this chlorine can become a human health risk and is a large component in the formation of acid rain. U.S. EPA has developed different requirements to control the emissions of chlorine from the different classes of combustion units.

Boilers and most industrial furnaces must follow a tiered system for the regulation of both hydrogen chloride and chlorine gas. The owner and operator determine the allowable feed or emission rate of total chlorine by selecting one of three approaches, called tiers. Each tier differs in the amount of monitoring, and in some cases, air dispersion modeling (i.e., modeling the air pathways through which pollutants may travel) that the owner and operator are required to conduct.

Each facility can select any of the three tiers. Factors that a facility may consider in selecting a tier include the physical characteristics of the facility and surrounding terrain, the anticipated waste compositions and feed rates, and the level of resources available for conducting the analysis. The main distinction between the tiers is the point of compliance. This is the point at which the owner and operator must ensure that chlorine concentrations will be below U.S. EPA's acceptable exposure levels. The owner and operator must determine if the cost of conducting monitoring and modeling is worth the benefit of possibly combusting waste with a higher concentration of chlorine.

12.8.2.1.3 Particulate Matter

The third combustion unit performance standard is for particulate matter. Particulate matter consists of small dust-like particles emitted from combustion units. The particles themselves are not normally toxic, but may become caught in the lungs (causing respiratory damage) if inhaled, or may enter into the environment where they can cause either ecological damage or, via food chain intake, can reenter the human health exposure pathway. In addition, particulate matter may provide a point of attachment for toxic metals and organic compounds. To minimize these adverse conditions, RCRA combustion units may not emit more than 180 mg/m^3 of dry particulate matter.

12.8.2.1.4 Metals

The final performance standard is for toxic metals. For RCRA combustion units, both carcinogenic and noncarcinogenic metals are regulated under the same type of tiered system as chlorine. The facility determines an appropriate tier for each regulated metal and assures that the facility meets these feed rate and emission standards. A different tier may be selected for each metal pollutant.

12.8.2.1.5 Additional Performance Standards

U.S. EPA may require owners and operators of hazardous waste combustion units to comply with additional performance standards by virtue of the omnibus authority. This authority allows U.S. EPA to incorporate additional terms and conditions into a facility's permit as necessary to protect human health and the environment.

U.S. EPA recommends that site-specific risk assessments, incorporating direct and indirect exposures, be considered during the combustion unit's permitting process. These risk assessments may be used to evaluate the unit's impact on the surrounding environment. If a site-specific risk assessment shows that additional protection should be afforded to the surrounding environment, U.S. EPA typically will use the omnibus authority to impose the necessary permit conditions.

12.8.2.1.6 Operating Requirements

The goal of setting operating requirements for hazardous waste combustion units is to ensure that the unit will operate in a way that meets the performance standards for organics, chlorine, particulate matter, and metal pollutants. The unit's permit will specify the operating conditions that have been shown to meet the performance standards for organics, chlorine gas, particulate matter, and metals.

An RCRA permit for a hazardous waste combustion unit sets operating requirements that specify allowable ranges for, and requires continuous monitoring of, certain critical parameters that will ensure compliance with the performance standards. Operation within these parameters ensures that combustion is performed in the most protective manner and the performance standards are achieved. These parameters, or operating requirements, may include

1. Maximum waste feed rates
2. Control of the firing system
3. Allowable ranges for temperature
4. Limits on variations of system design and operating procedures
5. Gas flow rate.

12.8.2.2 MACT Standards under the CAA

Hazardous waste burning incinerators, cement kilns, and lightweight aggregate kilns (LWAKs), hereafter referred to as MACT combustion units, must also comply with emission limitations. The MACT emission standards are found under the CAA regulations. Instead of using operating requirements as a way of ensuring that the unit meets the performance standards, owners or operators of combustion units subject to MACT standards may use a pollution control technology to achieve the stringent numerical emission limits.

12.8.2.2.1 Organics

To control the emission of organics, these units must comply with similar DRE requirements to the other hazardous waste combustion units. Owners or operators of MACT combustion units must select POHCs and demonstrate a DRE of 99.99% for each POHC in the hazardous wastestream. Sources that burn hazardous waste have a required DRE of 99.9999% for each POHC designated. Additionally, for dioxins and furans, U.S. EPA promulgated more stringent standards under MACT. For example, MACT incinerators and cement kilns that burn waste with dioxins and furans must not exceed an emission limitation of either 0.2 ng of toxicity equivalence per dry standard cubic meter (TEQ/m^3) or 0.4 ng TEQ/m^3 at the inlet to the dry particulate matter control device. This unit of measure is based on a method for assessing risks associated with exposures to dioxins and furans.

12.8.2.2.2 Hydrogen Chloride and Chlorine Gas

Rather than a tiered system to control hydrogen chloride and chlorine gas emissions, MACT combustion units must meet numerical emission limits for total chlorine. Owners and operators of these units must ensure that the total chlorine emission does not exceed specific limits, expressed in ppmv. For example, the allowable limit of total chlorine for a new incinerator is 21 ppmv. The owner or operator may choose to achieve this level by controlling the amount of chlorine entering the incinerator. By achieving the regulatory emission limit of chlorine, both hydrogen chloride and chlorine gas emissions will be reduced.

12.8.2.2.3 Particulate Matter

U.S. EPA developed more stringent standards for particulate matter in order to control certain metals. This surrogate is used because particulate matter may provide a point of attachment for toxic metals that can escape into the atmosphere from a combustion unit. For instance, a new LWAK cannot exceed an emission limit of 57 mg/m^3 of dry particulate matter.

12.8.2.2.4 Metals

Hazardous waste burning incinerators, cement kilns, and LWAKs do not follow a tiered approach to regulate the release of toxic metals into the atmosphere. The MACT rule finalized numerical emission standards for three categories of metals: mercury, low-volatile metals (arsenic, beryllium, and chromium), and semivolatile metals (lead and cadmium). Units must meet emission standards for the amount of metals emitted. For example, a new cement kiln must meet an emission limit of 120 μg/m^3 of mercury, 54 μg/m^3 of low-volatile metals, and 180 μg/m^3 of semivolatile metals.

12.8.2.2.5 Operating Requirements

Owners or operators of MACT units must ensure that the MACT emission standards are not exceeded. To do this, the unit must operate under parameters that are demonstrated in a CPT. The unit's operating parameters, such as temperature, pressure, and waste feed, are then set based on the result of the CPT and documented in a NOC. Continuous monitoring systems are used to monitor the operating parameters.

The facility may also choose to use an advanced type of monitoring known as continuous emissions monitoring systems (CEMS). CEMS directly measure the pollutants that are exiting the combustion unit stack at all times. If a facility chooses to use a CEMS, they do not need to comply with the operating parameter that would otherwise apply.

12.8.2.2.6 Additional Requirements

Because hazardous waste combustion units are a type of TSDF, they are subject to the general TSDF standards in addition to combustion unit performance standards and operating requirements. Combustion units are also subject to specific waste analysis, inspection and monitoring, and residue management requirements.

While combusting hazardous waste, the combustion process and equipment must be monitored and inspected to avoid potential accidents or incomplete combustion. The monitoring and inspection requirements for incinerators are detailed in the regulations, while the requirements for BIFs are determined on a site-specific basis. Possible inspection and monitoring requirements include

1. Monitoring the combustion temperature and hazardous waste feed rate.
2. Sampling and analyzing the waste and exhaust emissions to verify that the operating requirements established in the permit achieve the performance standards.
3. Conducting visual inspections of the combustion unit and its associated equipment.
4. Testing the emergency waste feed cutoff system and associated alarms.
5. Placing monitoring and inspection data in the operating log.

Residues from the combustion of hazardous waste are also potentially subject to RCRA regulation. If a combustion unit burns a listed hazardous waste, the ash could also be considered a listed waste via the derived-from rule. The owner and operator must also determine whether this ash exhibits any hazardous waste characteristics. The same is true if a unit burns waste that only exhibits a characteristic. Ash that exhibits a characteristic must be managed as a hazardous waste.

In addition, these units are also subject to the general TSDF facility standards under RCRA. Hazardous waste incinerators and hazardous waste burning cement kilns and LWAKs are also subject to the CAA MACT emission standards. A complete overview of the MACT standards and additional information about hazardous waste combustion can be found in Ref. 13.

12.9 PERMITTING, CORRECTIVE ACTION, AND AUTHORIZING STATES TO IMPLEMENT RCRA

12.9.1 PERMITTING

The RCRA regulations require hazardous waste TSDFs to obtain an operating permit that establishes the administrative and technical conditions under which hazardous waste at the facility must be managed. Such permits cover the full range of TSDF standards, including general facility provisions, unit-specific requirements, closure and financial assurance standards, and any applicable groundwater monitoring and air emissions provisions.

In order to obtain a permit, a TSDF owner and operator must comply with specific application procedures. The permitting process consists of the following stages[2]:

1. Informal meeting prior to application
2. Permit submission
3. Permit review
4. Preparation of the draft permit
5. Taking public comment
6. Finalizing the permit.

After issuance, permits may need to be modified to allow facilities to implement technological improvements, comply with new environmental standards, respond to changing wastestreams, and generally improve waste management practices. These modifications can be initiated by either the facility or the permitting agency.

Facilities that were existing and operating on the effective date of a regulation that required them to obtain an operating permit are considered interim status facilities. They are allowed to continue operating as long as they comply with certain general facility and unit-specific TSDF standards until the implementing agency makes a final permit determination.

Some waste management operations and practices require special permit provisions. These special forms of permits include[2]

1. Permits-by-rule
2. Emergency permits
3. Research, development, and demonstration (RD&D) permits
4. Land treatment demonstration permits
5. Combustion permits
6. Postclosure permits
7. Remedial action plans.

Additionally, U.S. EPA proposed another special type of permit called a "standardized permit." Additional information about RCRA permitting can be found in Ref. 14.

12.9.2 CORRECTIVE ACTION TO CLEAN UP HAZARDOUS WASTE CONTAMINATION

There are three essential elements to RCRA's enforcement program: compliance monitoring, enforcement actions, and compliance assistance and incentives.

Compliance monitoring is used to determine a handler's level of compliance with RCRA's regulatory requirements. The primary method of collecting compliance monitoring data is through an inspection. Either U.S. EPA or an authorized state may lead inspections. Inspections must be conducted annually at all federal- or state-operated facilities and at least once every two years at each TSDF. The six types of inspections conducted under the RCRA program are[2]

1. Compliance evaluation inspection
2. Case development inspection
3. Comprehensive groundwater monitoring evaluation
4. Compliance sampling inspection
5. Operations and maintenance inspection
6. Laboratory audit.

The primary goal of enforcement actions is to bring facilities into compliance and ensure future compliance. The enforcement options available under RCRA are

1. Administrative actions, including informal and formal actions
2. Civil actions
3. Criminal actions.

U.S. EPA uses the guidelines in the *Civil Penalty Policy* for assessing penalty amounts and uses the *Final U.S. EPA Supplemental Environmental Projects Policy* to allow for flexibility in assessing penalties. Enforcement of RCRA at federal facilities is now similar to enforcement at TSDFs, as a result of the Federal Facility Compliance Act of 1992.

To achieve greater compliance, U.S. EPA also offers compliance assistance through numerous policies, including *Final Policy on Compliance Incentives for Small Businesses* and *Incentives for Self-Policing: Discovery, Disclosure, Correction, and Prevention of Violations.*

The responsibility for the various enforcement actions is divided among different U.S. EPA Headquarters offices, U.S. EPA Regions, and authorized state agencies. Additional information about RCRA enforcement can be found in Refs 15 and 16.

12.9.3 Authorizing States to Implement RCRA

Congress intended states to assume responsibility for implementing RCRA, with oversight from the federal government. In order for a state to receive authorization to implement and enforce the hazardous waste regulations in lieu of federal U.S. EPA, the state must demonstrate that its program

1. Is equivalent to, no less stringent than, and consistent with the federal program (state requirements may be more stringent or broader in scope).
2. Provides adequate enforcement authority.
3. Provides for public availability of information in substantially the same manner and to the same degree as the federal program.

Any state that seeks final authorization for its hazardous waste program must submit an application to the U.S. EPA Administrator containing the following elements[2]:

1. A letter from the governor requesting program authorization.
2. A complete program description.
3. An attorney general's statement.
4. A Memorandum of Agreement (MOA).
5. Copies of all applicable state statutes and regulations.
6. Documentation of public participation activities.

Once a state's program has been authorized, it must revise its program, on an annual basis, to reflect both changes in the federal program, and state statutory or regulatory changes. State programs are also subject to review by U.S. EPA, and a state's authorized status can be withdrawn if the program does not comply with appropriate regulatory requirements. Without officially withdrawing authorization, U.S. EPA may take independent enforcement action by over-filing, or enforcing a provision for which a particular state has authorization. States may also choose to transfer program responsibility back to U.S. EPA.

U.S. EPA works closely with states in implementing the hazardous waste management program by offering grants to states, setting national goals and priorities, and providing program oversight. U.S. EPA Headquarters, U.S. EPA Regions, and states collect, compile, and track information on the RCRA hazardous waste program through RCRAInfo.

12.10 SUPERFUND: THE HAZARDOUS WASTE CLEANUP PROGRAM

This section focuses on the CERCLA that is a central part of the legislative framework for environmental protection. CERCLA is also known as Superfund.

CERCLA is designed to remedy the mistakes in hazardous waste management made in the past, while the RCRA waste management standards are concerned with avoiding such mistakes through proper management in the present and future. RCRA mainly regulates how wastes should be managed to avoid potential threats to human health and the environment. CERCLA, on the other hand, is relevant primarily when mismanagement occurs or has occurred (i.e., when there has been a release or a substantial threat of a release in the environment of a hazardous substance, or of a pollutant or contaminant, that presents an imminent and substantial threat to human health). More specifically, RCRA authorizes a general regulatory program to manage all hazardous wastes from cradle to grave (i.e., from generation to ultimate disposal), while CERCLA authorizes a number of government actions to remedy the conditions that could result in a release or the effects of a release itself. While the two programs use parallel, but not identical, procedures, both RCRA and CERCLA authorize U.S. EPA to act in the event of an imminent hazard.

12.10.1 DEFINITIONS

Both RCRA and CERCLA address hazards to the environment. However, CERCLA is the more comprehensive statute. CERCLA hazardous substances encompass RCRA hazardous wastes, as well as other toxic pollutants regulated by the CAA, the CWA, and the TSCA. Thus, all RCRA hazardous wastes may trigger CERCLA response actions when released into the environment. RCRA nonhazardous solid wastes, on the other hand, do not trigger CERCLA response actions unless they present an imminent and substantial danger as pollutants or contaminants (Figure 12.10).

In addition to hazardous substances, CERCLA addresses pollutants and contaminants, which are broadly defined to include any substance that is reasonably anticipated to cause illness or deformation in any organism. All three definitions specifically exclude petroleum and natural gas.

12.10.2 HISTORY AND PURPOSE OF CERCLA

CERCLA was established in response to the discovery, in the late 1970s, of a large number of abandoned, leaking, hazardous waste dumps that were threatening human health and contaminating the environment.[17] One of the best-known dumps was Love Canal in Niagara Falls, New York, where a chemical company had buried large amounts of hazardous waste in a canal originally designed to transport water. After the canal was capped with clay and soil, an elementary school was built over the site, and the city of Niagara Falls grew rapidly around it.

In the 1970s, an unusual number of community residents (especially those who attended the elementary school) developed serious health problems. Moreover, the residents complained of noxious fumes and of chemicals oozing out of the ground. Subsequent government investigations found extensive contamination of the area, including groundwater supplies. In 1978, President Carter declared Love Canal a federal disaster area, and most of the residents in the area around the site were relocated.

At the time, declaring the site as a federal disaster area was the only viable option available to the federal government. RCRA did not provide relief because the problem did not involve the current or future management of wastes. Legal actions against the responsible parties did not offer a solution because such action was too time consuming and costly. Unfortunately, subsequent investigations indicated that the scope of the waste dump problem went far beyond Love Canal, making the federal disaster relief option impractical. In late 1980, Congress passed CERCLA to address other uncontrollable hazardous waste sites similar to Love Canal throughout the country.

CERCLA, as originally enacted in 1980, authorized a five-year program by the federal government to perform the following primary tasks[2]:

1. Identify those sites where releases of hazardous substances had already occurred or might occur and posed a serious threat to human health, welfare, or the environment.

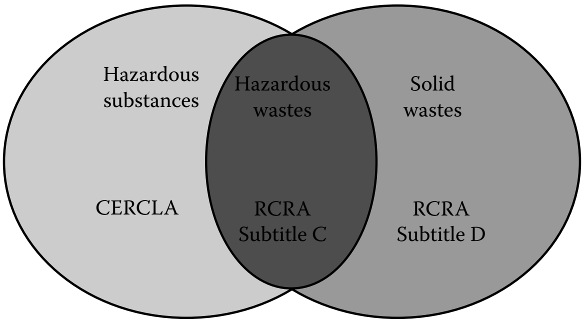

FIGURE 12.10 Relationship between CERCLA hazardous substances and RCRA hazardous wastes. (Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.)

2. Take appropriate action to remedy those releases.
3. Force those parties responsible for the release to pay for the cleanup actions.

To accomplish these tasks, CERCLA gave new cleanup authority to the federal government, created a $1.6 billion trust fund to pay for government cleanup, and imposed cleanup liability on those responsible. This "Superfund" consisted primarily of tax assessments on oil and designated chemicals.

During the five-year period of the original CERCLA program, two facts became increasingly clear: The problem of abandoned hazardous waste sites was more extensive than originally thought, and its solution would be more complex and time consuming. Unlike RCRA response actions where the owner and operator of a site are known, CERCLA may deal with environmental threats due to activities conducted long ago, and thus the responsible party may be unknown, no longer in existence (e.g., a defunct company), or unable to pay. To address these additional concerns, the Superfund Amendments and Reauthorization Act (SARA) not only extended CERCLA for another five years, but increased the fund from a total of $1.6 billion to $8.5 billion.[18] SARA also established new standards and schedules for site cleanup and also created new programs for informing the public of risks from hazardous substances in their community and preparing communities for hazardous substance emergencies.

12.10.3 TRIGGER FOR STATUTORY RESPONSE

CERCLA response authorities are triggered by a release or a substantial threat of release of dangerous substances into the environment (e.g., a chemical spill from a tank truck accident or a leak from a damaged drum). The release must involve either

1. A hazardous substance, as defined in the statute or
2. A pollutant or contaminant that may present an imminent or substantial danger to public health or welfare.

12.10.4 TYPES OF RESPONSE ACTIONS

Once a potential release has been discovered, the information is entered into the Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS), a computerized database used to track hazardous substance sites. After being entered into CERCLIS, each site undergoes a preliminary assessment (PA) to determine whether the site poses a potential hazard and whether further action is necessary. If the threat is immediate, a removal action may be conducted.

Removal actions are short-term cleanup actions that usually address problems only at the surface of a site. They are conducted in response to an emergency situation (e.g., to avert an explosion, to clean up a hazardous waste spill, or to stabilize a site until a permanent remedy can be found). Removal actions are limited to 12 months duration or $2 million in expenditures, although in certain cases these limits may be extended. Removals may occur at any point in time after the PA has been conducted.

Remedial actions are longer-term response actions that ultimately represent the final remedy for a site and generally are more expensive and of a longer duration than removals. This is because the remedial actions are intended to provide permanent solutions to hazardous substance threats. It is possible that both removal and remedial actions may be taken at the same site. In the event that longer-term cleanup is necessary, the site is referred to the remedial program for further investigation and assessment.

If the PA reveals that a contamination problem exists, but does not pose an immediate threat that warrants a removal, U.S. EPA will continue to study the site during a site inspection (SI). Based on data collected during the PA and the SI, U.S. EPA will evaluate the site using the hazard ranking system (HRS), a model and scoring system that determines the relative risk to public health and the environment posed by hazardous substances in groundwater, surface water, air, and soil. Only those sites with a score of 28.5 (on a scale from 0 to 100) are eligible for placement on the National Priorities List (NPL), U.S. EPA's priority hazardous substance sites for cleanup. U.S. EPA only funds remedial actions at hazardous waste sites on the NPL. As of May 2002, there are over 1200 sites either on the NPL or are proposed for inclusion. The majority of sites are placed on the NPL based on their HRS score. Under some circumstances, sites may also be placed on the NPL by the state in which the site is located or by the Agency for Toxic Substances and Disease Registry (ATSDR).

Once a site is placed on the NPL, the remedial process begins. The remedial process requires U.S. EPA to design a community involvement plan that will inform citizens of all remedial activities and provide opportunities for public comment. A remedial response has two main phases. The first phase, the remedial investigation/feasibility study (RI/FS), involves evaluating site conditions at the site, defining any problems, and comparing alternative site cleanup methods. After the remedy has been selected, the decision is documented in the record of decision (ROD). The second phase, the remedial design/remedial action (RD/RA), involves designing the chosen cleanup and beginning construction.

Following the implementation of the remedy, the state or the potentially responsible party (PRP) assumes responsibility for the operation and maintenance (O&M) of the site, which may include activities such as groundwater pump and treat, and cap maintenance. Once U.S. EPA has determined that all appropriate response actions have been taken and cleanup goals have been achieved, the site is deleted from the NPL through a formal rulemaking process.

12.10.5 RCRA and Remedy Selection under CERCLA

CERCLA assures that remedies are based on the cleanup standards and criteria that have been established by other laws, such as CAA, CWA, and RCRA. CERCLA specifically requires that on-site remedies attain any legally applicable or relevant and appropriate requirements (ARARs), standards, criteria, or limitations under federal or more stringent state environmental laws, including RCRA, unless site-specific waivers are obtained. This means, for example, that whenever a remedial action involves on-site treatment, storage, or disposal of hazardous waste, the action must meet RCRA's technical standards for such treatment, storage, or disposal. The National Oil and Hazardous Substances Pollution Contingency Plan (NCP), which is the regulatory blueprint for the CERCLA program, addresses the application of ARARs to CERCLA remedial actions.

Once hazardous wastes are transported from a CERCLA site, they are subject to full RCRA regulation. Therefore, all transportation and TSD requirements under RCRA must be followed. This means that off-site shipments must be accompanied by a manifest. In particular, the off-site disposal of hazardous wastes can occur only at an RCRA facility in a unit in full compliance with the requirements. U.S. EPA policy requires that the disposal facility be inspected six months prior to receiving the waste.

For off-site land disposal of wastes resulting from a CERCLA activity, the program contains two additional requirements. First, the unit in which the wastes are to be disposed must not be releasing hazardous wastes or constituents into groundwater, surface water, or soil. Second, any releases from other units of the facility must be under an approved RCRA corrective action program. This policy assures that wastes shipped off-site from CERCLA sites are sent to environmentally sound waste management facilities.

Finally, U.S. EPA may not take or fund remedial actions in a state unless the state ensures the availability of hazardous waste treatment and disposal capacity by submitting a capacity assurance plan (CAP) to U.S. EPA. This capacity must be for facilities that are in compliance with RCRA requirements and must be adequate to manage hazardous wastes projected to be generated within the state over 20 years. This requirement limits and manages the amount of hazardous waste generated in the United States by encouraging waste minimization and recycling, interstate agreements, and efficient and realistic hazardous waste management systems. Currently, every state in the nation had submitted a CAP to U.S. EPA.

12.10.6 RCRA Corrective Action versus CERCLA Response

The cleanup of a site with hazardous waste contamination may be handled under either CERCLA, as described above, or RCRA. RCRA authorizes U.S. EPA to require corrective action (under an enforcement order or as part of a permit) whenever there is, or has been, a release of hazardous waste or constituents at TSDFs. The RCRA statute also provides similar corrective action authority in response to releases at interim status facilities. Further, RCRA allows U.S. EPA to require corrective action beyond the facility boundary. U.S. EPA interprets the term "corrective action" to cover the full range of possible actions, from studies and interim measures to full cleanups. Anyone who violates a corrective action order can be fined up to $27,500/d of noncompliance and runs the risk of having their permit or interim status suspended or revoked.

RCRA and CERCLA cleanup programs follow roughly the same approach to cleanups. In both, examinations of available data are carried out after discovery of a release to determine whether an emergency action is warranted. Both programs authorize short-term measures to abate immediate adverse effects of a release. Once an emergency has been addressed, both programs provide for appropriate investigation and more investigation as needed to establish long-term cleanup options. One major difference between the two programs involves funding. CERCLA requires that site conditions be analyzed according to HRS and that only NPL sites receive any remedial action funding. There is no comparable requirement under the RCRA corrective action program because the owner or operator of the site is responsible for the cost of the cleanup.

The facility owner or operator implements RCRA corrective action. On the other hand, a number of different parties can implement a CERCLA remedial action in a number of different ways. For example, agreements may be reached that allow the PRPs, the State, or the federal government to assume the lead for certain portions of a response action.

Generally, cleanups under RCRA corrective action or CERCLA will substantively satisfy the requirements of both programs. It is U.S. EPA's general policy for facilities subject to both CERCLA and RCRA to be deferred to RCRA authority. In some cases, however, it may be more appropriate to use both RCRA and CERCLA authorities. U.S. EPA has many procedures in place to facilitate coordination between RCRA and CERCLA programs.

12.10.7 Imminent Hazards under RCRA and CERCLA

Both RCRA and CERCLA contain provisions that allow U.S. EPA to require persons contributing to an imminent hazard to take the necessary actions to clean up releases. RCRA's imminent and substantial endangerment provision addresses nonhazardous as well as hazardous solid waste releases. The authority under CERCLA is essentially the same, except that CERCLA's authority to abate an imminent or substantial danger to public health or the environment is limited to hazardous substance releases. In an enforcement action, the RCRA and CERCLA imminent hazard provisions may be used in tandem to ensure adequate protection of human health and the environment.

Additional and detailed information about the topics covered in this section can be found in Ref. 19.

12.11 LEGISLATIVE ENVIRONMENTAL STATUTES AND REGULATIONS

U.S. EPA's mission is to protect human health and the environment. In order to further this mission, Congress has enacted many environmental laws to address releases, or threats of releases, of hazardous constituents. An understanding of these laws is necessary to determine where RCRA fits into the national environmental protection program established by Congress and implemented by U.S.

EPA. Each environmental statute has its own particular focus, whether it is controlling the levels of pollutants introduced into a single environmental medium (i.e., air, soil, or water) or addressing a specific area of concern, such as pesticides or waste cleanup.

While the segmentation of environmental issues simplifies the drafting of legislation, it complicates the implementation of environmental protection regulations. The media-, practice-, and chemical-specific boundaries established in the nation's environmental statutes are often artificial. Many different types of practices may be responsible for the release into the environment of the same contaminant. Moreover, individual contaminants are not confined to specific media. Volatile organic compounds, such as benzene or toluene, can be released into and contaminate the air, soil, and water. Additionally, uncontrolled pollutants may travel long distances by natural means and change physically, affecting multiple media. Therefore, a media- or contaminant-specific approach cannot fully address the magnitude and complexities of the waste management problem.

Many of these statutes interact closely and even overlap with RCRA. In order to avoid overregulation of industry and coordinate environmental protection laws, Congress required that U.S. EPA, when promulgating RCRA regulations, ensure consistency with and avoid duplication of regulatory provisions promulgated under other environmental statutes.

One statute in particular, CERCLA or Superfund, has a close-fitting relationship with RCRA. Both programs are similar in that their primary purpose is to protect human health and the environment from the dangers of hazardous waste. However, these statutes address the hazardous waste problem from two fundamentally different approaches:

- RCRA has a regulatory focus and authorizes control over the management of wastes from the moment of generation until final disposal.
- CERCLA has a response focus. Whenever there has been a breakdown in the waste management system (e.g., a release or a potential threat of a release of a hazardous substance, pollutant, or contaminant), CERCLA authorizes cleanup actions.

The following subsections summarize each statute and highlight its interaction with RCRA (Table 12.4).

12.11.1 CLEAN AIR ACT

The CAA[20] limits the emission of pollutants into the atmosphere in order to protect human health and the environment from the effects of airborne pollution. For six criteria pollutants (sulfur dioxide, particulate matter, nitrogen dioxide, carbon monoxide, ozone, and lead), U.S. EPA established National Ambient Air Quality Standards (NAAQS). Regulation of these criteria pollutants affords the public some protection from toxic air pollutants. Congress also mandated that CAA control emissions from specific industrial sources. Using this statutory authority, U.S. EPA designated hazardous air pollutants and set National Emission Standards for Hazardous Air Pollutants (NESHAPs). Primary responsibility for implementing both the NAAQS and NESHAP requirements rests with states. The major interactions between RCRA and CAA include the following[2]:

1. In September 1999, U.S. EPA finalized a rule that established coordinated CAA and RCRA requirements for incinerators, cement kilns, and LWAKs, commonly known as the MACT rule. This rule ensures that these facilities will avoid two potentially different regulatory compliance schemes by integrating the monitoring, compliance testing, recordkeeping, and permitting requirements of CAA and RCRA.
2. U.S. EPA has also developed organic air emission regulations for TSDFs and LQGs under RCRA. However, these RCRA regulations have been designed to minimize, to the extent possible, any overlap with CAA regulations.

TABLE 12.4
Major RCRA Interactions with Other Environmental Laws

Law	RCRA Interactions
CAA	• RCRA hazardous waste combustion facilities are subject to CAA permit requirements • Air emissions from RCRA incinerators and other TSDFs must comply with applicable CAA NAAQS and emission limitations • Pollutants and sludges extracted from CAA air emission control devices are subject to RCRA hazardous waste regulations if hazardous • Hospital, infectious, and medical waste incinerators are subject to NSPS and emission guidelines under CAA
CWA	• Sludges resulting from CWA wastewater treatment and pretreatment are subject to RCRA hazardous waste regulations if hazardous • Discharges from RCRA-permitted facilities must comply with the limitations set forth in NPDES permits • RCRA-regulated USTs may also be subject to CWA SPCC requirements
EPCRA	• Some RCRA TSDFs must submit annual reports to EPA detailing releases of chemicals to air, land, and water
FIFRA	• FIFRA controls limit the level of toxic pesticides that are produced and thereby reduce the amount of waste that needs to be managed as hazardous under RCRA • FIFRA requires the registration of pesticides and disinfectants used in medical waste treatment technologies
MPRSA	• MPRSA prevents waste from an RCRA generator or TSDF from being deposited into the ocean, except in accordance with a separate MPRSA permit
OSHA	• RCRA hazardous waste generators and TSDFs may need to comply with OSHA training and planning standards • RCRA cleanup activities and hazardous waste operations at generator facilities and TSDFs may need to comply with HAZWOPER regulations
SDWA	• MCLs may be adopted by the RCRA program as cleanup standards for corrective action • RCRA contains provisions parallel to SDWA that prohibit the underground injection of hazardous wastes, unless such wastes have been treated to meet their respective LDR treatment standards
TSCA	• TSCA controls on the disposal methods of certain chemicals, such as PCBs, reduce the amount of waste that needs to be managed as hazardous under RCRA • TSCA controls on the manufacture and use of certain chemical substances also reduce the amount of waste that needs to be managed as hazardous under RCRA

Source: Adapted from U.S. EPA, *RCRA Orientation Manual*, www.epa.gov/waste/inforesources/pubs/orientat/rom1.pdf.

3. While medical waste is not subject to federal RCRA regulation, air emissions from new and existing hospital, infectious, and medical waste incinerators are subject to New Source Performance Standards (NSPS) and emission guidelines under CAA.
4. Extraction of pollutants from air emissions using CAA controls (e.g., scrubbers) can create hazardous wastes or sludges containing such wastes. Disposal of these materials must comply with RCRA.

12.11.2 CLEAN WATER ACT

The CWA[21] imposes pollutant limitations for all discharges of wastewater from identifiable ("point") sources into the nation's waterways. These discharges are defined as either direct discharges, indirect discharges, or zero discharges.

Direct discharges are discharges from "point sources" into surface water pursuant to a National Pollutant Discharge Elimination System (NPDES) permit. NPDES permits are granted on a case-by-case basis and limit the permissible concentration of toxic constituents or conventional pollutants in effluents discharged to a waterway. These limits are generally established on the basis of the best available treatment technology and, where necessary, to protect surface water quality standards.

Under indirect discharges, the wastewater is first sent to a publicly owned treatment works (POTW), and then, after treatment by the POTW, discharged pursuant to an NPDES permit. Under these requirements, the generator of the wastes cannot simply transfer the waste materials to a POTW. Rather, the wastes must satisfy applicable treatment and toxic control requirements known as pretreatment standards, where they exist. POTWs that receive hazardous wastes for treatment are also subject to certain RCRA permit-by-rule requirements, and remain subject to RCRA corrective action.

Zero discharges mean that the wastewater is not being discharged to a navigable water, but rather is being land disposed (e.g., through spray irrigation) or is disposed by underground injection. Zero discharge facilities are subject to federal or state regulatory limitations that are as strict as those that apply to direct and indirect dischargers.

CWA also includes provisions intended to prevent oil spills into the navigable waters of the United States. These spill prevention, control, and countermeasures (SPCC) regulations establish spill prevention procedures and equipment requirements for nontransportation-related facilities with certain aboveground or underground oil storage capacities that could reasonably be expected to discharge oil into or upon the navigable waters of the United States or adjoining shorelines. The SPCC regulations provide a basic framework for operational procedures, containment requirements, and spill response procedures.

The major interactions between RCRA and CWA include the following[2]:

1. Sludge resulting from wastewater treatment and pretreatment under CWA must be handled as an RCRA waste under Subtitle C, if hazardous.
2. Discharges to surface waters from an RCRA-permitted facility must comply with the limitations set forth in an NPDES permit. This means that either the facility itself has obtained an NPDES permit or the wastes meet CWA pretreatment standards and have been transported to a POTW.
3. Dredged materials subject to the requirement of a CWA permit are not considered hazardous wastes under RCRA.
4. USTs that are subject to the technical requirements of RCRA's UST program may also be subject to CWA SPCC requirements.

12.11.3 EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT

Congress amended CERCLA in 1986 with the enactment of the SARA. These amendments improved the Superfund program and added an important section that focused on strengthening the rights of citizens and communities in the face of potential hazardous substance emergencies. This section, SARA Title III, or the EPCRA, was enacted in response to the more than 2000 deaths caused by the release of a toxic chemical in Bhopal, India.

EPCRA[22] is intended to help communities prepare to respond in the event of a chemical emergency, and to increase the public's knowledge of the presence and threat of hazardous chemicals. To this end, EPCRA requires the establishment of state and local committees to prepare communities for potential chemical emergencies. The focus of the preparation is a community emergency response plan that must

1. Identify the sources of potential emergencies.
2. Develop procedures for responding to emergencies.
3. Designate who will coordinate the emergency response.

EPCRA also requires facilities to notify the appropriate state and local authorities if releases of certain chemicals occur. Facilities must also compile specific information about hazardous chemicals they have on-site and the threats posed by those substances. Some of this information must be provided to state and local authorities. More specific data must be made available upon request from those authorities or from the general public.

The primary interaction between RCRA and EPCRA is that some RCRA TSDFs treating hazardous waste are required to submit annual reports to U.S. EPA of their releases of chemicals to air, land, and water.[2]

12.11.4 FEDERAL INSECTICIDE, FUNGICIDE, AND RODENTICIDE ACT

The FIFRA provides procedures for the registration of pesticide products to control their introduction into the marketplace. As such, its regulatory focus is different from most of the statutes discussed in this chapter. While the other statutes attempt to minimize and manage waste by-products at the end of the industrial process, FIFRA controls whether (and how) certain products are manufactured or sold in the first place.

FIFRA[23] imposes a system of pesticide product registrations. Such requirements include premarket review of potential health and environmental effects before a pesticide can be introduced in the United States, reregistration of products introduced prior to the enactment of FIFRA to assess their safety in light of current standards, and classification of pesticides for restricted or general use. Restricted products can be used only by those whose competence has been certified by a state program.

The major interactions between RCRA and FIFRA include the following[2]:

1. FIFRA controls limit the level of toxic pesticides that are produced, and thereby reduce the amount of waste that needs to be managed under RCRA.
2. FIFRA requires the registration of pesticides and disinfectants used in medical waste treatment technologies.

12.11.5 MARINE PROTECTION, RESEARCH, AND SANCTUARIES ACT

The MPRSA requires a permit for any material that is transported from a U.S. port or by a U.S. vessel for deposition at sea.[24]

There are two major areas of overlap between MPRSA and RCRA. MPRSA prevents waste from an RCRA generator or TSDF from being deposited into the ocean, except in accordance with a separate MPRSA permit. In addition, dredged materials subject to the requirement of an MPRSA permit are not considered as hazardous wastes under RCRA.[2]

12.11.6 OCCUPATIONAL SAFETY AND HEALTH ACT

The mission of the OSHA is to save lives, prevent injuries, and protect the health of employees in the workplace.[25] OSHA accomplishes these goals through several regulatory requirements including the hazard communication standard (HCS) and the Hazardous Waste Operations and Emergency Response Worker Protection Standard (HAZWOPER).

The HCS was promulgated to provide workers with access to information about the hazards and identities of the chemicals they are exposed to while working, as well as the measures they can take to protect themselves. OSHA's HCS requires employers to establish hazard communication programs to transmit information on the hazards of chemicals to their employees by means of labels on containers, material safety data sheets, and training programs.

The HAZWOPER was developed to protect the health and safety of workers engaged in operations at hazardous waste sites, hazardous waste treatment facilities, and emergency response locations. HAZWOPER covers issues such as training, medical surveillance, and maximum exposure limits.

The major interactions between RCRA and OSHA include the following[2]:

1. Hazardous waste generators and TSDFs may need to comply with OSHA training and planning standards, in addition to RCRA requirements.
2. HAZWOPER regulations may be applicable to RCRA corrective action cleanup activities and to hazardous waste operations at generator facilities and TSDFs.

12.11.7 SAFE DRINKING WATER ACT

The SDWA protects the nation's drinking water supply by establishing national drinking water standards (maximum concentration limits, MCLs, or specific treatment techniques) and by regulating underground injection control (UIC) wells.[26] The UIC program bans some types of underground disposal of RCRA hazardous wastes. With some exceptions, other materials cannot be injected underground without a UIC permit.

The major interactions between RCRA and SDWA include the following[2]:

1. MCLs may be adopted by the RCRA program as cleanup standards for corrective action. Selected MCLs are also used under the RCRA groundwater monitoring program for land disposal units.
2. RCRA also contains provisions parallel to SDWA that prohibit the underground injection of hazardous wastes, unless such wastes have been treated to meet their respective LDR treatment standards. RCRA also contains a ban on any injection of hazardous waste into "shallow" wells.

12.11.8 TOXIC SUBSTANCES CONTROL ACT

The primary focus of the TSCA is similar to that of FIFRA in that the statute provides authorities to control the manufacture and sale of certain chemical substances.[27] These requirements include testing of chemicals that are currently in commercial production or use, premarket screening and regulatory tracking of new chemical products, and controlling unreasonable risks once a chemical substance is determined to have an adverse effect on health or the environment. TSCA controls on such unreasonable risks include prohibiting the manufacture or certain uses of the chemical, requiring labeling, limiting volume of production or concentration, requiring replacement or repurchase of products, and controlling disposal methods. The major interactions between RCRA and TSCA include the following[2]:

1. TSCA has a direct effect on RCRA through controls on the disposal methods of certain chemicals, such as PCBs. For example, while TSCA regulates PCB disposal, RCRA also regulates PCB disposal when the PCBs are mixed with hazardous waste.
2. TSCA also regulates used oil that contains quantifiable levels of PCBs.
3. TSCA's indirect effect on RCRA is the same as FIFRA's. TSCA controls the manufacture and use of certain chemical substances, which limits the amount of waste that needs to be managed under RCRA.
4. U.S. EPA has proposed TSCA standards for the disposal of lead-based paint (LBP) debris to replace RCRA regulations. The new standards would establish disposal standards for LBP debris and identify recycling and incineration activities that would be controlled or prohibited. To avoid duplicative regulation, the waste that is subject to these new standards would not be subject to RCRA hazardous waste determination.

ACRONYMS

APA	Administrative Procedures Act
API	American Petroleum Institute

ARAR	Applicable or relevant and appropriate requirement
ATS	Alternative treatment standards
ATSDR	Agency for Toxic Substances and Disease Registry
BATF	Bureau of Alcohol, Tobacco, and Firearms
BDAT	Best demonstrated available technology
BIF	Boiler and industrial furnace
CAA	Clean Air Act
CAP	Capacity assurance plan
CCP	Commercial chemical product
CDC	Center for Disease Control
CEMS	Continuous Emissions Monitoring Systems
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act or Superfund
CERCLIS	Comprehensive Environmental Response, Compensation, and Liability Information System
CESQG	Conditionally exempt small quantity generator
CFC	Chlorofluorocarbon
CFR	Code of Federal Regulations
CPG	Comprehensive Procurement Guideline
CPT	Comprehensive Performance Test
CWA	Clean Water Act
DOT	Department of Transportation
DRE	Destruction and removal efficiency
EPA ID	U.S. EPA Identification
EPCRA	Emergency Planning and Community Right-to-Know Act
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FOIA	Freedom of Information Act
H	Hazard code
HAZWOPER	Hazardous waste operations and emergency response worker protection standard
HRS	Hazard ranking system
HSWA	Hazardous and Solid Waste Amendments
ID	Identification number
LBP	Lead-based paint
LDR	Land disposal restrictions
LQG	Large quantity generator
LQHUW	Large quantity handler of universal waste
LUST	Leaking underground storage tank
LWAK	Lightweight aggregate kiln
MACT	Maximum achievable control technology
MCL	Maximum contaminant level
MOA	Memorandum of Agreement
MPRSA	Marine Protection, Research, and Sanctuaries Act
MSWLF	Municipal solid waste landfill
NAAQS	National Ambient Air Quality Standards
NCAPS	National Corrective Action Prioritization System
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NESHAP	National Emission Standards for Hazardous Air Pollutants
NOC	Notification of compliance
NPDES	National Pollutant Discharge Elimination System
NPL	National priorities list
NSPS	New source performance standards

O&M	Operation and maintenance
OECD	Organization for Economic Cooperation and Development
OPA	Oil Pollution Act
OSHA	Occupational Safety and Health Act
OSW	U.S. EPA's Office of solid waste
PA	Preliminary assessment
PBT	Persistent, bioaccumulative, and toxic
PCB	Polychlorinated biphenyl
POHC	Principal organic hazardous constituent
POTW	Publicly owned treatment works
ppmv	parts per million by volume
PRP	Potentially responsible party
RCRA	Resource Conservation and Recovery Act
RCRIS	Resource Conservation and Recovery Act Information System
RD&D	Research, development, and demonstration
RD/RA	Remedial design/remedial action
RI/FS	Remedial investigation/feasibility study
RIC	RCRA information center
RMAN	Recovered Materials Advisory Notice
ROD	Record of decision
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SIC	Standard industrial classification
SI	Site inspection
SPCC	Spill prevention, control, and countermeasures
SQG	Small quantity generator
SQHUW	Small quantity handler of universal waste
SWDA	Solid Waste Disposal Act
TC	Toxicity characteristic
TCLP	Toxicity characteristic leaching procedure
TEQ	Toxicity equivalence
TSCA	Toxic Substances Control Act
TSD	Treatment, storage, and disposal
TSDF	Treatment, storage, and disposal facility
UIC	Underground injection control
U.S. EPA	United States Environmental Protection Agency
UST	Underground storage tank
UTS	Universal treatment standards

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APPENDIX: UNIVERSAL TREATMENT STANDARDS (UTS): 40 CFR 268.48

Constituent Name	CAS Number	Wastewater, Concentration (mg/L)	Nonwastewater Concentration (mg/kg unless noted as mg/L TCLP)*
Organic Constituents			
Acenaphthylene	208-96-8	0.059	3.4
Acenaphthene	83-32-9	0.059	3.4
Acetone	67-64-1	0.28	160
Acetonitrile	75-05-8	5.6	38
Acetophenone	96-86-2	0.01	9.7
2-Acetylaminofluorene	53-96-3	0.059	140
Acrolein	107-02-8	0.29	NA
Acrylamide	79-06-1	19	23
Acrylonitrile	107-13-1	0.24	84
Aldicarb sulfone	1646-83-4	0.056	0.28
Aldrin	309-00-2	0.021	0.066
4-Aminobiphenyl	92-67-1	0.13	NA
Aniline	62-53-3	0.81	14
Anthracene	120-12-7	0.059	3.4
Aramite	140-57-8	0.36	NA
α-BHC	319-84-6	0.00014	0.066
β-BHC	319-85-7	0.00014	0.066
δ-BHC	319-36-8	0.023	0.066
γ-BHC	58-89-9	0.0017	0.066
Benomyl	17804-35-2	0.056	1.4
Benzene	71-43-2	0.14	10
Benz(*a*)anthracene	56-55-3	0.059	3.4
Benzal chloride	98-87-3	0.055	6
Benzo(*b*)fluoranthene	205-99-2	0.11	6.8
Benzo(*k*)fluoranthene	207-08-9	0.11	6.8
Benzo(*ghi*)perylene	191-24-2	0.0055	1.8
Benzo(*a*)pyrene	50-32-8	0.061	3.4
Bromodichloromethane	75-27-4	0.35	15
Bromomethane/methyl bromide	74-83-9	0.11	15
4-Bromophenyl phenyl ether	101-55-3	0.055	15
n-Butyl alcohol	71-36-3	5.6	2.6
Butylate	2008-41-5	0.042	1.4
Butyl benzyl phthalate	85-68-7	0.017	28
2-sec-Butyl-4,6-dinitrophenol/ Dinoseb	88-85-7	0.066	2.5
Carbaryl	63-25-2	0.006	0.14
Carbenzadim	10605-21-7	0.056	1.4
Carbofuran	1563-66-2	0.006	0.14
Carbofuran phenol	1563-38-8	0.056	1.4
Carbon disulfide	75-15-o	3.8	4.8 mg/L TCLP
Carbon tetrachloride	56-23-5	0.057	6
p-Chloroaniline	106-47-8	0.46	16
Chlorobenzene	108-90-7	0.057	6

continued

Constituent Name	CAS Number	Wastewater, Concentration (mg/L)	Nonwastewater Concentration (mg/kg unless noted as mg/L TCLP)*
Chlorobenzilate	510-15-6	0.1	NA
2-Chloro-1,3-butadiene	126-99-8	0.057	0.28
Chlorodibromomethane	124-48-1	0.057	15
Chloroethane	75-00-3	0.27	6
bis(2-Chloroethoxy)methane	111-91-1	0.036	7.2
bis(2-Chloroethyl)ether	111-44-4	0.033	6
Chloroform	67-66-3	0.046	6
bis(2-Chloroisopropyl)ether	39638-32-9	0.055	7.2
p-Chloro-*m*-cresol	59-50-7	0.018	14
2-Chloroethyl vinyl ether	110-75-8	0.062	NA
Chloromethane/methyl chloride	74-87-3	0.19	30
2-Chloronaphthalene	91-58-7	0.055	5.6
2-Chlorophenol	95-57-8	0.044	5.7
3-Chloropropylene	107-05-1	0.036	30
Chrysene	218-01-9	0.059	3.4
o-Cresol	95-48-7	0.11	5.6
m-Cresol	108-39-4	0.77	5.6
p-Cresol	106-44-5	0.77	5.6
m-Cumenyl methylcarbamate	64-00-6	0.056	1.4
p,p′-DDD	72-54-8	0.023	0.087
o,p′-DDE	3424-82-6	0.031	0.087
p,p′-DDE	72-55-9	0.031	0.087
o,p′-DDT	789-02-6	0.0039	0.087
p,p′-DDT	50-29-3	0.0039	0.087
Dibenz(*ah*)anthracene	53-70-3	0.055	8.2
Dibenz(*ae*)pyrene	192-65-4	0.061	NA
1,2-Dibromo-3-chloropropane	96-12-8	0.11	15
1,2-Dibromoethane (ethylene dibromide)	106-93-4	0.028	15
Dibromomethane	74-95-3	0.11	15
m-Dichlorobenzene	541-73-1	0.036	6
o-Dichlorobenzene	95-50-1	0.088	6
p-Dichlorobenzene	106-46-7	0.09	6
Dichlorodifluoromethane	75-71-8	0.23	7.2
1,1-Dichloroethane	75-34-3	0.059	6
1,2-Dichloroethane	107-06-2	0.21	6
1,1-Dichloroethylene	75-35-4	0.025	6
trans-1,2-Dichloroethylene	156-60-5	0.054	30
2,4-Dichlorophenol	120-83-2	0.044	14
2,6-Dichlorophenol	87-65-0	0.044	14
2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	0.72	10
1,2-Dichloropropane	78-87-5	0.85	18
Dieldrin	60-57-1	0.017	0.13
Diethyl phthalate	84-66-2	0.2	28
p-Dimethylaminoazobenzene	60-11-7	0.13	NA
2-4-Dimethyl phenol	105-67-9	0.036	14
Dimethyl phthalate	131-11-3	0.047	28

continued

Constituent Name	**CAS Number**	**Wastewater, Concentration (mg/L)**	**Nonwastewater Concentration (mg/kg unless noted as mg/L TCLP)***
Di-*n*-butyl phthalate	84-74-2	0.057	28
1,4-Dinitrobenzene	100-25-4	0.32	2.3
4,6-Dinitro-*o*-cresol	534-52-1	0.28	160
2,4-Dinitrophenol	51-28-5	0.12	160
2,4-Dinitrotoluene	121-14-2	0.32	140
2,6-Dinitrotoluene	606-20-2	0.55	28
Di-*n*-octyl phthalate	117-84-0	0.017	28
Di-*n*-propylnitrosamine	621-64-7	0.4	14
1,4-Dioxane	123-91-1	12	170
Diphenylamine	122-39-4	0.92	13
Diphenylnitrosamine	86-30-6	0.92	13
1,2-Diphenylhydrazine	122-66-7	0.087	NA
Disulfoton	298-04-4	0.017	6.2
Dithiocarbamates (total)	NA	0.028	28
Endosulfan I	959-98-8	0.023	0.066
Endosulfan II	33213-65-9	0.029	0.13
Endrin aldehyde	7421-93-4	0.025	0.13
EPTC	759-94-4	0.042	1.4
Ethyl acetate	141-78-6	0.34	33
Ethyl benzene	100-41-4	0.057	10
Ethyl cyanide/propanenitrile	107-12-0	0.24	360
Ethyl ether	60-29-7	0.12	160
Ethyl methacrylate	97-63-2	0.14	160
Ethylene oxide	75-21-8	0.12	NA
Famphur	52-85-7	0.017	15
Fluoranthene	206-44-0	0.068	3.4
Fluorene	86-73-7	0.059	3.4
Formetanate hydrochloride	23422-53-9	0.056	1.4
Heptachlor	76-44-8	0.0012	0.066
Heptachlor epoxide	1024-57-3	0.016	0.066
Hexachlorobenzene	118-74-1	0.055	10
Hexachlorobutadiene	87-68-3	0.055	5.6
Hexachlorocyclopentadiene	77-47-4	0.057	2.4
HXCDDS (hexachlorodibenzo-*p*-dioxins)	NA	0.000063	0.001
HxCDFs (hexachlorodibenzofurans)	NA	0.000063	0.001
Hexachloroethane	67-72-1	0.055	30
lndeno (1,2,3-cd) pyrene	193-39-5	0.0055	3.4
lsodrin	465-73-6	0.021	0.066
lsosafrole	120-58-1	0.081	2.6
Repone	143-50-0	0.0011	0.13
Methacrylonitrile	126-98-7	0.24	84
Methanol	67-56-1	5.6	0.75 mg/L TCLP
Methapyrilene	91-80-5	0.081	1.5
Methiocarb	2032-65-7	0.056	1.4
Methomyl	16752-77-5	0.028	0.14
Methoxychlor	72-43-5	0.25	0.18

continued

Constituent Name	CAS Number	Wastewater, Concentration (mg/L)	Nonwastewater Concentration (mg/kg unless noted as mg/L TCLP)*
3-Methylcholanthrene	56-49-5	0.0055	15
4,4-Methylene bis(2-chloroaniline)	101-14-4	0.5	30
Methylene chloride	75-09-2	0.089	30
Methyl ethyl ketone	78-93-3	0.28	36
Methyl isobutyl ketone	108-10-1	0.14	33
Methyl methacrylate	80-62-6	0.14	160
Methyl methanesulfonate	66-27-3	0.018	NA
Methyl parathion	298-00-0	0.014	4.6
Metolcarb	1129-41-5	0.056	1.4
Mexacarbate	315-18-4	0.056	1.4
Molinate	2212-67-1	0.042	1.4
Naphthalene	91-20-3	0.059	5.6
2-Naphthylamine	91-59-8	0.52	NA
Nitrobenzene	98-95-3	0.068	14
5-Nitro-*o*-toluidine	99-55-8	0.32	28
o-nitrophenol	88-75-5	0.028	13
p-nitrophenol	100-02-7	0.12	29
N-nitrosodiethylamine	55-18-5	0.4	28
N-nitrosodimethylamine	62-75-9	0.4	2.3
N-nitroso-di-*n*-butylamine	924-16-3	0.4	17
N-nitrosomethylethylamine	10595-95-6	0.4	2.3
N-nitrosomorpholine	59-89-2	0.4	2.3
N-nitrosopiperidine	100-75-4	0.013	35
N-nitrosopyrrolidine	930-55-2	0.013	35
Oxamyl	23135-22-0	0.056	0.28
Parathion	56-38-2	0.014	4.6
Total PCBs	1336-36-3	0.1	10
Pebulate	1114-71-2	0.042	1.4
Pentachlorobenzene	608-93-5	0.055	10
PeCDFs (pentachlorodibenzofurans)	NA	0.000035	0.001
Pentachloroethane	76-01-7	0.055	6
Pentachloronitrobenzene	82-68-8	0.055	4.8
Pentachlorophenol	87-86-5	0.089	7.4
Phenol	108-95-2	0.039	6.2
Phorate	298-02-2	0.021	4.6
Phthalic acid	100-21-0	0.055	28
Phthalic anhydride	85-44-9	0.055	28
Physostigmine	57-47-6	0.056	1.4
Physostigmine salicylate	57-64-7	0.056	1.4
Promecarb	2631-37-0	0.056	1.4
Pronamide	23950-58-5	0.093	1.5
Propham	122-42-9	0.056	1.4
Propoxur	114-26-1	0.056	1.4
Prosulfocarb	52888-80-9	0.042	1.4
Pyrene	129-00-0	0.067	8.2
Pyridine	110-86-1	0.014	16

continued

Constituent Name	CAS Number	Wastewater, Concentration (mg/L)	Nonwastewater Concentration (mg/kg unless noted as mg/L TCLP)*
Safrole	94-59-7	0.081	22
Silvex/2,4,5-TP	93-72-1	0.72	7.9
1,2,4,5-Tetrachlorobenzene	95-94-3	0.055	14
TCDDs (tetrachlorodibenzo-*p*-dioxins)	NA	0.000063	0.001
TCDFs (tetrachlorodibenzofurans)	NA	0.000063	0.001
1,1,1,2-Tetrachloroethane	630-20-6	0.057	6
1,1,2,2-Tetrachloroethane	79-34-5	0.057	6
Tetrachloroethylene	127-18-4	0.056	6
2,3,4,6-Tetrachlorophenol	58-90-2	0.03	7.4
Toluene	108-88-3	0.08	10
Toxaphene	8001-35-2	0.0095	2.6
Triallate	2303-17-5	0.042	1.4
Tribromomethane (bromoform)	75-25-2	0.63	15
2,4,6-Tribromophenol	118-79-6	0.035	7.4
1,2,4-Trichlorobenzene	120-82-1	0.055	19
1,1,1-Trichloroethane	71-55-6	0.054	6
1,1,2-Trichloroethane	79-00-5	0.054	6
Trichloroethylene	79-01-6	0.054	6
Trichlorofluoromethane	75-69-4	0.02	30
2,4,5-Trichlorophenol	95-95-4	0.18	7.4
2,4,6-Trichlorophenol	88-06-2	0.035	7.4
2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	0.72	7.9
1,2,3-Trichloropropane	96-18-4	0.85	30
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.057	30
Triethylamine	121-44-3	0.081	1.5
tris-(2,3-Dibromopropyl) phosphate	126-72-7	0.11	0.1
Vernolate	1929-77-7	0.042	1.4
Vinyl chloride	75-01-4	0.27	6
Xylenes-mixed isomers (sum of *o*-, *m*-, and *p*-xylene concentrations)	1330-20-7	0.32	30
Inorganic Constituents			
Antimony	7440-36-0	1.9	1.15 mg/L TCLP
Arsenic	7440-38-2	1.4	5 mg/L TCLP
Barium	7440-39-3	1.2	21 mg/L TCLP
Beryllium	7440-41-7	0.82	1.22 mg/L TCLP
Cadmium	7440-43-g	0.69	0.11 mg/L TCLP
Chromium (total)	7440-47-3	2.77	0.60 mg/L TCLP
Cyanides (total)	57-12-5	1.2	590
Cyanides (amenable)	57-12-5	0.86	30
Fluorides	16984-48-8	35	NA
Lead	7439-92-1	0.69	0.75 mg/L TCLP

continued

Constituent Name	CAS Number	Wastewater, Concentration (mg/L)	Nonwastewater Concentration (mg/kg unless noted as mg/L TCLP)*
Mercury—nonwastewater from Retort	7439-97-6	NA	0.20 mg/L TCLP
Mercury—all others	7439-97-6	0.15	0.025 mg/L TCLP
Nickel	7440-02-0	3.98	11 mg/L TCLP
Selenium	7782-49-2	0.82	5.7 mg/L TCLP
Silver	7440-22-4	0.43	0.14 mg/L TCLP
Sulfides	18496-25-8	14	NA
Thallium	7440-28-0	1.4	0.20 mg/L TCLP
Vanadium	7440-62-2	4.3	1.6 mg/L TCLP
Zinc	7440-66-6	2.61	4.3 mg/L TCLP

Source: U.S. EPA.

[*] TCLP = toxicity characteristic leaching procedure.

13 Characteristics of Hazardous Industrial Waste

Nazih K. Shammas

CONTENTS

13.1 INTRODUCTION

The improper management of hazardous waste poses a serious threat to both the health of people and the environment. When the United States Environmental Protection Agency (U.S. EPA) began developing the hazardous waste management regulations in the late 1970s, the Agency estimated that only 10% of all hazardous waste was managed in an environmentally sound manner.

Proper identification of a hazardous waste can be a difficult and confusing task, as the Resource Conservation and Recovery Act (RCRA) regulations establish a complex definition of the term "hazardous waste." To help make sense of what is and is not a hazardous waste, this chapter presents the steps involved in the process of identifying, or "characterizing," a hazardous waste.

This chapter will introduce the entire hazardous waste identification process, but will focus particularly on the final steps and the characteristics and properties of hazardous wastes. After reading this chapter, one will be able to understand the hazardous waste identification process and the definition of hazardous waste, and be familiar with the following concepts:

1. Hazardous waste listings
2. Hazardous waste characteristics
3. The "mixture" and "derived-from" rules
4. The "contained-in" policy
5. The Hazardous Waste Identification Rules (HWIR)

13.2 HAZARDOUS WASTE IDENTIFICATION PROCESS

A hazardous waste is a waste with a chemical composition or other properties that make it capable of causing illness, death, or some other harm to humans and other life forms when mismanaged or released into the environment.[1] Developing a regulatory program that ensures the safe handling of such dangerous wastes, however, demands a far more precise definition of the term. U.S. EPA therefore created a series of hazardous waste identification regulations, which outline the process to determine whether any particular material is a hazardous waste for the purposes of RCRA.

Proper hazardous waste identification is essential to the success of the hazardous waste management program. The RCRA regulations require that any person who produces or generates a waste must determine if that waste is hazardous. For this purpose, the RCRA includes the following steps in the hazardous waste identification process[2]:

1. Is the waste a "solid waste"?
2. Is the waste specifically excluded from the RCRA regulations?
3. Is the waste a "listed" hazardous waste?
4. Does the waste exhibit a characteristic of hazardous waste?

Hazardous waste identification begins with an obvious point: in order for any material to be a hazardous waste, it must first be a waste. However, deciding whether an item is or is not a waste is not always easy. For example, a material (like an aluminum can) that one person discards could seem valuable to another person who recycles that material. U.S. EPA therefore developed a set of regulations to assist in determining whether a material is a waste. RCRA uses the term "solid waste" in place of the common term "waste." Under RCRA, the term "solid waste" means any waste, whether it is a solid, semisolid, or liquid. The first section of the RCRA hazardous waste identification regulations focuses on the definition of solid waste. For this chapter, you need only understand in general terms the role that the definition of solid waste plays in the RCRA hazardous waste identification process.

Only a small fraction of all RCRA solid wastes actually qualify as hazardous wastes. According to U.S. EPA estimates, of the 12 billion tons (metric) of industrial, agricultural, commercial, and household wastes generated annually, 254 million tons (2%) are hazardous, as defined by RCRA regulations.[3] At first glance, one would imagine that distinguishing between hazardous and nonhazardous wastes is a simple matter of chemical and toxicological analysis. Other factors must be considered, however, before evaluating the actual hazard posed by a waste's chemical composition. Regulation of certain wastes may be impractical, unfair, or otherwise undesirable, regardless of the hazards they pose. For instance, household waste can contain dangerous chemicals, such as solvents and pesticides, but making households subject to the strict RCRA waste management regulations would create a number of practical problems. Congress and U.S. EPA have exempted or excluded certain wastes, including household wastes, from the hazardous waste definition and regulations. Determining whether or not a waste is excluded or exempted from hazardous waste regulation is the second step in the RCRA hazardous waste identification process. Only after determining that a solid waste is not somehow excluded from hazardous waste regulation should the analysis proceed to evaluate the actual chemical hazard of a waste.

The final steps in the hazardous waste identification process determine whether a waste poses a sufficient chemical or physical hazard to merit regulation. These steps in the hazardous waste identification process involve evaluating the waste in light of the regulatory definition of hazardous waste. The remainder of this chapter explains the definition, characteristics, and properties of hazardous wastes.

13.3 EXCLUSIONS FROM SOLID AND HAZARDOUS WASTES

The statutory definition points out that whether a material is a solid waste is not based on the physical form of the material (i.e., whether or not it is a solid as opposed to a liquid or gas), but rather that the material is a waste. The regulations further define solid waste as any material that is discarded by being either *abandoned*, *inherently waste-like*, a certain *military munition*, or *recycled* (Figure 13.1). These terms are defined as follows:

1. *Abandoned.* This simply means "thrown away." A material is abandoned if it is disposed of, burned, or incinerated.
2. *Inherently waste-like.* Some materials pose such a threat to human health and the environment that they are always considered solid wastes; these materials are considered to be inherently waste-like. Examples of inherently waste-like materials include certain dioxin-containing wastes.

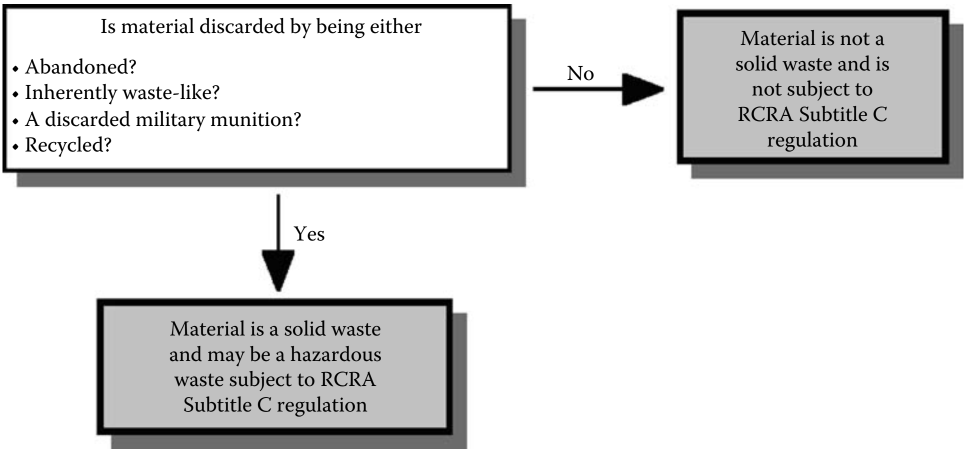

FIGURE 13.1 Determination of whether a waste is a solid waste. *Source:* U.S. EPA, Resource Conservation and Recovery Act—Orientation Manual, Report EPA 530-R-02-016, U.S. EPA, Washington, DC, January 2003.

3. *Military munitions.* Military munitions are all ammunition products and components produced for or used by the U.S. Department of Defense (DOD) or U.S. Armed Services for national defense and security. Unused or defective munitions are solid wastes when abandoned (i.e., disposed of, burned, incinerated) or treated prior to disposal; rendered nonrecyclable or nonuseable through deterioration; or declared a waste by an authorized military official. Used (i.e., fired or detonated) munitions may also be solid wastes if collected for storage, recycling, treatment, or disposal.
4. *Recycled.* A material is recycled if it is used or reused (e.g., as an ingredient in a process), reclaimed, or used in certain ways (used in a manner constituting disposal, burned for energy recovery, or accumulated speculatively).

13.3.1 RECYCLED MATERIALS

Materials that are recycled are a special subset of the solid waste universe. When recycled, some materials are not solid wastes, and therefore not hazardous wastes, but others are solid and hazardous waste, but are subject to less-stringent regulatory controls. The level of regulation that applies to recycled materials depends on the material and the type of recycling (Figure 13.2). Because some types of recycling pose threats to human health and the environment, RCRA does not exempt all recycled materials from the definition of solid waste. As a result, the manner in which a material is recycled will determine whether or not the material is a solid waste, and therefore whether it is

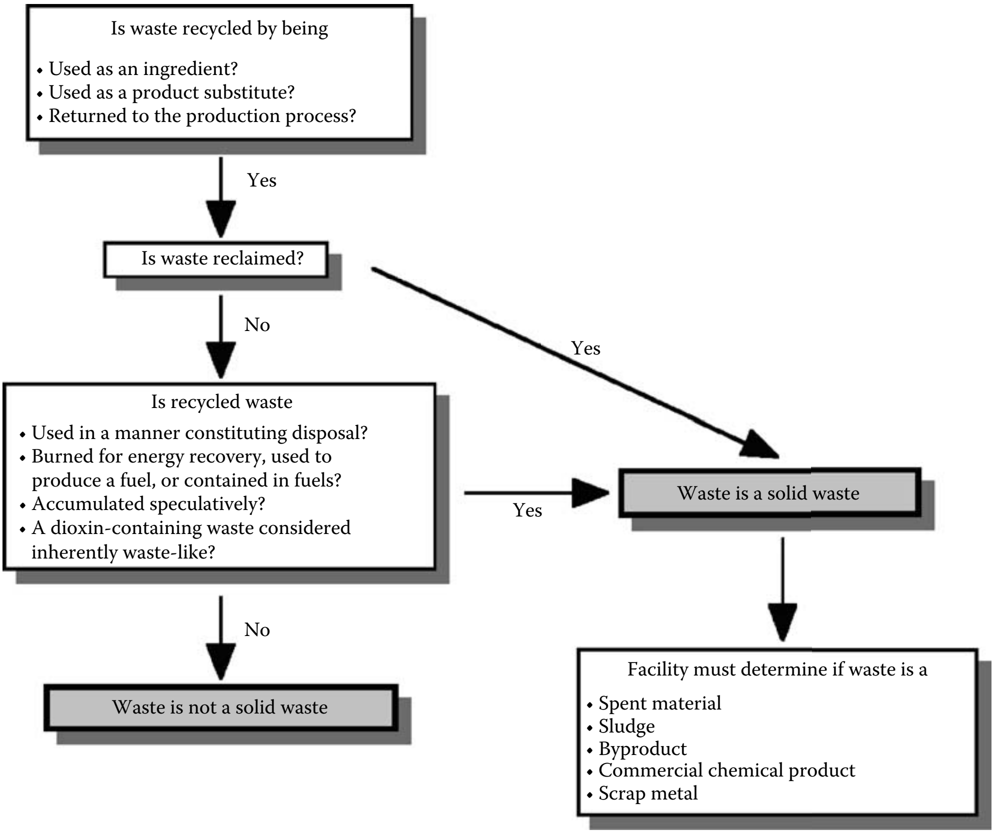

FIGURE 13.2 Determination of whether recycled wastes are hazardous wastes. *Source:* U.S. EPA, Resource Conservation and Recovery Act—Orientation Manual, Report EPA 530-R-02-016, U.S. EPA, Washington, DC, January 2003.

regulated as a hazardous waste. In order to encourage waste recycling, RCRA exempts three types of wastes from the definition of solid waste[2]:

1. *Wastes used as an ingredient.* If a material is directly used as an ingredient in a production process without first being reclaimed, then that material is not a solid waste.
2. *Wastes used as a product substitute.* If a material is directly used as an effective substitute for a commercial product (without first being reclaimed), it is exempt from the definition of solid waste.
3. *Wastes returned to the production process.* When a material is returned directly to the production process (without first being reclaimed) for use as a feedstock or raw material, it is not a solid waste.

Materials, however, are solid wastes and are not exempt if they are recycled in certain other ways. For example, materials recycled in the following ways are defined as solid wastes:

1. *Waste used in a manner constituting disposal.* Use constituting disposal is the direct placement of wastes or products containing wastes (e.g., asphalt with petroleum-refining wastes as an ingredient) on the land.
2. *Waste burned for energy recovery, used to produce a fuel, or contained in fuels.* Burning hazardous waste for fuel (e.g., burning for energy recovery) and using wastes to produce fuels are regulated activities. However, commercial products intended to be burned as fuels are not considered solid wastes. For example, off-specification jet fuel (e.g., a fuel with minor chemical impurities) is not a solid waste when it is burned for energy recovery, because it is itself a fuel.
3. *Waste accumulated speculatively.* In order to encourage recycling of wastes as well as to ensure that materials are recycled and not simply stored to avoid regulation, U.S. EPA established a provision to encourage facilities to recycle sufficient amounts in a timely manner. This provision designates as solid wastes those materials that are accumulated speculatively. A material is accumulated speculatively (e.g., stored in lieu of expeditious recycling) if it has no viable market or if the person accumulating the material cannot demonstrate that at least 75% of the material is recycled in a calendar year, commencing on January 1.
4. *Dioxin-containing wastes considered inherently waste-like.* Dioxin-containing wastes are considered inherently waste-like because they pose significant threats to human health and the environment if released or mismanaged. As a result, RCRA does not exempt such wastes from the definition of solid waste even if they are recycled through direct use or reuse without prior reclamation. This is to ensure that such wastes are subject to the most protective regulatory controls.

13.3.2 Secondary Materials

Not all materials can be used directly or reused without reclamation. A material is reclaimed if it is processed to recover a usable product (e.g., smelting a waste to recover valuable metal constituents), or if it is regenerated through processing to remove contaminants in a way that restores them to their useable condition (e.g., distilling dirty spent solvents to produce clean solvents). If secondary materials are reclaimed before use, their regulatory status depends on the type of material. For this solid waste determination process, U.S. EPA groups all materials into five categories: spent materials, sludges, byproducts, commercial chemical products (CCPs), and scrap metal.

13.3.2.1 Spent Materials

Spent materials are materials that have been used and can no longer serve the purpose for which they were produced without processing. For example, a solvent used to degrease metal parts will eventually become contaminated such that it cannot be used as a solvent until it is regenerated. If a spent material must be reclaimed, it is a solid waste and is subject to hazardous waste regulation. Spent materials are also regulated as solid wastes when used in a manner constituting disposal, when burned for energy recovery, when used to produce a fuel or contained in fuels, or when accumulated speculatively (see Table 13.1).

13.3.2.2 Sludges

Sludges are any solid, semisolid, or liquid wastes generated from a wastewater treatment plant, water supply treatment plant, or air pollution control device (e.g., filters, baghouse dust). Sludges from specific industrial processes or sources (known as listed sludges) are solid wastes when reclaimed, when used in a manner constituting disposal, when burned for energy recovery, used to produce a fuel, or contained in fuels, or when accumulated speculatively. On the other hand, characteristic sludges (those that exhibit certain physical or chemical properties) are not solid wastes when reclaimed, unless they are used in a manner constituting disposal, are burned for energy recovery, used to produce a fuel, or contained in fuels, or are accumulated speculatively (Table 13.1).

13.3.2.3 Byproducts

Byproducts are materials that are not one of the intended products of a production process. An example is the sediment remaining at the bottom of a distillation column. *Byproduct* is a catch-all term and includes most wastes that are not spent materials or sludges. Listed byproducts are solid wastes when reclaimed; used in a manner constituting disposal; burned for energy recovery, used to produce a fuel, or contained in fuels; or accumulated speculatively. On the other hand, characteristic byproducts are not solid wastes when reclaimed, unless they are used in a manner constituting disposal; burned for energy recovery, used to produce a fuel, or contained in fuels; or accumulated speculatively (Table 13.1).

13.3.2.4 Commercial Chemical Products

These are unused or off-specification chemicals (e.g., chemicals that have exceeded their shelf-life), spill or container residues, and other unused manufactured products that are not typically considered

TABLE 13.1
Regulatory Status of Secondary Materials

	These Materials are Solid Wastes When			
	Reclaimed	Used in a Manner Constituting Disposal	Burned for Energy Recovery, Used to Produce a Fuel, or Contained in Fuels	Accumulated Speculatively
Spent materials	X	X	X	X
Listed sludges	X	X	X	X
Characteristic sludges		X	X	X
Listed byproducts	X	X	X	X
Characteristic byproducts		X	X	X
Commercial chemical products		X[a]	X[a]	
Scrap metal	X	X	X	X

Source: U.S. EPA, Resource Conservation and Recovery Act—Orientation Manual, Report EPA 530-R-02-016, U.S. EPA, Washington, DC, January 2003.

[a] If such management is consistent with the product's normal use, then commercial chemical products used in a manner constituting disposal or burned for energy recovery, used to produce a fuel, or contained in fuels are not solid wastes.

chemicals. Commercial chemical products are not solid wastes when reclaimed, unless they are used in a manner constituting disposal; or burned for energy recovery, used to produce a fuel, or contained in fuels (Table 13.1).

13.3.2.5 Scrap Metal

Scrap metal comprises worn or extra bits and pieces of metal parts, such as scrap piping and wire, or worn metal items, such as scrap automobile parts and radiators. If scrap metal is reclaimed, it is a solid waste and is subject to hazardous waste regulation. Scrap metal is also regulated as a solid waste when used in a manner constituting disposal; burned for energy recovery, used to produce a fuel, or contained in fuels; or accumulated speculatively. This does not apply to processed scrap metal, which is excluded from hazardous waste generation entirely.

13.3.3 SHAM RECYCLING

For all recycling activities, the above rules are based on the premise that legitimate reclamation or reuse is taking place. U.S. EPA rewards facilities recycling some wastes by exempting them from regulation, or by subjecting them to less stringent regulation. Some facilities, however, may claim that they are recycling a material in order to avoid being subject to RCRA regulation, when in fact the activity is not legitimate recycling. U.S. EPA has established guidelines for what constitutes legitimate recycling and has described activities it considers to be illegitimate or sham recycling. Considerations in making this determination include whether the secondary material is effective for the claimed use, if the secondary material is used in excess of the amount necessary, and whether or not the facility has maintained records of the recycling transactions. Sham recycling may include situations when a secondary material falls into the following categories:

1. It is ineffective or only marginally effective for the claimed use (e.g., using certain heavy metal sludges in concrete when such sludges do not contribute any significant element to the concrete's properties).
2. It is used in excess of the amount necessary (e.g., using materials containing chlorine as an ingredient in a process requiring chlorine, but in excess of the required chlorine levels).
3. It is handled in a manner inconsistent with its use as a raw material or commercial product substitute (e.g., storing materials in a leaking surface impoundment as compared to a tank in good condition that is intended for storing raw materials).

13.3.4 EXEMPTIONS FROM HAZARDOUS WASTES

Not all RCRA solid wastes qualify as hazardous wastes. Other factors must be considered before deciding whether a solid waste should be regulated as a hazardous waste. Regulation of certain wastes may be impractical or otherwise undesirable, regardless of the hazards that the waste might pose. For instance, household waste can contain dangerous chemicals, such as solvents and pesticides, but subjecting households to the strict RCRA waste management regulations would create a number of practical problems. As a result, Congress and U.S. EPA exempted or excluded certain wastes, such as household wastes, from the hazardous waste definition and regulations. Determining whether or not a waste is excluded or exempted from hazardous waste regulation is the second step in the RCRA hazardous waste identification process. There are five categories of exclusions[2]:

1. Exclusions from the definition of solid waste
2. Exclusions from the definition of hazardous waste
3. Exclusions for waste generated in raw material, product storage, or manufacturing units
4. Exclusions for laboratory samples and waste treatability studies
5. Exclusions for dredged material regulated under the Marine Protection Research and Sanctuaries Act or the Clean Water Act

If the waste fits one of these categories, it is not regulated as an RCRA hazardous waste, and the hazardous waste requirements do not apply.

13.3.4.1 Solid Waste Exclusions

A material cannot be a hazardous waste if it does not meet the definition of a solid waste. Thus, wastes that are excluded from the definition of solid waste are not subject to the RCRA Subtitle C hazardous waste regulation. There are 20 exclusions from the definition of solid waste:

1. *Domestic sewage and mixtures of domestic sewage.* Domestic sewage, or sanitary waste, comes from households, office buildings, factories, and any other place where people live and work. These wastes are carried by sewer to a municipal wastewater treatment plant (called a publicly owned treatment works [POTW]). The treatment of these wastes is regulated under the Clean Water Act (CWA). Mixtures of sanitary wastes and other wastes (including hazardous industrial wastes) that pass through a sewer system to a POTW are also excluded from Subtitle C regulation once they enter the sewer. In certain circumstances, this exclusion may be applied to domestic sewage and mixtures of domestic sewage that pass through a federally owned treatment works (FOTW).
2. *Industrial wastewater discharges (point source discharges).* Another exclusion from RCRA designed to avoid overlap with CWA regulations applies to point source discharges. Point source discharges are discharges of pollutants (e.g., from a pipe, sewer, or pond) directly into a lake, river, stream, or other water body. CWA regulates such discharges under the National Pollutant Discharge Elimination System (NPDES) permitting program. Under this exclusion from the definition of solid waste, wastewaters that are subject to CWA regulations are exempt from Subtitle C regulation at the point of discharge. Any hazardous waste generation, treatment, or storage prior to the discharge is subject to RCRA regulation. Many industrial facilities that treat wastewater on site utilize this point source discharge exclusion.
3. *Irrigation return flows.* When farmers irrigate agricultural land, water not absorbed into the ground can flow into reservoirs for reuse. This return flow often picks up pesticide or fertilizer constituents, potentially rendering it hazardous. Because this water may be reused on the fields, it is excluded from the definition of solid waste.
4. *Radioactive waste.* Radioactive waste is regulated by either the Nuclear Regulatory Commission or the U.S. Department of Energy (DOE) under the Atomic Energy Act (AEA). To avoid duplicative regulation under RCRA and AEA, RCRA excludes certain radioactive materials from the definition of solid waste. However, RCRA excludes only the radioactive components of the waste. If a radioactive waste is mixed with a hazardous waste, the resultant mixture is regulated by both AEA and RCRA as a mixed waste. Similarly, if a facility generates a hazardous waste that is also radioactive, the material is a mixed waste and is subject to regulation under both RCRA and AEA.
5. In situ *mining waste. In situ* mining of certain minerals may involve the application of solvent solutions directly to a mineral deposit in the ground. The solvent passes through the ground, collecting the mineral as it moves. The mineral and solvent mixtures are then collected in underground wells where the solution is removed. Such solvent-contaminated earth, or any nonrecovered solvent, is excluded from the definition of solid waste when left in place.
6. *Pulping liquors.* Pulping liquor, also called black liquor, is a corrosive material used to dissolve wood chips for the manufacturing of paper and other materials. To promote waste minimization and recycling, U.S. EPA excluded pulping liquors from the definition of solid waste if they are reclaimed in a recovery furnace and then reused in the pulping process. If the liquors are recycled in another way, or are accumulated speculatively, they are not excluded.

7. *Spent sulfuric acid.* Spent sulfuric acid may be recycled to produce virgin sulfuric acid. To promote waste reduction and recycling, such recycled spent sulfuric acid is excluded from the definition of solid waste, unless the facility accumulates the material speculatively.
8. *Closed-loop recycling.* To further promote waste reduction and recycling, spent materials that are reclaimed and returned to the original process in an enclosed system of pipes and tanks are excluded from the definition of solid waste, provided that the following conditions are met:
   (a) Only tank storage is involved, and the entire process, through reclamation, is closed to the air (i.e., enclosed).
   (b) Reclamation does not involve controlled flame combustion, such as that which occurs in boilers, industrial furnaces, or incinerators.
   (c) Waste materials are never accumulated in tanks for more than 12 months without being reclaimed.
   (d) Reclaimed materials are not used to produce a fuel, or used to produce products that are used in a manner constituting disposal.

   An example of such a closed-loop system might include a closed solvent recovery system in which the dirty solvents are piped from the degreasing unit to a solvent still where the solvent is cleaned, and then piped back to the degreasing unit.
9. *Spent wood preservatives.* Many wood-preserving plants recycle their wastewaters and spent wood-preserving solutions. These materials are collected on drip pads and sumps, and are in many cases returned directly to the beginning of the wood-preserving process where they are reused in the same manner. Although the process resembles a closed-loop recycling process, the closed-loop recycling exclusion does not apply because drip pads are open to the air. Consistent with their objective to encourage recycling hazardous waste, U.S. EPA developed two specific exclusions for spent wood-preserving solutions and wastewaters containing spent preservatives, provided that the materials have been reclaimed and are reused for their original purpose. In addition, wood-preserving solutions and wastewaters are excluded from the definition of solid waste prior to reclamation. To use this exclusion, a facility is required to reuse the materials for their intended purpose and manage them in a way that prevents releases to the environment.
10. *Coke byproduct wastes.* Coke, used in the production of iron, is made by heating coal in high-temperature ovens. Throughout the production process many byproducts are created. The refinement of these coke byproducts generates several listed and characteristic wastestreams. However, to promote recycling of these wastes, U.S. EPA provided an exclusion from the definition of solid waste for certain coke byproduct wastes that are recycled into new products.
11. *Splash condenser dross residue.* The treatment of steel production pollution control sludge generates a zinc-laden residue, called dross. This material, generated from a splash condenser in a high-temperature metal recovery process, is known as a splash condenser dross residue. Because this material contains 50 to 60% zinc, it is often reclaimed, reused, or processed as a valuable recyclable material. Facilities commonly handle this material as a valuable commodity by managing it in a way that is protective of human health and the environment, so U.S. EPA excluded this residue from the definition of solid waste.
12. *Hazardous oil-bearing secondary materials and recovered oil from petroleum-refining operations.* Petroleum-refining facilities sometimes recover oil from oily wastewaters and reuse this oil in the refining process. In order to encourage waste minimization and recycling, U.S. EPA excluded such recovered oil from the definition of solid waste when it is returned to the refinery. Oil-bearing hazardous wastes that are recycled back into the petroleum-refining process are also excluded. In 2002, U.S. EPA proposed to conditionally exclude oil-bearing secondary materials that are processed in a gasification system to

produce synthesis gas fuel and other nonfuel chemical byproducts. Condensates from the Kraft process steam strippers, the most commonly used pulping process today, utilizes various chemicals to break down wood into pulp. This process generates overhead gases that are condensed and often recycled as fuel. To encourage the recycling of these condensates, U.S. EPA excluded them from the definition of solid waste provided the condensate is combusted at the mill that generated it.

13. *Comparable fuels.* In order to promote the recycling of materials with high fuel values, certain materials that are burned as fuels are excluded from the definition of solid waste, provided that they meet certain specifications (i.e., are of a certain degree of purity). This is to ensure that the material does not exceed certain levels of toxic constituents and physical properties that might impede burning. Materials that meet this specification are considered comparable to pure or virgin fuels.
14. *Processed scrap metal.* Scrap metal includes, but is not limited to, pipes, containers, equipment, wire, and other metal items that are no longer of use. To facilitate recycling, scrap metal that has been processed to make it easier to handle or transport and is sent for metals recovery is excluded from the definition of solid waste. Unprocessed scrap metal is still eligible for an exemption from hazardous waste regulation when recycled.
15. *Shredded circuit boards.* Circuit boards are metal boards that hold computer chips, thermostats, batteries, and other electronic components. Circuit boards can be found in computers, televisions, radios, and other electronic equipment. When this equipment is thrown away, these boards can be removed and recycled. Whole circuit boards meet the definition of scrap metal, and are therefore exempt from hazardous waste regulation when recycled. On the other hand, some recycling processes involve shredding the board. Such shredded boards do not meet the exclusion for recycled scrap metal. In order to facilitate the recycling of such materials, U.S. EPA excluded recycled shredded circuit boards from the definition of solid waste, provided that they are stored in containers sufficient to prevent release to the environment, and are free of potentially dangerous components, such as mercury switches, mercury relays, nickel–cadmium batteries, and lithium batteries.
16. *Mineral processing spent materials.* Mineral processing generates spent materials that may exhibit hazardous waste characteristics. Common industry practice is to recycle these mineral processing wastes back into the processing operations to recover mineral value. U.S. EPA created a conditional exclusion from the definition of solid waste for these spent materials when recycled in the mineral processing industry, provided the materials are stored in certain types of units and are not accumulated speculatively.
17. *Petrochemical recovered oil.* Organic chemical manufacturing facilities sometimes recover oil from their organic chemical industry operations. U.S. EPA excluded petrochemical recovered oil from the definition of solid waste when the facility inserts the material into the petroleum-refining process of an associated or adjacent petroleum refinery. Only petrochemical recovered oil that is hazardous because it exhibits the characteristic of ignitability or exhibits the toxicity characteristic for benzene (or both) is eligible for the exclusion.
18. *Spent caustic solutions from petroleum refining.* Petrochemical refineries use caustics to remove acidic compounds such as mercaptans from liquid petroleum streams to reduce produced odor and corrosivity as well as to meet product sulfur specifications. Spent liquid treating caustics from petroleum refineries are excluded from the definition of solid waste if they are used as a feedstock in the manufacture of napthenic and cresylic acid products. U.S. EPA believes that spent caustic, when used in this manner, is a valuable commercial feedstock in the production of these particular products, and is therefore eligible for exclusion.
19. *Glass frit and fluoride-rich baghouse dust generated by vitrification.* In July 2000, U.S. EPA proposed that glass frit and fluoride-rich baghouse dust generated by vitrification be classified as products and excluded from the definition of solid waste. Glass frit is useable

as a commercial chemical product, and fluoride-rich baghouse dust can be recycled back into the aluminum reduction pots as electrolyte or sold as a product for other industrial uses such as steel making.

20. *Zinc fertilizers made from recycled hazardous secondary materials.* U.S. EPA promulgated a conditional exclusion from the definition of solid waste for hazardous secondary materials that are recycled to make zinc fertilizers or zinc fertilizer ingredients. Zinc, an important micronutrient for plants and animals, can be removed from zinc-rich manufacturing residue and used to produce zinc micronutrient fertilizer. A second conditional exclusion applies to the zinc fertilizer products made from these secondary materials.

13.3.4.2 Hazardous Waste Exclusions

U.S. EPA also exempts certain solid wastes from the definition of hazardous waste. If a material meets an exemption from the definition of hazardous waste, it cannot be a hazardous waste, even if the material technically meets a listing or exhibits a characteristic. There are 16 exemptions from the definition of hazardous waste:

1. *Household hazardous waste.* Households often generate solid wastes that could technically be hazardous wastes (e.g., solvents, paints, pesticides, fertilizer, poisons). However, it would be impossible to regulate every house in the U.S. that occasionally threw away a can of paint thinner or a bottle of rat poison. Therefore, U.S. EPA developed the household waste exemption. Under this exemption, wastes generated by normal household activities (e.g., routine house and yard maintenance) are exempt from the definition of hazardous waste. U.S. EPA has expanded the exemption to include household-like areas, such as bunkhouses, ranger stations, crew quarters, campgrounds, picnic grounds, and day-use recreation areas. Although household hazardous waste is exempt from Subtitle C, it is regulated under Subtitle D as a solid waste.
2. *Agricultural waste.* To prevent overregulation of farms and promote waste recycling, solid wastes generated by crop or animal farming are excluded from the definition of hazardous waste provided that the wastes are returned to the ground as fertilizers or soil conditioners. Examples of such wastes are crop residues and manures.
3. *Mining overburden.* After an area of a surface mine has been depleted, it is common practice to return to the mine the earth and rocks (overburden) that were removed to gain access to ore deposits. When the material is returned to the mine site, it is not a hazardous waste under RCRA.
4. *Bevill and Bentsen wastes.* In the Solid Waste Disposal Act Amendments of 1980, Congress amended RCRA by exempting oil, gas, and geothermal exploration, development, and production wastes (Bentsen wastes); fossil fuel combustion wastes; mining and mineral processing wastes; and cement kiln dust wastes (Bevill wastes) from the definition of hazardous waste pending further study by U.S. EPA. These wastes were temporarily exempted because they were produced in very large volumes, were thought to pose less of a hazard than other wastes, and were generally not amenable to the management practices required under RCRA. Items 5 to 8 (following) describe these exemptions in detail.
5. *Fossil fuel combustion waste.* In order to accommodate effective study, fossil fuel combustion wastes were divided into two categories, large-volume coal-fired utility wastes and the remaining wastes. After studying these wastes, in 1993 U.S. EPA decided to permanently exempt large-volume coal-fired utility wastes, including fly ash, bottom ash, boiler slag, and flue gas emission control waste from the definition of hazardous waste. Further study by U.S. EPA, in 2000, indicated that all remaining fossil fuel combustion wastes need not be regulated under RCRA Subtitle C. However, U.S. EPA determined that national

nonhazardous waste regulations under RCRA Subtitle D are appropriate for coal combustion wastes disposed in surface impoundments and landfills and used as mine-fill. These regulations have now been proposed and subsequently finalized by U.S. EPA.

6. *Oil, gas, and geothermal wastes.* Certain wastes from the exploration and production of oil, gas, and geothermal energy are excluded from the definition of hazardous waste. These wastes include those that have been brought to the surface during oil and gas exploration and production operations, and other wastes that have come into contact with the oil and gas production stream (e.g., during removal of waters injected into the drill well to cool the drill bit).
7. *Mining and mineral processing wastes.* Certain wastes from the mining, refining, and processing of ores and minerals are excluded from the definition of hazardous waste.
8. *Cement kiln dust.* Cement kiln dust is a fine-grained solid byproduct generated during the cement manufacturing process and captured in a facility's air pollution control system. After study, U.S. EPA decided to develop specific regulatory provisions for cement kiln dust. Until U.S. EPA promulgates these new regulatory controls, however, cement kiln dust will generally remain exempt from the definition of hazardous waste.
9. *Trivalent chromium wastes.* The element chromium exists in two forms, hexavalent and trivalent. U.S. EPA determined that, although hexavalent chromium poses enough of a threat to merit regulation as a characteristic hazardous waste, trivalent chromium does not. Therefore, to prevent unnecessary regulation, U.S. EPA excluded from the definition of hazardous waste trivalent chromium-bearing hazardous wastes from certain leather-tanning, shoe-manufacturing, and leather-manufacturing industries.
10. *Arsenically treated wood.* Discarded arsenically treated wood or wood products that are hazardous only because they exhibit certain toxic characteristics (e.g., contain harmful concentrations of metal or pesticide constituents), are excluded from the definition of hazardous waste. Once such treated wood is used, it may be disposed of by the user (commercial or residential) without being subject to hazardous waste regulation. This exclusion is based on the fact that the use of such wood products on the land is similar to the common disposal method, which is landfilling. This exclusion applies only to end-users and not to manufacturers.
11. *Petroleum-contaminated media and debris from underground storage tanks (USTs).* USTs are used to store petroleum (e.g., oil) and hazardous substances (e.g., ammonia). When these tanks leak, the UST program under RCRA Subtitle I provides requirements for cleaning up such spills. To facilitate the corrective action process under the UST regulations, contaminated media (soils and groundwater) and debris (tanks and equipment) at sites undergoing UST cleanup that are hazardous only because they exhibit certain toxic characteristics (e.g., contain a harmful concentrations of leachable organic constituents) are excluded from the definition of hazardous waste.
12. *Spent chlorofluorocarbon refrigerants.* Chlorofluorocarbons (CFCs) released to the atmosphere damage the stratospheric ozone layer. To promote recycling and discourage the practice of venting used CFCs to the atmosphere as a means of avoiding Subtitle C regulation, U.S. EPA excluded recycled CFCs from the definition of hazardous waste because the refrigerants are generally reclaimed for reuse.
13. *Used oil filters.* In order to promote the recycling and recovery of metals and other products from used oil filters, U.S. EPA exempted used oil filters that have been properly drained to remove the used oil.
14. *Used oil distillation bottoms.* When used oil is recycled, residues (called distillation bottoms) form at the bottom of the recycling unit. To promote the recycling of used oil and the beneficial reuse of waste materials, U.S. EPA excluded these residues from the definition of hazardous waste when the bottoms are used as ingredients in asphalt paving and roofing materials.

15. *Landfill leachate or gas condensate derived from listed waste.* Landfill leachate and landfill gas condensate derived from previously disposed wastes that now meet the listing description of one or more of the petroleum refinery listed wastes would be regulated as a listed hazardous waste. However, U.S. EPA temporarily excluded such landfill leachate and gas condensate from the definition of hazardous waste provided their discharge is regulated under the CWA. The exclusion will remain effective while U.S. EPA studies how the landfill leachate and landfill gas condensate are currently managed, and the effect of future CWA effluent limitation guidelines for landfill wastewaters.
16. *Project XL pilot project exclusions.* U.S. EPA has provided two facilities with site-specific hazardous waste exclusions pursuant to the Project XL pilot program. The waste generated from the copper metallization process at the IBM Vermont XL project is excluded from the listing. Byproducts resulting from the production of automobile air bag gas generants at the Autoliv ASP Inc. XL project in Utah are also exempt from regulation as hazardous waste. In addition to these finalized exclusions, in July 2001 U.S. EPA proposed a site-specific exclusion for mixed wastes generated at the Ortho-McNeil Pharmaceutical Inc. facility in Spring House, PA, under the Project XL program.

13.3.4.3 Raw Material, Product Storage, and Process Unit Waste Exclusions

Hazardous wastes generated in raw material, product storage, or process (e.g., manufacturing) units are exempt from Subtitle C hazardous waste regulation while the waste remains in such units. These units include tanks, pipelines, vehicles, and vessels used either in the manufacturing process or for storing raw materials or products, but specifically do not include surface impoundments. Once the waste is removed from the unit, or when a unit temporarily or permanently ceases operation for 90 days, the waste is considered generated and is subject to regulation.

13.3.4.4 Sample and Treatability Study Exclusions

Hazardous waste samples are small, discrete amounts of hazardous waste that are essential to ensure accurate characterization and proper hazardous waste treatment. In order to facilitate the analysis of these materials, RCRA exempts characterization samples and treatability study samples from Subtitle C hazardous waste regulation:

1. *Waste characterization samples.* Samples sent to a laboratory to determine whether or not a waste is hazardous are exempt from regulation. Such samples (typically less than one gallon of waste) are excluded from Subtitle C regulation, provided that these samples are collected and shipped for the sole purpose of determining hazardous waste characteristics or composition. Storage, transportation, and testing of the sample are excluded from RCRA regulation even when the laboratory testing is complete, provided the sample is returned to the generator, and other specific provisions are met. When shipping the sample to or from the laboratory, the sample collector must comply with certain labeling requirements, as well as any applicable U.S. Postal Service (USPS) or U.S. Department of Transportation (DOT) shipping requirements.
2. *Treatability study samples.* To determine if a particular treatment method will be effective on a given waste or what types of wastes remain after the treatment is complete, facilities send samples of waste to a laboratory for testing. U.S. EPA conditionally exempts those who generate or collect samples for the sole purpose of conducting treatability studies from the hazardous waste regulations, provided that certain requirements, including packaging, labeling, and record-keeping provisions, are met. In addition, under specific conditions, laboratories conducting such treatability studies may also be exempt from Subtitle C regulation.

13.3.4.5 Dredge Materials Exclusions

Dredge materials subject to the permitting requirements of Section 404 of the Federal Water Pollution Control Act of Section 103 of the Marine Protection, Research, and Sanctuaries Act of 1972 are not considered hazardous wastes.

13.4 DEFINITION OF HAZARDOUS WASTE

According to Congress, the original statutory definition of the term *hazardous waste* is as follows:

> A solid waste, or combination of solid waste, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

This broad statutory definition provides a general indication of which wastes Congress intended to regulate as hazardous, but it obviously does not provide the clear distinctions necessary for industrial waste handlers to determine whether their wastes pose a sufficient threat to warrant regulation or not. Congress instructed U.S. EPA to develop more specific criteria for defining hazardous waste. There are therefore two definitions of hazardous waste under the RCRA program: a statutory definition and a regulatory definition. The statutory definition cited above is seldom used today. It served primarily as a general guideline for U.S. EPA to follow in developing the regulatory definition of hazardous waste. The regulatory definition is an essential element of the current RCRA program. It precisely identifies which wastes are subject to RCRA waste management regulations.

Congress asked U.S. EPA to fulfill the task of developing a regulatory definition of hazardous waste by using two different mechanisms: by listing certain specific wastes as hazardous and by identifying characteristics that, when present in a waste, make it hazardous. Following its statutory mandate, U.S. EPA developed a regulatory definition of hazardous waste that incorporates both listings and characteristics. In regulatory terms, a RCRA hazardous waste is a waste that appears on one of the four hazardous wastes lists (F list, K list, P list, or U list), or exhibits at least one of four characteristics—ignitability, corrosivity, reactivity, or toxicity.[4]

13.4.1 HAZARDOUS WASTE LISTINGS

A hazardous waste listing is a narrative description of a specific type of waste that U.S. EPA considers dangerous enough to warrant regulation. Hazardous waste listings describe wastes from various industrial processes, wastes from specific sectors of industry, or wastes in the form of specific chemical formulations. Before developing a hazardous waste listing, U.S. EPA thoroughly studies a particular wastestream and the threat it can pose to human health and the environment. If the waste poses enough of a threat, U.S. EPA includes a precise description of that waste on one of the hazardous waste lists in the regulations. Thereafter, any waste fitting that narrative listing description is considered hazardous, regardless of its chemical composition or any other potential variable. For example, one of the current hazardous waste listings is: "API separator sludge from the petroleum refining industry." An API separator is a device commonly used by the petroleum-refining industry to separate contaminants from refinery wastewaters. After studying the petroleum-refining industry and typical sludges from API separators, U.S. EPA decided these sludges were dangerous enough to warrant regulation as hazardous waste under all circumstances. The listing therefore designates all petroleum-refinery API separator sludges as hazardous. Chemical composition or other factors about a specific sample of API separator sludge are not relevant to its status as hazardous waste under the RCRA program.

Using listings to define hazardous wastes presents certain advantages and disadvantages. One advantage is that listings make the hazardous waste identification process easy for industrial waste handlers. Only knowledge of a waste's origin is needed to determine if it is listed; laboratory analysis is unnecessary. By comparing any waste to narrative listing descriptions, one can easily determine whether or not the waste is hazardous. U.S. EPA's use of listings also presents certain disadvantages. For example, listing a waste as hazardous demands extensive study of that waste by U.S. EPA. U.S. EPA lacks the resources to investigate the countless types of chemical wastes produced in the U.S., and therefore the hazardous waste listings simply cannot address all dangerous wastes. Another disadvantage of the hazardous waste listings is their lack of flexibility. Listings designate a waste as hazardous if it falls within a particular category or class. The actual composition of the waste is not a consideration as long as the waste matches the appropriate listing description. For instance, some API separator sludges from petroleum refining might contain relatively few hazardous constituents and pose a negligible risk to human health and the environment. Such sludges are still regulated as hazardous, however, because the listing for this wastestream does not consider the potential variations in waste composition. Thus, the hazardous waste listings can unnecessarily regulate some wastes that do not pose a significant health threat. It is also possible for industries to substantially change their processes so that wastes would no longer meet a listing description in spite of the presence of hazardous constituents. The hazardous waste characteristics provide an important complement to listings by addressing most of the shortcomings of the listing methodology of hazardous waste identification.

13.4.2 HAZARDOUS WASTE CHARACTERISTICS

A hazardous waste characteristic is a property that, when present in a waste, indicates that the waste poses a sufficient threat to merit regulation as hazardous. When defining hazardous waste characteristics, U.S. EPA does not study particular wastestreams from specific industries. Instead, U.S. EPA asks the question, "What properties or qualities can a waste have which cause that waste to be dangerous?" For example, U.S. EPA found that ignitability, or the tendency for a waste to easily catch fire and burn, is a dangerous property. Thus, ignitability is one of the hazardous waste characteristics, and a waste displaying that property is regulated as hazardous, regardless of whether the waste is listed. When defining hazardous waste characteristics, U.S. EPA identifies, where practicable, analytical tests capable of detecting or demonstrating the presence of the characteristic. For instance, U.S. EPA regulations reference a laboratory flash-point test to be used when deciding if a liquid waste is ignitable. Whether or not a waste displays a hazardous characteristic generally depends on how it fares in one of the characteristics tests. Therefore, the chemical makeup or other factors about the composition of a particular waste typically determine whether or not it tests as hazardous for a characteristic.

Using characteristics to define hazardous wastes presents certain advantages over designating hazardous wastes by listings. One advantage is that hazardous characteristics and the tests used to evaluate their presence have broad applicability. Once U.S. EPA has defined a characteristic and selected a test for use in identifying it, waste handlers can evaluate any wastestream to see if it is classified as a hazardous waste. Furthermore, use of characteristics can be a more equitable way of designating wastes as hazardous. Instead of categorizing an entire group of wastes as hazardous, characteristics allow a waste handler to evaluate each waste sample on its own merits and classify it according to the actual danger it poses. Aware of these advantages, U.S. EPA originally planned to use characteristics as the primary means of identifying hazardous waste. U.S. EPA hoped to define and select test methods for identifying all hazardous characteristics, including organic toxicity, mutagenicity (the tendency to cause mutations), teratogenicity (the tendency to cause defects in offspring), bioaccumulation potential, and phytotoxicity (toxicity to plants). U.S. EPA encountered problems, however, when trying to develop regulatory definitions of these properties. One primary problem was that no straightforward testing protocols were available for use in determining if a

TABLE 13.2
Typical Hazardous Wastes Generated by Selected Industries

Waste Generators	Waste Type
Chemical manufacturers	Strong acids and bases Reactive wastes Ignitable wastes Discarded commercial chemical products
Vehicle maintenance shops	Paint wastes Ignitable wastes Spent solvents Acids and bases
Printing industry	Photography waste with heavy metals Heavy metal solutions Waste inks Spent solvents
Paper industry	Ignitable wastes Corrosive wastes Ink wastes, including solvents and metals
Construction industry	Ignitable wastes Paint wastes Spent solvents Strong acids and bases
Cleaning agents and cosmetic manufacturing	Heavy metal dusts and sludges Ignitable wastes Solvents Strong acids and bases
Furniture and wood manufacturing and refinishing	Ignitable wastes Spent solvents Paint wastes
Metal manufacturing	Paint wastes containing heavy metals Strong acids and bases Cyanide wastes Sludges containing heavy metals

Source: U.S. EPA, Hazardous Waste, available at http://www.epa.gov/epaoswer/osw/hazwaste.htm#hazwaste, 2008.

waste possessed any of these characteristics. For example, deciding if a particular wastestream poses an unacceptable cancer risk demands extensive laboratory experimentation. Requiring such analysis on a routine basis from industrial waste handlers would be impractical. Therefore, U.S. EPA developed a hazardous waste definition that relies on both listings and characteristics to define hazardous wastes. Table 13.2 shows some typical hazardous wastes generated by selected industries.[3]

13.4.3 LISTED HAZARDOUS WASTES

U.S. EPA has studied and listed as hazardous hundreds of specific industrial wastestreams. These wastes are described or listed on four different lists that are found in the regulations (RCRA Part 261, Subpart D). These four lists are as follows[2]:

1. *The F list.* The F list designates as hazardous particular wastes from certain common industrial or manufacturing processes. Because the processes producing these wastes

can occur in different sectors of industry, the F list wastes are known as wastes from nonspecific sources.

2. *The K list.* The K list designates as hazardous particular wastestreams from certain specific industries. K-list wastes are known as wastes from specific sources.
3. *The P list and the U list.* These two lists are similar in that both list as hazardous pure or commercial grade formulations of certain specific unused chemicals.

These four lists each designate anywhere from 30 to a few hundred wastestreams as hazardous. Each waste on the lists is assigned a waste code consisting of the letter associated with the list followed by three numbers. For example, the wastes on the F list are assigned the waste codes F001, F002, and so on. These waste codes are an important part of the RCRA regulatory system. Assigning the correct waste code to a waste has important implications for the management standards that apply to the waste.

13.4.4 LISTING CRITERIA

Before listing any waste as hazardous, U.S. EPA developed a set of criteria to use as a guide when determining whether or not a waste should be listed. These listing criteria provide a consistent frame of reference when U.S. EPA considers listing a wastestream. Remember that U.S. EPA only uses these criteria when evaluating whether to list a waste; the listing criteria are not used by waste handlers, who refer to the actual hazardous waste lists for hazardous waste identification purposes. There are four different criteria upon which U.S. EPA may base its determination to list a waste as hazardous. Note that these four criteria do not directly correspond to the four different lists of hazardous waste. The four criteria U.S. EPA may use to list a waste as follows[1]:

1. The waste typically contains harmful chemicals, and other factors indicate that it could pose a threat to human health and the environment in the absence of special regulation. Such wastes are known as toxic listed wastes.
2. The waste contains such dangerous chemicals that it could pose a threat to human health and the environment even when properly managed. Such wastes are known as acutely hazardous wastes.
3. The waste typically exhibits one of the four characteristics of hazardous waste described in the hazardous waste identification regulations (ignitability, corrosivity, reactivity, or toxicity).
4. When U.S. EPA has a cause to believe for some other reason, the waste typically fits within the statutory definition of hazardous waste developed by Congress.

U.S. EPA may list a waste as hazardous for any and all of the above reasons. The majority of listed wastes fall into the toxic waste category. To decide if a waste should be a toxic listed waste, U.S. EPA first determines whether it typically contains harmful chemical constituents. An appendix to RCRA contains a list of chemical compounds or elements that scientific studies have shown to have toxic, carcinogenic, mutagenic, or teratogenic effects on humans or other life forms. If a waste contains chemical constituents found on the appendix list, U.S. EPA then evaluates 11 other factors to determine if the wastestream is likely to pose a threat in the absence of special restrictions on its handling. These additional considerations include a risk assessment and study of past cases of damage caused by the waste.

Acutely hazardous wastes are the second most common type of listed waste. U.S. EPA designates a waste as acutely hazardous if it contains the appendix constituents that scientific studies have shown to be fatal to humans or animals in low doses. In a few cases, acutely hazardous wastes contain no appendix constituents, but are extremely dangerous for another reason. An example is a listed waste that designates unused discarded formulations of nitroglycerine as acutely hazardous. Although nitroglycerine is not an appendix hazardous constituent, wastes containing unused nitroglycerine are so unstable that they pose an acute hazard. The criteria for designating a waste as acutely hazardous require only that U.S. EPA considers the typical chemical makeup of the wastestream. U.S. EPA is not required to study other factors, such as relative risk and evidence of harm, when listing a waste as acutely hazardous.

To indicate its reason for listing a waste, U.S. EPA assigns a hazard code to each waste listed on the F, K, P, and U lists. These hazard codes are listed below. The last four hazard codes apply to wastes that have been listed because they typically exhibit one of the four regulatory characteristics of hazardous waste. There will be more about the four characteristics of hazardous waste later in this chapter. The hazard codes indicating the basis for listing a waste are as follows[2]:

1. Toxic waste (T)
2. Acute hazardous waste (H)
3. Ignitable waste (I)
4. Corrosive waste (C)
5. Reactive waste (R)
6. Toxicity characteristic waste (E)

The hazard codes assigned to listed wastes affect the regulations that apply to handling the waste. For instance, acute hazardous wastes accompanied by the hazard code (H) are subject to stricter management standards than most other wastes.

13.4.5 The F List: Wastes from Nonspecific Sources

The F list designates as hazardous particular wastestreams from certain common industrial or manufacturing processes. F-list wastes usually consist of chemicals that have been used for their intended purpose in an industrial process. That is why F-list wastes are known as "manufacturing process wastes." The F list wastes can be divided into seven groups, depending on the type of manufacturing or industrial operation that creates them. The seven categories of F-listed wastes are as follows[1]:

1. Spent solvent wastes (F001 to F005)
2. Wastes from electroplating and other metal-finishing operations (F006 to F012, F019)
3. Dioxin-bearing wastes (F020 to F023 and F026 to F028)
4. Wastes from the production of certain chlorinated aliphatic hydrocarbons (F024, F025)
5. Wastes from wood preserving (F032, F034, and F035)
6. Petroleum refinery wastewater treatment sludges (F037 and F038)
7. Multisource leachate (F039)

13.4.5.1 Spent Solvent Wastes

Spent solvent wastes apply to wastestreams from the use of certain common organic solvents. Solvents are chemicals with many uses, although they are most often used in degreasing or cleaning. The solvents covered by the F listings are commonly used in industries ranging from mechanical repair to dry cleaning to electronics manufacturing. U.S. EPA decided that only certain solvents used in certain ways produce wastestreams that warrant a hazardous waste listing. Therefore, a number of key factors must be evaluated in order to determine whether the spent solvent wastes apply to a particular waste solvent. First, one or more of the 31 specific organic solvents designated in the spent solvent wastes listing description must have been used in the operation that created the waste. Second, the listed solvent must have been used in a particular manner; it must have been used for its "solvent properties," as U.S. EPA defines that expression. Finally, U.S. EPA decided that only a wastestream created through the use of concentrated solvents should be listed. Thus, the concentration of the solvent formulation or product before its use in the process that created the waste is also a factor in determining the applicability of the spent solvent wastes listing.

The spent solvent listings provide a good illustration of a principle common to all listed hazardous wastes. To determine whether a waste qualifies as listed, knowledge of the process that created the waste is essential, and information about the waste's chemical composition is often irrelevant. For example, the F005 listing description can allow two different wastes with identical chemical contents to be regulated differently because of subtle differences in the processes that created the wastes. A waste made up of toluene and paint is F005 if the toluene has been used to clean the paint from brushes or some other surface. A waste with the same chemical composition is not F005 if the toluene has been used as an ingredient (such as a thinner) in the paint. U.S. EPA considers use as a cleaner to be "use as a solvent"; use as an ingredient does not qualify as solvent use. As can be seen, knowledge of the process that created a waste is the key in evaluating whether a waste can be a hazardous spent solvent or other listed hazardous waste.

13.4.5.2 Wastes from Electroplating and Other Metal-Finishing Operations

The listed hazardous wastes from electroplating and other metal-finishing operations are wastes commonly produced during electroplating and other metal-finishing operations. Diverse industries use electroplating and other methods to change the surface of metal objects in order to enhance the appearance of the objects, make them more resistant to corrosion, or impart some other desirable property to them. Industries involved in plating and metal finishing range from jewelry manufacture to automobile production. A variety of techniques can be used to amend a metal's surface. For example, electroplating uses electricity to deposit a layer of a decorative or protective metal on the surface of another metal object. Chemical conversion coating also amends the surface of a metal, but does so by chemically converting (without use of electricity) a layer of the original base metal into a protective coating. Because each of these processes produces different types of wastes, U.S. EPA only designated wastes from certain metal-finishing operations as hazardous. The first step in determining whether one of the wastes from electroplating and other metal-finishing operations listings applies to a waste is identifying the type of metal-finishing process involved in creating the waste from the following list:

1. Electroplating operations
2. Metal heat-treating operations
3. Chemical conversion coating of aluminum

13.4.5.3 Dioxin-Bearing Wastes

The listings for dioxin-bearing wastes describe a number of wastestreams that U.S. EPA believes are likely to contain dioxins, which are considered to be among the most dangerous known chemical compounds. The dioxin listings apply primarily to manufacturing process wastes from the production of specific pesticides or specific chemicals used in the production of pesticides. One listing (F027) deserves special notice, because it does not apply to used manufacturing wastes. It applies only to certain unused pesticide formulations. This is in fact the only listing on the F list or the K list that describes an unused chemical rather than an industrial wastestream consisting of chemicals that have served their intended purpose. With the exception of one other listing (F028), all of the dioxin-bearing wastes are considered acute hazardous wastes and are designated with the hazard code (H). These wastes are therefore subject to stricter management standards than other hazardous wastes.

13.4.5.4 Wastes from the Production of Certain Chlorinated Aliphatic Hydrocarbons

Wastes from the production of certain chlorinated aliphatic hydrocarbons listings designate as hazardous certain wastestreams produced in the manufacture of chlorinated aliphatic hydrocarbons. These listings stand out on the F list (the list of wastes from nonspecific sources), because they focus on wastes from a very narrow industrial sector. Many other wastestreams from the manufacture of organic chemicals are listed on the K list, the list of wastes from specific sources, including two chlorinated aliphatic wastes.

13.4.5.5 Wood-Preserving Wastes

The wood-preserving wastes listings apply to certain wastes from wood-preserving operations. Many types of wood used for construction or other nonfuel applications are chemically treated to slow the deterioration caused by decay and insects. Such chemical treatment is commonly used in telephone poles, railroad ties, and other wood products prepared to withstand the rigors of outdoor use. Wood preservation typically involves pressure treating the lumber with pentachlorophenol, creosote, or preservatives containing arsenic or chromium. (It should be noted that, from January 1, 2004, many wood treaters have no longer been using arsenic- or chromium-based inorganic preservatives.) The wood-preserving process creates a number of common wastestreams containing these chemicals. For example, once wood has been treated with a preservative excess preservative drips from the lumber. The wood-preserving wastes listings designate this preservative drippage as listed hazardous waste. These listings also apply to a variety of other residues from wood preserving. Whether these listings apply to a particular wood-preserving waste depends entirely on the type of preservative used at the facility (waste generated from wood-preserving processes using pentachlorophenol is F032, waste from the use of creosote is F034, and waste from treating wood with arsenic or chromium is F035). The K list also includes the waste code K001, which applies to bottom sediment sludge from treating wastewaters associated with processes using pentachlorophenol or creosote.

13.4.5.6 Petroleum Refinery Wastewater Treatment Sludges

The petroleum refinery wastewater treatment sludges listings apply to specific wastestreams from petroleum refineries. The petroleum-refining process typically creates large quantities of contaminated wastewater. Before this wastewater can be discharged to a river or sewer, it must be treated to remove oil, solid material, and chemical pollutants. Gravity provides a simple way of separating these pollutants from refinery wastewaters. Over time, solids and heavier pollutants precipitate from wastewaters to form sludge. Other less dense pollutants accumulate on the surface of wastewaters, forming a material known as float. These gravitational separation processes can be encouraged using chemical or mechanical means. Some of the listings apply to sludge and float created by gravitational treatment of petroleum refinery wastewaters; other listings apply to sludge and float created during the chemical or physical treatment of refinery wastewaters. The K list also includes waste for certain petroleum wastestreams generated by the petroleum-refining industry.

13.4.5.7 Multisource Leachate

The multisource leachate listing applies to the liquid material that accumulates at the bottom of a hazardous waste landfill. Understanding the natural phenomenon known as leaching is essential to understanding a number of key RCRA regulations. Leaching occurs when liquids such as rainwater filter through soil or buried materials, such as wastes placed in a landfill. When this liquid comes into contact with buried wastes, it leaches or draws chemicals out of those wastes. This liquid (called leachate) can then carry the leached chemical contaminants further into the ground, eventually depositing them elsewhere in the subsurface or in groundwater. The leachate that percolates through landfills, particularly hazardous waste landfills, usually contains high concentrations of chemicals, and is often collected to minimize the potential that it may enter the subsurface environment and contaminate soil or groundwater.

13.4.6 THE K LIST: WASTES FROM SPECIFIC SOURCES

The K list of hazardous wastes designates particular wastes from specific sectors of industry and manufacturing as hazardous. The K list wastes are therefore known as wastes from specific sources. Like F list wastes, K list wastes are manufacturing process wastes. They contain chemicals that have been used for their intended purpose. To determine whether a waste qualifies as K-listed, two primary questions must be answered. First, is the facility that created the waste within one of the industrial or manufacturing categories on the K list? Second, does the waste match one of the specific K list waste descriptions? There are 13 industries that can generate K-list wastes[1]:

1. Wood preservation
2. Inorganic pigment manufacturing
3. Organic chemicals manufacturing
4. Inorganic chemicals manufacturing
5. Pesticides manufacturing
6. Explosives manufacturing
7. Petroleum refining
8. Iron and steel production
9. Primary aluminum production
10. Secondary lead processing
11. Veterinary pharmaceuticals manufacturing
12. Ink formulation
13. Coking (processing of coal to produce coke, a material used in iron and steel production)

It should be noted that not all wastes from these 13 industries are hazardous, only those specifically described in the detailed K-list descriptions.

In general, the K listings target much more specific wastestreams than the F listings. For example, U.S. EPA has added a number of listings to the petroleum-refining category of the K list. U.S. EPA estimates that 100 facilities nationwide produce wastestreams covered by these new K listings. In contrast, F-listed spent solvent wastes are commonly generated in thousands of different plants and facilities. It should also be noticed that industries generating K-listed wastes, such as the wood-preserving and petroleum-refining industries, can also generate F-listed wastes. Typically, K listings describe more specific wastestreams than F listings applicable to the same industry. For example, two K listings designate as hazardous two very specific types of petroleum refinery wastewater treatment residues: wastewater treatment sludges created in API separators and wastewater treatment float created using dissolved air flotation (DAF) pollution control devices. There are two F listings that complement these two K listings by designating as hazardous all other types of petroleum refinery wastewater treatment sludges and floats. These petroleum refinery listings illustrate that the K listings are typically more specific than the F listings. They also illustrate that the two lists are in many ways very similar.

13.4.7 THE P AND U LISTS: DISCARDED COMMERCIAL CHEMICAL PRODUCTS

The P and U lists designate as hazardous pure or commercial-grade formulations of certain unused chemicals. The P and U listings are quite different from the F and K listings. For a waste to qualify as P- or U-listed, a waste must meet the following three criteria:

1. The waste must contain one of the chemicals listed on the P or U list.
2. The chemical in the waste must be unused.
3. The chemical in the waste must be in the form of a "commercial chemical product."

It has already been explained that hazardous waste listings are narrative descriptions of specific wastestreams and that a waste's actual chemical composition is generally irrelevant to whether a listing applies to it. At first glance, the P and U listings seem inconsistent with these principles. Each P and U listing consists only of the chemical name of a compound known to be toxic or otherwise dangerous; no description is included. U.S. EPA adopted this format because the same narrative description applies to all P and U list wastes. Instead of appearing next to each one of the hundreds of P and U list waste codes, this description is found in the regulatory text that introduces the two lists.

The generic P and U list waste description involves two key factors. First, a P or U listing applies only if one of the listed chemicals is discarded unused. In other words, the P and U lists do not apply to manufacturing process wastes, as do the F and K lists. The P and U listings apply to unused chemicals that become wastes. Unused chemicals become wastes for a number of reasons. For example, some unused chemicals are spilled by accident. Others are intentionally discarded because they are off-specification and cannot serve the purpose for which they were originally produced.

The second key factor governing the applicability of the P or U listings is that the listed chemical must be discarded in the form of a "commercial chemical product." U.S. EPA uses the phrase commercial chemical product to describe a chemical that is in pure form, that is in commercial-grade form, or that is the sole active ingredient in a chemical formulation. The pure form of a chemical is a formulation consisting of 100% of that chemical. The commercial-grade form of a chemical is a formulation in which the chemical is almost 100% pure, but contains minor impurities. A chemical is the sole active ingredient in a formulation if that chemical is the only ingredient serving the function of the formulation. For instance, a pesticide made for killing insects may contain a poison such as heptachlor as well as various solvent ingredients that act as carriers or lend other desirable properties to the poison. Although all of these chemicals may be capable of killing insects, only the heptachlor serves the primary purpose of the insecticide product. The other chemicals involved are present for other reasons, not because they are poisonous. Therefore, heptachlor is the sole active ingredient in such a formulation, even though it may be present in low concentrations.

As can be seen, the P and U listings apply only to a very narrow category of wastes. For example, an unused pesticide consisting of pure heptachlor is listed waste P059 when discarded. An unused pesticide consisting of pure toxaphene is listed waste P123 when discarded. An unused pesticide made up of 50% heptachlor and 50% toxaphene as active ingredients, while being just as deadly as the first two formulations, is not a listed waste when discarded. That is because neither compound is discarded in the form of a commercial chemical product. The reason U.S. EPA chose such specific criteria for designating P- or U-listed chemicals as hazardous is that when U.S. EPA was first developing the definition of hazardous waste, it was not able to identify with confidence all the different factors that can cause a waste containing a known toxic chemical to be dangerous. It was obvious, however, that those wastes consisting of pure, unadulterated forms of certain chemicals were worthy of regulation. U.S. EPA used the P and U lists to designate hazardous wastes consisting of pure or highly concentrated forms of known toxic chemicals. As shall be seen in the following section of this chapter, wastes that remain unregulated by listings may still fall under protective hazardous waste regulation due to the four characteristics of hazardous waste.

13.5 CHARACTERISTIC HAZARDOUS WASTES

A hazardous waste characteristic is a property that indicates that a waste poses a sufficient threat to deserve regulation as hazardous. U.S. EPA tried to identify characteristics that, when present in a waste, can cause death or illness in humans or ecological damage. U.S. EPA also decided that the presence of any characteristic of hazardous waste should be detectable by using a standardized test method or by applying general knowledge of the waste's properties. U.S. EPA believed that unless generators were provided with widely available and uncomplicated test methods for determining whether their wastes exhibited hazardous characteristics, this system of identifying hazardous wastes would be unfair and impractical. Given these criteria, U.S. EPA only finalized four hazardous waste characteristics. These characteristics are a necessary supplement to the hazardous waste listings. They provide a screening mechanism that waste handlers must apply to all wastes from all industries. In this sense, the characteristics provide a more complete and inclusive means of identifying hazardous wastes than do the hazardous waste listings. The four characteristics of hazardous waste are as follows[4]:

1. Ignitability
2. Corrosivity
3. Reactivity
4. Toxicity

The regulations explaining these characteristics and the test methods to be used in detecting their presence are found in RCRA (Part 261, Subpart C). Note that although waste handlers can use the test methods referenced in Subpart C to determine whether a waste displays characteristics, they are not required to do so. In other words, any handler of industrial waste may apply knowledge of the waste's properties to determine if it exhibits a characteristic, instead of sending the waste for expensive laboratory testing. As with listed wastes, characteristic wastes are assigned waste codes. Ignitable, corrosive, and reactive wastes carry the waste codes D001, D002, and D003, respectively. Wastes displaying the characteristic of toxicity can carry any of the waste codes D004 through D043.

13.5.1 IGNITABILITY

Ignitable wastes are wastes that can readily catch fire and sustain combustion. Many paints, cleaners, and other industrial wastes pose such a fire hazard. Most ignitable wastes are liquid in physical form. U.S. EPA selected a flash point test as the method for determining whether a liquid waste is combustible enough to deserve regulation as hazardous. The flash point test determines the lowest temperature at which a chemical ignites when exposed to flame. Many wastes in solid or nonliquid physical form (e.g., wood, paper) can also readily catch fire and sustain combustion, but U.S. EPA did not intend to regulate most of these nonliquid materials as ignitable wastes. A nonliquid waste is only hazardous due to ignitability if it can spontaneously catch fire under normal handling conditions and can burn so vigorously that it creates a hazard. Certain compressed gases and chemicals called oxidizers can also be ignitable. Ignitable wastes are among the most common hazardous wastes.

13.5.2 CORROSIVITY

Corrosive wastes are acidic or alkaline (basic) wastes which can readily corrode or dissolve flesh, metal, or other materials. They are also among the most common hazardous wastestreams. Waste sulfuric acid from automotive batteries is an example of a corrosive waste. U.S. EPA uses two criteria to identify corrosive hazardous wastes. The first is a pH test. Aqueous wastes with a pH greater than or equal to 12.5, or less than or equal to 2 are corrosive under U.S. EPA's rules. A waste may also be corrosive if it has the ability to corrode steel in a specific U.S. EPA-approved test protocol.

13.5.3 REACTIVITY

A reactive waste is one that readily explodes or undergoes violent reactions. Common examples are discarded munitions or explosives. In many cases, there is no reliable test method to evaluate a waste's potential to explode or react violently under common handling conditions. Therefore, U.S. EPA uses narrative criteria to define most reactive wastes and allows waste handlers to use their best judgment in determining if a waste is sufficiently reactive to be regulated. This is possible because reactive hazardous wastes are relatively uncommon and the dangers they pose are well known to the few waste handlers who deal with them. A waste is reactive if it meets any of the following criteria:

1. It can explode or violently react when exposed to water or under normal handling conditions.
2. It can create toxic fumes or gases when exposed to water or under normal handling conditions.
3. It meets the criteria for classification as an explosive under DOT rules.
4. It generates toxic levels of sulfide or cyanide gas when exposed to a pH range of 2 to 12.5.

13.5.4 TOXICITY CHARACTERISTICS

The leaching of toxic compounds or elements into groundwater drinking supplies from wastes disposed of in landfills is one of the most common ways the general population can be exposed to the chemicals found in industrial wastes. U.S. EPA developed a characteristic designed to identify wastes likely to leach dangerous concentrations of certain known toxic chemicals into groundwater. In order to predict whether any particular waste is likely to leach chemicals into groundwater in the absence of special restrictions on its handling, U.S. EPA first designed a laboratory procedure that replicates the leaching process and other effects that occur when wastes are buried in a typical municipal landfill. This laboratory procedure is known as the "toxicity characteristic leaching procedure" (TCLP). Using the TCLP on a waste sample creates a liquid leachate that is similar to the liquid U.S. EPA would expect to find in the ground near a landfill containing the same waste. Once the leachate is created in the laboratory, a waste handler must determine whether it contains any of 39 different toxic chemicals above specified regulatory levels. If the leachate sample contains a sufficient concentration of one of the specified chemicals, the waste exhibits the toxicity characteristic (TC). U.S. EPA used groundwater modeling studies and toxicity data for a number of common toxic compounds and elements to set these threshold concentration levels. Much of the toxicity data were originally developed under the Safe Drinking Water Act (SDWA).

However, there is one exception to using the TCLP to identify a waste as hazardous. The DC Circuit Court, in *Association of Battery Recyclers vs. U.S. EPA*, vacated the use of the TCLP to determine whether manufactured gas plant (MGP) wastes exhibit the characteristic of toxicity. As previously stated, the TCLP replicates the leaching process in municipal landfills. The court found that U.S. EPA did not produce sufficient evidence that co-disposal of MGP wastes from remediation sites with municipal solid waste (MSW) has happened or is likely to happen. On March 13, 2002, in response to the court vacatur, U.S. EPA codified language exempting MGP waste from the toxicity characteristic regulation.

To recap, determining whether a waste exhibits the toxicity characteristic involves two principal steps[1]:

1. Creating a leachate sample using the TCLP
2. Evaluating the concentration of 39 chemicals in that sample against the regulatory levels listed in Table 13.3.

If a waste exhibits the TC, it carries the waste code associated with the compound or element that exceeded the regulatory level. Table 13.3 presents the toxicity characteristic waste codes, regulated constituents, and regulatory levels.

TABLE 13.3
Toxicity Characteristic Constituents and Regulatory Levels

Waste Code	Contaminants	Concentration (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D018	Benzene	0.5
D006	Cadmium	1.0
D019	Carbon tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D007	Chromium	5.0
D023	o-Cresol[a]	200.0
D024	m-Cresol[a]	200.0
D025	p-Cresol[a]	200.0
D026	Total cresols[a]	200.0
D016	2,4-D	10.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D012	Endrin	0.02
D031	Heptachlor (and its epoxide)	0.008
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D008	Lead	5.0
D013	Lindane	0.4
D009	Mercury	0.2
D014	Methoxychlor	10.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D010	Selenium	1.0
D011	Silver	5.0
D039	Tetrachloroethylene	0.7
D015	Toxaphene	0.5
D040	Trichloroethylene	0.5
D041	2,4,5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D017	2,4,5-TP (Silvex)	1.0
D043	Vinyl chloride	0.2

Source: U.S. EPA, Introduction to Hazardous Waste Identification (40 CFR, Part 261), Report U.S. EPA 530-K-05-012, U.S. EPA, Washington, DC, September 2005.

[a] If o-, m-, and p-cresols cannot be individually measured, the regulatory level for total cresols is used.

13.6 WASTES LISTED SOLELY FOR EXHIBITING THE CHARACTERISTIC OF IGNITABILITY, CORROSIVITY, OR REACTIVITY

Hazardous wastes listed solely for exhibiting the characteristic of ignitability, corrosivity, or reactivity are not regulated in the same way that other listed hazardous wastes are regulated under RCRA. When wastes are generated that meet a listing description for one of the 29 wastes listed only for exhibiting the characteristic of ignitability, corrosivity, or reactivity, the waste is not hazardous if it does not exhibit a characteristic.[5,6] This concept is consistent with the mixture and derived-from rules, which will be discussed in the following section. For example, F003 is listed for the characteristic of ignitability. If a waste is generated and meets the listing description for F003 but does not exhibit the characteristic of ignitability, it is not regulated as a hazardous waste. However, such wastes are still subject to the land disposal restrictions unless they do not exhibit a characteristic at the point of generation.

13.7 THE MIXTURE AND DERIVED-FROM RULES

So far, this chapter has introduced the fundamentals of the hazardous waste identification process and an overview of the hazardous waste listings and characteristics. One should now be able to explain in general terms which solid wastes are hazardous wastes. What remains to be explained is when these hazardous wastes cease being regulated as hazardous wastes. The regulations governing this issue are commonly known as the mixture and derived-from rules.

13.7.1 BACKGROUND

When U.S. EPA first developed the RCRA regulations and the definition of hazardous waste in the late 1970s, the Agency focused on establishing the listings and characteristics, criteria allowing industry to identify which wastes deserved regulation as hazardous wastes. Commenters on U.S. EPA's original proposed regulations brought up other key questions about the hazardous waste identification process. For example, these commenters asked, "Once a waste is identified as hazardous, what happens if that waste changes in some way? If the hazardous waste is changed, either by mixing it with other wastes or by treating it to modify its chemical composition, should it still be regulated as hazardous?" U.S. EPA developed a fairly simple and strict answer and presented it in the mixture and derived-from rules.

13.7.2 LISTED HAZARDOUS WASTES

The mixture and derived-from rules operate differently for listed wastes and characteristic wastes. The mixture rule for listed wastes states that a mixture made up of any amount of a nonhazardous solid waste and any amount of a listed hazardous waste is considered a listed hazardous waste. In other words, if a small vial of listed waste is mixed with a large quantity of nonhazardous waste, the resulting mixture bears the same waste code and regulatory status as the original listed component of the mixture. This principle applies regardless of the actual health threat posed by the waste mixture or the mixture's chemical composition. The derived-from rule governs the regulatory status of materials that are created by treating or changing a hazardous waste in some way. For example, ash created by burning a hazardous waste is considered "derived-from" that hazardous waste. The derived-from rule for listed wastes states that any material derived from a listed hazardous waste is also a listed hazardous waste. Thus, ash produced by burning a listed hazardous waste bears that same waste code and regulatory status as the original listed waste, regardless of the ash's actual properties.

The net effect of the mixture and derived-from rules for listed wastes can be summarized as follows: once a waste matches a listing description, it is forever a listed hazardous waste, regardless of how it is mixed, treated, or otherwise changed. Furthermore, any material that comes in contact with the listed waste will also be considered listed, regardless of its chemical composition.

Although the regulations do provide a few exceptions to the mixture and derived-from rules, most listed hazardous wastes are subject to the strict principles outlined above. To understand the logic behind the mixture and derived-from rules, one must consider the fact that if U.S. EPA relied solely on the narrative listing descriptions to govern when a waste ceased being hazardous, industry might easily circumvent RCRA's protective regulation. For example, a waste handler could simply mix different wastes and claim that they no longer exactly matched the applicable hazardous waste listing descriptions. These wastes would no longer be regulated by RCRA, even though the chemicals they contained would continue to pose the same threats to human health and the environment. U.S. EPA was not able to determine what sort of treatment or concentrations of chemical constituents indicated that a waste no longer deserved regulation. U.S. EPA therefore adopted the simple, conservative approach of the mixture and derived-from rules, while admitting that these rules might make some waste mixtures and treatment residues subject to unnecessary regulation. Adopting the mixture and derived-from rules also presented certain advantages. For instance, the mixture rule gives waste handlers a clear incentive to keep their listed hazardous wastes segregated from other nonhazardous or less dangerous wastestreams. The greater the volumes of hazardous waste the more expensive it is to store, treat and dispose.

13.7.3 Characteristic Wastes

The mixture and derived-from rules apply differently to listed and characteristic wastes. A mixture involving characteristic wastes is hazardous only if the mixture itself exhibits a characteristic. Similarly, treatment residues and materials derived from characteristic wastes are hazardous only if they themselves exhibit a characteristic. Unlike listed hazardous wastes, characteristic wastes are hazardous because they possess one of four unique and measurable properties. U.S. EPA decided that once a characteristic waste no longer exhibits one of these four dangerous properties, it no longer deserves regulation as hazardous. Thus, a characteristic waste can be made nonhazardous by treating it to remove its hazardous property; however, U.S. EPA places certain restrictions on the manner in which a waste can be treated. One can learn more about these restrictions in the U.S. EPA *Land Disposal Restrictions Module*.[7] Handlers who render characteristic wastes nonhazardous must consider these restrictions when treating wastes to remove their hazardous properties.

13.7.4 Waste Listed Solely for Exhibiting the Characteristic of Ignitability, Corrosivity, or Reactivity

All wastes listed solely for exhibiting the characteristic of ignitability, corrosivity, or reactivity (including mixtures, derived-from, and as-generated wastes) are not regulated as hazardous wastes once they no longer exhibit a characteristic.[5,8] U.S. EPA can list a waste as hazardous if that waste typically exhibits one or more of the four hazardous waste characteristics. If a hazardous waste listed only for the characteristics of ignitability, corrosivity, or reactivity is mixed with a solid waste, the original listing does not carry through to the resulting mixture if that mixture does not exhibit any hazardous waste characteristics. For example, U.S. EPA listed the spent solvents as hazardous because these wastes typically display the ignitability characteristic. If this waste is treated by mixing it with another waste, and the resulting mixture does not exhibit a characteristic, the listing no longer applies.

If a waste derived from the treatment, storage, or disposal of a hazardous waste listed for the characteristics of ignitability, corrosivity, or reactivity no longer exhibits one of those characteristics, it is not a hazardous waste. For example, if sludge is generated from the treatment of a listed waste and that sludge does not exhibit the characteristic of ignitability, corrosivity, or reactivity, the listing will not apply to the sludge.

13.7.5 MIXTURE RULE EXEMPTIONS

There are a few situations in which U.S. EPA does not require strict application of the mixture and derived-from rules. U.S. EPA determined that certain mixtures involving listed wastes and certain residues from the treatment of listed wastes typically do not pose enough of a health or environmental threat to deserve regulation as listed wastes. The principal regulatory exclusions from the mixture and derived-from rules are summarized below.

There are eight exemptions from the mixture rule. The first exemption from the mixture rule applies to mixtures of characteristic wastes and specific mining wastes excluded under RCRA. This narrow exemption allows certain mixtures to qualify as nonhazardous wastes, even if the mixtures exhibit one or more hazardous waste characteristics. The mining waste exclusion is explained in more detail in a U.S. EPA module.[9]

The remaining exemptions from the mixture rule apply to certain listed hazardous wastes that are discharged to wastewater treatment facilities. Many industrial facilities produce large quantities of nonhazardous wastewaters as their primary wastestreams. These wastewaters are typically discharged to a water body or local sewer system after being treated to remove pollutants, as required by the CWA. At many of these large facilities, on-site cleaning, chemical spills, or laboratory operations also create relatively small secondary wastestreams that are hazardous due to listings or characteristics. For example, a textile plant producing large quantities of nonhazardous wastewater can generate a secondary wastestream of listed spent solvents from cleaning equipment. Routing such secondary hazardous wastestreams to the facility's wastewater treatment system is a practical way of treating and getting rid of these wastes. This management option triggers the mixture rule, however, as even a very small amount of a listed wastestream combined with very large volumes of nonhazardous wastewater causes the entire mixture to be listed. U.S. EPA provided exemptions from the mixture rule for a number of these situations where relatively small quantities of listed hazardous wastes are routed to large-volume wastewater treatment systems. To qualify for this exemption from the mixture rule, the amount of listed waste introduced into a wastewater treatment system must be very small relative to the total amount of wastewater treated in the system, and the wastewater system must be regulated under the CWA.

13.7.6 DERIVED-FROM RULE EXEMPTIONS

There are five regulatory exemptions from the derived-from rule. The first of these derived-from rule exemptions applies to materials that are reclaimed from hazardous wastes and used beneficially. Many listed and characteristic hazardous wastes can be recycled to make new products or be processed to recover useable materials with economic value. Such products derived from recycled hazardous wastes are no longer solid wastes. Using the hazardous waste identification process discussed at the beginning of this chapter, if the materials are not solid wastes, then whether they are derived from listed wastes or whether they exhibit hazardous characteristics is irrelevant. A U.S. EPA module[10] explains which residues derived from hazardous wastes cease to be wastes and qualify for this exemption.

The other four exemptions from the derived-from rule apply to residues from the treatment of specific wastes using specific treatment processes. For example, one listing describes spent pickle liquor from the iron and steel industry. Pickle liquor is an acid solution used to finish the surface of steel. When pickle liquor is spent and becomes a waste, it usually contains acids and toxic heavy metals. This waste can be treated by mixing it with lime to form sludge. This treatment, called stabilization,[11,12] neutralizes the acids in the pickle liquor and makes the metals less dangerous by chemically binding them within the sludge. U.S. EPA studied this process and determined that the waste treated in this manner no longer poses enough of a threat to warrant hazardous waste regulation. Therefore, lime-stabilized waste pickle liquor sludge derived from the listed waste is not a listed hazardous waste. The other exemptions from the derived-from rule for listed wastes are also quite specific and include waste derived-from the burning of exempt recyclable fuels, biological treatment sludge derived-from treatment of listed waste, catalyst inert support media separated from a listed waste, and residues from high-temperature metal recovery of listed wastes, provided certain conditions are met.

13.7.7 DELISTING

The RCRA regulations provide another form of relief from the mixture and derived-from rule principles for listed hazardous wastes. Through a site-specific process known as “delisting,” a waste handler can submit to U.S. EPA a petition demonstrating that while a particular wastestream generated at their facility may meet a hazardous waste listing description, it does not pose sufficient hazard to deserve RCRA regulation. If U.S. EPA grants such a petition, the particular wastestream at that facility will not be regulated as a listed hazardous waste. Because the delisting process is difficult, time-consuming, and expensive, it is not considered a readily available exception to the mixture and derived-from from rules.

The hazardous waste listings, the hazardous waste characteristics, and the mixture and derived-from rules are all essential parts of the definition of hazardous waste, but these key elements are all described in different sections of the RCRA regulations. Only one regulatory section unites all four elements to establish the formal definition of hazardous waste. This section is entitled “Definition of Hazardous Waste,” which states that all solid wastes exhibiting one of the four hazardous characteristics are hazardous wastes. This section also states that all solid wastes listed on one of the four hazardous waste lists are hazardous wastes. Finally, this section explains in detail the mixture and derived-from rules and the regulatory exemptions from these rules. Thus, although the section is entitled Definition of Hazardous Waste, it serves primarily as a guide to the mixture and derived-from rules.

13.8 THE CONTAINED-IN POLICY

The contained-in policy is a special, more flexible version of the mixture and derived-from rules that applies to environmental media and debris contaminated with hazardous waste. *Environmental media* is the term U.S. EPA uses to describe soil, sediments, and groundwater. *Debris* is a term U.S. EPA uses to describe a broad category of larger manufactured and naturally occurring objects that are commonly discarded. Examples of debris include the following:

1. Dismantled construction materials such as used bricks, wood beams, and chunks of concrete
2. Decommissioned industrial equipment such as pipes, pumps, and dismantled tanks
3. Other discarded manufactured objects such as personal protective equipment (e.g., gloves, coveralls, eyewear)
4. Large, naturally occurring objects such as tree trunks and boulders

Environmental media and debris are contaminated with hazardous waste in a number of ways. Environmental media are usually contaminated through accidental spills of hazardous waste or spills of product chemicals that, when spilled, become hazardous wastes. Debris can also be contaminated through spills. Most debris in the form of industrial equipment and personal protective gear becomes contaminated with waste or product chemicals during normal industrial operations. Contaminated media and debris are primary examples of “remediation wastes.” In other words, they are not wastestreams created during normal industrial or manufacturing operations. They are typically created during cleanups of contaminated sites and during the decommissioning of factories. Handlers of contaminated media and debris usually cannot control or predict the composition of these materials, which have become contaminated though accidents or past negligence. In contrast, handlers of “as-generated wastes,” the term often used to describe chemical wastestreams created during normal industrial or manufacturing operations, can usually predict or control the creation of these wastes through the industrial process. Examples of as-generated wastes include concentrated spent chemicals, industrial wastewaters, and pollution control residues such as sludges.

The hazardous waste identification principles, including the mixture and derived-from rules, apply to as-generated industrial wastes. U.S. EPA decided that a more flexible version of these principles should apply to the primary remediation wastes: environmental media and debris. In particular, U.S. EPA determined that strict application of the mixture and derived-from rules was inappropriate for media and debris, especially when listed wastes were involved. Applying the mixture and derived-from rules to media and debris would present certain disadvantages, as the following examples illustrate. First, under the traditional mixture and derived-from rules, environmental media and debris contaminated with any amount of listed hazardous waste would be forever regulated as hazardous. Such a strict regulatory interpretation would require excavated or dismantled materials to be handled as listed hazardous wastes and could discourage environmental cleanup efforts. Second, most spills of chemicals into soil or groundwater produce very large quantities of these media containing relatively low concentrations of chemicals. Strict application of the mixture and derived-from principles to media would therefore cause many tons of soil to be regulated as listed hazardous waste, despite containing low concentrations of chemicals and posing little actual health threat. Finally, one of the main benefits of the mixture and derived-from rules is not relevant to media and debris. The mixture and derived-from principles encourage handlers of as-generated wastes to keep their listed wastes segregated from less hazardous wastestreams to avoid creating more listed wastes. Handlers of contaminated media and debris generally have no control over the process by which these materials come into contact with hazardous waste.

For all of the above reasons, U.S. EPA chose to apply a special, more flexible, version of the mixture and derived-from rules to environmental media and debris. Contaminated soil, groundwater, and debris can still present health threats if they are not properly handled or disposed. Therefore, U.S. EPA requires that any medium and debris contaminated with a listed waste or exhibiting a hazardous characteristic be regulated like any other hazardous waste. Media and debris contaminated with listed hazardous wastes can, however, lose their listed status and become nonhazardous. This occurs after a demonstration that the particular medium or debris in question no longer poses a sufficient health threat to deserve RCRA regulation. The requirements for making this demonstration are explained below. Once the demonstration is made, the medium or debris in question is no longer considered to contain a listed hazardous waste and is no longer regulated. In addition, contaminated media that contain a waste listed solely for the characteristics of ignitability, corrosivity, or reactivity, would no longer be managed as a hazardous waste when no longer exhibiting a characteristic.[5,13] This concept that media and debris can contain or cease to contain a listed hazardous waste accounts for the name of the policy.

The contained-in policy for environmental media is not actually codified in the RCRA regulations. In legal terms, it is merely a special interpretation of the applicability of the mixture and derived-from rules to soil and groundwater that has been upheld in federal court. These principles for the management of contaminated media are therefore known as a policy instead of a rule. The terms of the contained-in policy are relatively general. In order for environmental media contaminated with a listed waste to no longer be considered hazardous, the handler of that media must demonstrate to U.S. EPA's satisfaction that it no longer poses a sufficient health threat to deserve RCRA regulation. Although handlers of listed media must obtain U.S. EPA's concurrence before disposing of such media as nonhazardous, the current contained-in policy provides no guidelines on how this demonstration to U.S. EPA should be made. The contained-in policy is a far easier option for eliminating unwarranted hazardous waste regulation for low-risk listed wastes than the process of delisting a hazardous waste mentioned previously. The delisting process demands extensive sampling and analysis, submission of a formal petition, and a complete rulemaking by U.S. EPA. A determination that an environmental medium no longer contains a listed hazardous waste can be granted on a site-specific basis by U.S. EPA officials without any regulatory procedure.

Debris contaminated with hazardous waste has traditionally been governed by the same nonregulatory contained-in policy explained above. In 1992, U.S. EPA codified certain aspects of the contained-in policy for debris in the definition of hazardous waste regulations.[14,15] In particular, U.S. EPA included a regulatory passage that explains the process by which handlers of debris contaminated with listed hazardous waste can demonstrate that the debris is nonhazardous. This passage also references certain treatment technologies for decontaminating listed debris so that it no longer contains a listed waste. Thus, the term contained-in policy is now something of a misnomer for contaminated debris, since a contained-in rule for debris now exists.

13.9 REGULATORY DEVELOPMENTS

The hazardous waste identification process is subject to critical review, and adjusted accordingly to reflect technology changes and new information. The hazardous waste listings are particularly dynamic as U.S. EPA conducts further research to incorporate new listings. The following is a brief discussion of several developments to hazardous waste identification.

13.9.1 THE HAZARDOUS WASTE IDENTIFICATION RULES

U.S. EPA proposed to significantly impact the RCRA hazardous waste identification process through a rulemaking effort called the Hazardous Waste Identification Rules (HWIR). The first rule, HWIR-media, was finalized on November 30, 1998, and addressed contaminated media.[16] The second rule, HWIR-waste, was finalized on May 16, 2001, and modified the mixture and derived-from rules, as well as the contained-in policy for listed wastes.[5] Both the HWIR-media rule and the HWIR-waste rule attempt to increase flexibility in the hazardous waste identification system by providing a regulatory mechanism for certain hazardous wastes with low concentrations of hazardous constituents to exit the RCRA Subtitle C universe.

The final HWIR-media rule addresses four main issues:

1. The Agency promulgated a streamlined permitting process for remediation sites that will simplify and expedite the process of obtaining a permit.
2. U.S. EPA created a new unit, called a “staging pile,” that allows more flexibility when storing remediation wastes during cleanups.
3. U.S. EPA promulgated exclusion for dredged materials permitted under the CWA, or the Marine Protection, Research, and Sanctuaries Act.
4. The rule finalized provisions that enable states to more easily receive authorization when their RCRA programs are updated in order to incorporate revisions to the federal RCRA regulations.

On July 18, 2000, the Agency released HWIR-waste exemption levels for 36 chemicals that were developed using a risk model known as the Multimedia, Multi-pathway and Multi-receptor Risk Assessment (3MRA) Model.[17] The May 16, 2001, HWIR-waste rule revised and retained the hazardous waste mixture and derived-from rules as previously discussed in this module. In addition, the rule finalized provisions that conditionally exempt mixed waste (waste that is both radioactive and hazardous), if the mixed waste meets certain conditions in the rule.[5]

13.9.2 FINAL HAZARDOUS WASTE LISTING DETERMINATIONS

U.S. EPA first signed a proposed consent decree with the Environmental Defense Fund (EDF), following a suit concerning U.S. EPA’s obligations to take certain actions pursuant to RCRA. A consent decree is a legally binding agreement, approved by the Court, which details the agreements of the parties in settling a suit. The proposed consent decree, commonly known as the “mega-deadline,” settles some of the outstanding issues from the case by creating a schedule for U.S. EPA to take action on its RCRA obligations. The consent decree, which has been updated periodically, requires U.S. EPA to evaluate specified wastestreams and determine whether or not to add them to the hazardous waste listings.

On November 8, 2000, U.S. EPA listed as hazardous two wastes generated by the chlorinated aliphatics industry.[18] The two wastes are wastewater treatment sludges from the production of ethylene dichloride or vinyl chloride monomer (EDC/VCM), and wastewater treatment sludges from the production of vinyl chloride monomer using mercuric chloride catalyst in an acetylene-based process.

On November 20, 2001, U.S. EPA published a final rule listing three wastes generated from inorganic chemical manufacturing processes as hazardous wastes.[19] The three wastes are baghouse filters from the production of antimony oxide, slag from the production of antimony oxide that is speculatively accumulated or disposed, and residues from manufacturing and manufacturing-site storage of ferric chloride from acids formed during the production of titanium dioxide using the chloride-ilmenite process.

U.S. EPA proposed a concentration-based hazardous waste listing for certain waste solids and liquids generated from the production of paint on February 13, 2001.[20] Following a review of the public comments and supplemental analyses based on those public comments, U.S. EPA determined that the paint wastes identified in the proposal do not present a substantial hazard to human health or the environment. Therefore, U.S. EPA did not list these paint production wastes as hazardous. See the April 4, 2002, final determination regarding these hazardous waste listings for additional information.[21]

On February 24, 2005, U.S. EPA published a final rule listing nonwastewaters from the production of certain dyes, pigments, and food, drug, and cosmetic colorants[22] as hazardous, using a mass loading-based approach. Under the mass loading approach, these wastes are hazardous if they contain any of the constituents of concern at annual mass loading levels that meet or exceed the regulatory levels. The listing focuses on seven hazardous constituents: aniline, o-anisidine, 4-chloroaniline, p-cresidine, 1,2-phenylenediamine, 1,3-phenylenediamine, and 2,4-dimethylaniline. Waste that contains less than the specified threshold levels of constituents of concern are not hazardous. This listing is U.S. EPA's final obligation under the consent decree.

13.9.3 Proposed Revision to Wastewater Treatment Exemption for Hazardous Waste Mixtures

On April 8, 2003, U.S. EPA proposed to add benzene and 2-ethoxyethanol to the list of solvents whose mixtures with wastewater are exempted from the definition of hazardous waste.[23] U.S. EPA is proposing to provide flexibility in the way compliance with the rule is determined by adding the option of directly measuring solvent chemical levels at the headworks of the wastewater treatment system. In addition, U.S. EPA is proposing to include scrubber waters derived from the combustion of spent solvents to the headworks exemption. Finally, U.S. EPA is finalizing the "Headworks Rule," as follows[24]:

- adds benzene and 2-ethoxyethanol to the list of solvents whose mixtures with wastewaters are exempted from the definition of hazardous waste,
- exempts scrubber waters derived from the combustion of any of the exempted solvents,
- adds an option to allow generators to directly measure solvent chemical levels at the headworks of the wastewater treatment system to determine whether the wastewater mixture is exempt from the definition of hazardous waste, and
- extends the eligibility for the de minimis exemption to other listed hazardous wastes (beyond discarded commercial chemical products) and to non-manufacturing facilities.

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20. U.S. EPA, Rule 66 FR 10060, U.S. EPA, Washington, DC, February 13, 2001.
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22. U.S. EPA, Rule 70 FR 9138, U.S. EPA, Washington, DC, February 24, 2005.
23. U.S. EPA, Rule 70 68 FR 17234, U.S. EPA, Washington, DC, April 8, 2003.
24. U.S. EPA, Revision of Wastewater Treatment Exemptions for Hazardous Waste Mixtures (“Headworks Exemptions”), http://www.epa.gov/epaoswer/hazwaste/id/headworks/index.htm, November 14, 2007.

14 Soil Remediation

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14.1 INTRODUCTION

14.1.1 CONTAMINATION OF SOILS

Soil can be defined as the top layer of the Earth's crust, consisting of mineral particles, organic matter, water, air, and living organisms. As the interface between the Earth's atmosphere and the lithosphere, soil performs a number of diverse functions essential for life preservation and human activities; it is the substrate necessary for the growth of plants and animals and the basis for all agricultural production, and it serves as a protection and filtering layer necessary for clean groundwater supplies. The rate of soil formation and regeneration is very slow, so soil is practically a nonrenewable resource. In view of the high rates of soil degradation, it has become essential that soil resources be protected against the factors that degrade its quality and limit its availability. Human activities can greatly affect the geochemical cycles of soil constituents, resulting in the contamination of soil with heavy metals and other toxic compounds. Soil contamination is mainly the result of improper environmental management in chemical industries, mining and mineral processing operations, industrial waste disposal sites, municipal landfills, and other facilities, both during operation and after closure. Additionally, widespread soil contamination may occur as a result of emissions from transport and industry, which re-deposit onto the soil surface, as well as from overuse of agricultural chemicals. The result of this diffuse soil contamination is the accumulation of the various contaminants in the soil surface layer and their dissolution and transportation into deeper soil layers and groundwater under the effect of the infiltrating water. In some cases, uncontrolled urban expansion has led to changes in land use, and former mining or industrial sites have been gradually transformed into residential, recreational, or even agricultural areas; in these cases, contaminated land may pose a high risk to human health and agricultural production.

Soil contamination was not perceived as a problem until the 1970s, when incidents in the U.S. and Europe (Love Canal, NY; Times Beach, MO; Lekkerkerk, the Netherlands) awakened public awareness about the serious threats posed to human health and the environment by abandoned or improperly managed hazardous wastes. In response to the growing public concern, the U.S., the Netherlands, and a number of other European countries started a systematic effort beginning in 1980 to identify potentially contaminated sites, assess the level of contamination, establish priorities for remediation based on risk assessment studies and gradually implement the required remedial actions.

In the U.S., three federal programs are currently in progress for identifying and cleaning up contaminated sites[1]:

1. In 1980, Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Commonly known as Superfund, the program under this law is focused on the remediation of *abandoned or uncontrolled hazardous waste sites*. Since 1980, Superfund has assessed nearly 44,400 sites. To date, 33,100 sites have been removed from the Superfund inventory to aid their economic redevelopment, and 11,300 sites remain active with the site assessment program or are included in the National Priorities List (NPL) for the implementation of remedial actions. By September 2000, 1509 sites were included in the NPL with ongoing or completed cleanup activities.
2. The second program is directed at corrective actions at *currently operating industrial facilities*. This program is authorized by the Resource Conservation and Recovery Act (RCRA) of 1980 and its subsequent amendments. At the time of writing, there are no statistical data about the progress of this program. Approximately 2000 sites were included in the RCRA Corrective Action Baseline by the end of September 2007. Amongst these sites, remedy constructions were completed for 560 sites and remedy decisions were made for 726 sites.
3. The third cleanup program, also authorized by the RCRA, addresses contamination resulting from leaks and spills (mainly petroleum products) from *underground storage tanks* (USTs). This law has compelled cleanup activities at many UST sites. By February 1999, over 385,000 releases had been reported, 327,000 cleanup projects initiated, and 211,000 projects completed.

Many policies and practices have been adopted by European countries for the management of contaminated sites. Information about the various national polices, the technical approaches for risk assessment, and the progress of rehabilitation activities in Europe has been compiled in the framework of two European networks—CARACS (Concerted Action for Risk Assessment for Contaminated Sites) and CLARINET (Contaminated Land Rehabilitation Network for Environmental Technologies)—which were funded by the European Commission. A detailed description of European national policies can be found in relevant publications[2,3] and in the CLARINET website (http://www.clarinet.at).

Table 14.1 summarizes the available data related to the registration, assessment, and remediation of contaminated sites in the U.S. and several European countries. The number of sites presented

TABLE 14.1
Available Data for the Registration, Assessment, and Remediation of Contaminated Sites in the U.S. and Europe

Country	Number of Sites Suspected Contamination	Confirmed Contamination	Cleanup Initiated or Completed	Data Till
U.S., Superfund	44,400	11,300	1,509	2000
U.S., UST		385,000	211,000	1999
U.K.	100,000			1995
The Netherlands	110,000			1998
Belgium	10,500		86	1998
France	250,000	896	125	1997
Spain	18,000	4,900	77	1995
Italy	9,000	1,570		1997
Germany	300,000			1997
Austria	2,476	145	97	1999
Switzerland	50,000	3,000	200	1998
Denmark	14,500	4,048	800	1997
Norway	3,350	2,100	99	1999
Finland	25,000	1,200		1995
Sweden	20,000	12,000		1999
Hungary	10,000	200		1998
Czech Republic	12,000	1,000	210	1998

Source: From NATO/CCMS, Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater, NATO CCMS Pilot Study, Phase III, 1999 Annual Report, EPA 542/R-99/007, no. 235, 1999; Ferguson, C. and Kasamas, H., Eds., *Risk Assessment for Contaminated Sites in Europe*, *Vol. 2. Policy Frameworks*, LGM Press, Nottingham, UK, 1999. With permission.

in the table changes yearly, because the entire process is in a state of continuous progression. It has been suggested that the real extent of the problem has become clear only recently. For example, in 1980 about 350 sites in the Netherlands were thought to be contaminated. This number increased to 1600 in 1986 and 110,000 in 1999. The estimated costs[1] for rehabilitation of these sites was 0.5 billion Euros in 1980, 3 billion Euros in 1986, and between 15 and 25 billion Euros in 1999.

14.1.2 REMEDIATION TECHNOLOGIES

Until recently, a common practice for the remediation of contaminated sites was to excavate the contaminated soil, replace it with clean soil, and then dispose of the contaminated material at municipal waste landfills. This practice, however, was gradually discouraged by the environmental authorities, which issued very strict regulations for landfilling and increased the corresponding disposal costs. In many industrial countries, the cost for disposal in a municipal waste landfill ranges from 80 to 150 USD/ton. If contaminated soil is characterized as hazardous waste, landfilling in state-of-the-art hazardous waste landfills may cost[4] between 500 and 800 USD/ton. The high disposal costs and the limited availability of clean soil has led to the development of alternative remediation methods, which permit the reuse of treated soil following the removal or immobilization of contaminants.

Soil remediation technologies can be classified according to the type of treatment processes taking place[5–7]:

1. *Biological processes.* These are based on the use of living organisms (e.g., microorganisms or plants).

2. *Chemical processes*. These destroy, fix, or remove toxic compounds by using one or more types of chemical reactions.
3. *Physical processes*. These separate contaminants from the soil matrix by exploiting physical differences between the soil and the contaminants (e.g., volatility) or between contaminated and uncontaminated soil particles.
4. *Solidification and stabilization processes*. These immobilize the contaminants through physical or chemical processes. Solidification involves the entrapment of contaminants into a consolidated mass and stabilization is the conversion of contaminants to a chemical form that is less available.
5. *Thermal processes*. These exploit physical and chemical processes at elevated temperatures.

Another classification of remediation technologies describes where the action is taking place. *Ex situ* methods are those applied to excavated soil and *in situ* processes are those applied to the soil in its original location. *On-site* techniques are those that take place on the contaminated site; they can be either *ex situ* or *in situ*. *Off-site* processes treat the excavated soil in fixed industrial facilities, away from the contaminated site.

The following categories of technologies are predominately *ex situ*:

1. Soil washing and related chemical treatment techniques
2. Solidification–stabilization
3. Thermal processes
4. Vitrification
5. Bioremediation using landfarming or biopile techniques

The most common *in situ* technologies are as follows:

1. Soil vapor extraction (SVE)
2. Air sparging
3. *In situ* bioremediation techniques combined with SVE and air sparging
4. Soil flushing
5. Electroremediation
6. Phytoremediation

Currently, most remediation projects are carried out using *ex situ* technologies, both in the U.S. and in Europe. However, there is an increasing trend toward the application of *in situ* technologies because of their considerable advantages over *ex situ* techniques, such as less disturbance of the site, lower treatment costs, and so on.

Published data for the cost of remediation technologies are highly variable. One reason for this variability is that remediation costs depend on several case-specific parameters, such as type of contaminants, geotechnical and geochemical characteristics of the soil matrix, and the hydrogeology of the site for *in situ* techniques. Differences in the reported cost data for the same technology between two countries may also reflect a different degree of commercialization for the specific technology. Indicative cost ranges for characteristic remediation technologies are presented in Table 14.2, based on the U.S. and European Union (EU) experiences.

This chapter presents a detailed description of five technologies: soil vapor extraction, bioremediation, phytoremediation, soil washing, and soil flushing. Information about other categories of proven or emerging technologies is available on several websites. An overview of the technologies currently applied in the U.S., with detailed cost and performance data from characteristic case studies, can be found at the FRTR (Federal Remediation Technologies Roundtable) website (http://www.frtr.gov). Detailed information on several soil remediation technologies can also be found on the United States Environmental Protection Agency's (U.S. EPA) Cleanup Information site (http://www.clu-in.org).

TABLE 14.2
Indicative Costs of Remediation Technologies

Remediation Technology	Range of Costs in the U.S.[a] (USD/t)	Range of Costs in the EU[b] (Euro/t)
Bioremediation	50–150	20–40
Soil washing	80–120	20–200
Stabilization–solidification	240–340	80–150
Thermal treatment	120–300	30–100
Incineration	200–1500	170–350
Soil vapor extraction	20–220	20–60
Phytoremediation	10–35	

[a] *Source*: Schnoor, J.L., Phytoremediation. Technology Evaluation Report TE-98-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA, 1997. With permission.

[b] *Source*: Vic, E.A. and Bardos, P., Remediation of Contaminated Land. Technology Implementation in Europe, Federal Environmental Agency, Austria. CLARINET Report, available at www.clarinet.at, 2002. With permission.

14.2 SOIL VAPOR EXTRACTION

14.2.1 General Description

Soil vapor extraction (SVE) is a relatively new yet widely applied technology for the remediation of soils contaminated with volatile organic compounds (VOC) in the unsaturated zone above the water table (vadose zone). The process consists of generating an airstream through the contaminated soil subsurface in order to enhance the volatilization of organic contaminants and thus remove them from the soil matrix.[9–13]

Figure 14.1 presents the main components of a typical *in situ* SVE system.[9,10] Vertical extraction wells are installed inside the contaminated zone at appropriate distances from one another. The SVE wells are typically constructed of PVC pipe, with a screened interval, which is placed within the contaminated zone. The wells are connected to blowers or vacuum pumps, which induce a continuous airflow through the pores of the unsaturated zone. The soil surface is sometimes covered with an impermeable seal, made from high density polyethylene (HDPE) or bentonite clay for example, to prevent the vertical influx of air from the surface, which might cause short-circuiting problems, and promote horizontal gas flow through the contaminated area. The airstream, which contains the contaminant vapors, passes initially through an air–water separation unit to remove the entrained moisture and is then directed to the gas treatment unit, where the contaminants are thermally destroyed or removed by adsorption.

There are three main prerequisites for the successful application of SVE technology:

1. The contamination should be trapped in the vadose zone.
2. The contaminants should have high volatility.
3. The contaminated zone should have high permeability.

A general simple rule is that SVE can be applied successfuly for contaminants with vapor pressure greater than 0.5 mmHg and for soils with air permeability coefficients ranging between 1×10^{-2} and 1×10^{-5} cm/s.[11]

Many modifications and additional treatment options have been proposed to enhance the performance and extend the applicability of SVE systems, examples of which include the following:

1. Pumping of the groundwater to lower the water table and enlarge the vadose zone, with simultaneous treatment of contaminated groundwater.[10]
2. The combination of SVE with *air sparging* technology. Air sparging involves the injection of air into the saturated zone of contaminated groundwater. The air bubbles enhance the

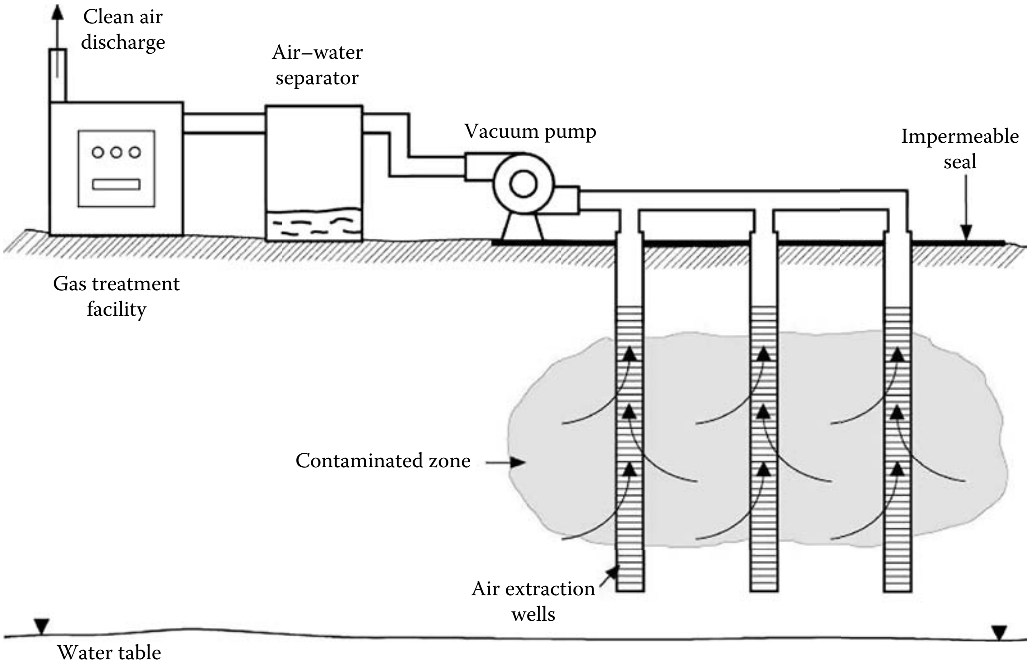


FIGURE 14.1 Schematic representation of an SVE system.

volatilization of dissolved contaminants, especially those with low solubility in water, and then migrate upward to the vadose zone to be captured by the SVE system.[14–17]

3. Combination of SVE with the *bioventing* technology.[17–19] Bioventing uses a system configuration similar to SVE but with a different objective. In bioventing, the induced airflow aims to provide sufficient oxygen for the aerobic biodegradation of contaminants. It is thus possible to remove contaminants with relatively low volatility and high biodegradability.
4. Thermal enhancement of volatilization.[19–21] Volatility of contaminants increases greatly with temperature, so several techniques have been developed to raise soil temperature, including the injection of hot air or steam, electrical resistance heating, and radio frequency heating.

Soil vapor extraction has become a very popular technology since the mid-1990s, because it has several important advantages:

1. It is an *in situ* technology and can even be applied below existing buildings, roads, and so on, thus causing minor disturbance to ongoing site operations.
2. The whole installation may be achieved using low-cost and easily available equipment, and the operation of the system is quite simple.
3. Although it is focused on the treatment of volatile contaminants trapped in the vadose zone, SVE can be integrated easily with other technologies targeting the remediation of groundwater or less volatile compounds, and this flexibility enables the application of the technology to a broad range of sites.

14.2.2 DESIGN CONSIDERATIONS

The most important parameters for the preliminary design of an SVE system are the VOC concentration in the extracted air, the air flow rate, and the radius of influence of each extraction well. These parameters determine the number of wells that must be installed to remediate the whole contaminated area, the time required to obtain the cleanup goals, the size and characteristics of the gas treatment facility and auxiliary equipment, and finally the cost of the whole remediation project.

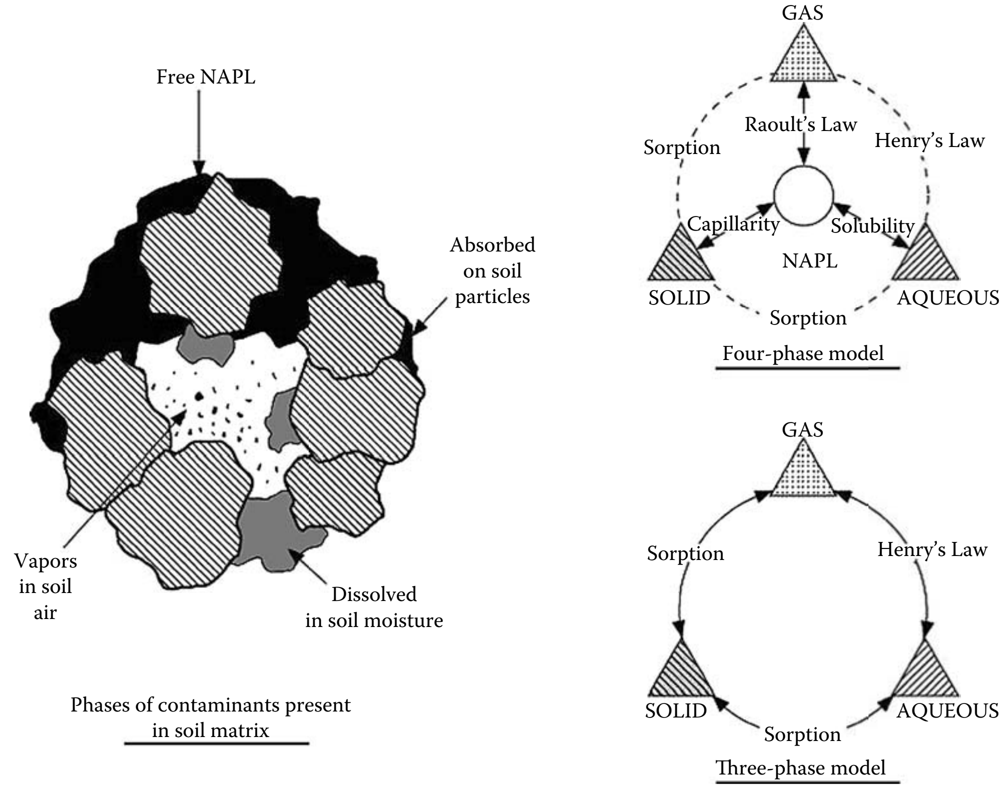
The design of SVE systems can be based on relatively simple mathematical models that describe the two basic phenomena governing the performance of SVE technology: the phase distribution of the organic contaminants and the characteristics of the airflow in the vadose zone.[11–13,22,23] A simplified modeling approach, providing valuable tools for preliminary design calculations, will be presented in the following sections.

14.2.2.1 Phase Distribution of Organic Contaminants in the Vadose Zone

Organic contaminants can be present in the vadose zone in four distinct phases (Figure 14.2):

1. As an immiscible organic liquid retained by capillary forces in the pore space between the soil particles. This free organic phase is often referred to with the abbreviation NAPL (nonaqueous phase liquid).
2. As dissolved compounds in soil pore water.
3. As an adsorbed film on the surface of soil particles.
4. As vapor in soil air present in the pore space.

The distribution of a contaminant among the four phases depends on (1) the physical and chemical properties of the compound and (2) the characteristics of the soil, and can be described by relatively simple equations (see Table 14.3).



Phases of contaminants present in soil matrix

Four-phase model

Three-phase model

FIGURE 14.2 Phase distribution of organic contaminants in the vadose zone. The solid arrows in the three- and four-phase models represent the equilibria taken into consideration in the equations of Table 14.3.

TABLE 14.3
Basic Equations and Required Data for Calculating the Phase Distribution of Contaminants under Equilibrium Conditions

In the presence of NAPL in the soil matrix		Without NAPL in the soil matrix	
$C_\mathrm{t} = \rho_\mathrm{b} C_\mathrm{s} + \theta_\mathrm{w} C_\mathrm{w} + \theta_\mathrm{a} C_\mathrm{a} + \theta_\mathrm{or} C_\mathrm{or}$	(1)	$C_\mathrm{t} = \rho_\mathrm{b} C_\mathrm{s} + \theta_\mathrm{w} C_\mathrm{w} + \theta_\mathrm{a} C_\mathrm{a}$	(7)
$C_\mathrm{a} = P^\mathrm{o} \times X \times \gamma_i \times \mathrm{MW}/(RT)$	(2)	$C_\mathrm{a} = K_\mathrm{H} \times C_\mathrm{w}$	(8)
$C_\mathrm{or} = m \times \rho_\mathrm{or} \times 10^6$	(3)	$C_\mathrm{s} = K_\mathrm{oc} \times f_\mathrm{oc} \times C_\mathrm{w}$	(5)
$C_\mathrm{w} = C_\mathrm{w}^\mathrm{o} \times X \times \gamma_i$	(4)	$\theta_\mathrm{t} = \theta_\mathrm{w} + \theta_\mathrm{a}$	(9)
$C_\mathrm{s} = K_\mathrm{oc} \times f_\mathrm{oc} \times C_\mathrm{w}$	(5)		
$\theta_\mathrm{t} = \theta_\mathrm{w} + \theta_\mathrm{a} + \theta_\mathrm{or}$	(6)		

Phase distribution values for calculation

C_s = adsorbed concentration of contaminant in the soil particle (mg/kg)

C_w = dissolved concentration in pore water (mg/L)

C_a = vapor concentration in pore air (mg/L)

C_or = concentration of contaminant in NAPL (mg/L)

θ_a = pore volume occupied by the gas phase (L/L)

θ_or = pore volume occupied by NAPL (L/L)

Required data

Contaminant properties[a]

MW = molecular weight (g/mol)

P^o = vapor pressure of the compound (mmHg)

C_w^o = water solubility (mg/L)

K_H = Henry's constant (dimensionless)

K_oc = organic carbon partitioning coefficient (L/kg)

Soil characteristics[b]

ρ_b = soil bulk density (kg/L)

θ_t = total porosity of soil (L/L)

θ_w = pore volume occupied by water (L/L)

f_oc = fraction of organic carbon in soil

Contamination data[b]

C_t = total quantity of contaminant per unit soil volume (mg/L)

ρ_or = specific density of the NAPL mixture (kg/L)

m = mass fraction of contaminant in the NAPL mixture

X = moles of contaminant in the NAPL mixture

γ_i = activity coefficient of contaminant in NAPL

[a] Data for these properties and for a long list of organic compounds can be found in several environmental engineering textbooks and handbooks.[9,10,24–27]

[b] Soil characteristics and data related to the concentration levels and the composition of organic contaminants should be collected during the investigation of the specific contaminated site.

When a single organic compound is present in the soil matrix as NAPL, its concentration in soil air (C_a) can be directly calculated from the vapor pressure of this compound (P^o) and the Ideal Gas Law:

$$C_\mathrm{a} = P^\mathrm{o} \times \mathrm{MW}/(RT) \tag{14.1}$$

where MW is the molecular weight of the compound, R is the ideal gas constant, and T is the absolute temperature. For a mixture of compounds, such as gasoline, the partial pressure (P_i) of each constituent i in the soil air depends on the composition of the mixture according to Raoult's Law:

$$P_i = P_i^{\mathrm{o}} \times X_i \times \gamma_i \tag{14.2}$$

where P_i^{o} is the vapor pressure of the pure constituent, X_i is the mole fraction of the constituent, and γ_i is the activity coefficient, representing the deviation from the properties of an ideal mixture.

Temperature has a strong influence on the vapor pressure of the contaminants. This effect can be described by the Clausius–Clapeyron equation:

$$\ln\left(\frac{P}{P^{\mathrm{o}}}\right) = \frac{\lambda}{R}\left(\frac{1}{T^{\mathrm{o}}} - \frac{1}{T}\right), \tag{14.3}$$

where P is the vapor pressure at T, P^{o} the vapor pressure at T^{o}, and λ is the molar heat of vaporization.

In the presence of NAPL, the concentration of contaminants in the soil moisture (C_{w}) can be calculated simply from the solubility of the compounds (equation 3 in Table 14.3). Adsorption of contaminants to the soil particles is a much more complex phenomenon, which depends both on contaminant properties and on soil characteristics. The simplest model for describing adsorption is based on the observation that organic compounds are preferentially bound to the organic matter of soil, and the following linear equation is proposed for calculating the adsorbed concentration (C_{s}):

$$C_{\mathrm{s}} = K_{\mathrm{oc}} \times f_{\mathrm{oc}} \times C_{\mathrm{w}}, \tag{14.4}$$

where K_{oc} is the organic carbon partitioning coefficient of the contaminant and f_{oc} is the fraction of organic carbon in the soil.

When the SVE technology is applied in a contaminated site, the NAPL is gradually removed. Towards the end of the remediation and when NAPL is no longer present, a three-phase model should be considered to calculate the phase distribution of contaminants (see Table 14.3). In this case, the vapor concentration in pore air (C_{a}) is calculating using the Henry's Law equation (Equation 14.5), which describes the equilibrium established between gas and aqueous phases:

$$C_{\mathrm{a}} = K_{\mathrm{H}} \times C_{\mathrm{w}}, \tag{14.5}$$

where K_{H} is the Henry's Law constant of the contaminant. Note, however, that during this phase the process is often governed by nonequilibrium rate-limiting conditions.

14.2.2.2 Basic Airflow Equations

The movement of air in the subsurface during the application of SVE is caused by the pressure gradient that is applied in the extraction wells. The lower pressure inside the well, generated by a vacuum blower or pump, causes the soil air to move toward the well. Three basic equations are required to describe this airflow: the mass balance of soil air, the flow equation due to the pressure gradient, and the Ideal Gas Law.

The mass balance of soil air may be described by the classic continuity equation for compressible fluids:

$$\theta_{\mathrm{a}}\frac{\partial \rho_{\mathrm{a}}}{\partial t} = -\left(\frac{\partial(\rho_{\mathrm{a}} u_x)}{\partial x} + \frac{\partial(\rho_{\mathrm{a}} u_y)}{\partial y} + \frac{\partial(\rho_{\mathrm{a}} u_z)}{\partial z}\right) = -\nabla(\rho_{\mathrm{a}} u), \tag{14.6}$$

where θ_a is the pore volume occupied by the gas phase, ρ_a is the density of air, which is not constant due to air compressibility, and u_x is the air velocity in the x-direction.

For a radial flow from a circumference of radius r toward the well, Equation 14.6 may be simplified as follows:

$$\theta_a r \frac{\partial \rho_a}{\partial t} = -\frac{\partial(\rho_a u_r r)}{\partial r}. \tag{14.7}$$

The air velocity due to the pressure gradient can be described by Darcy's Law:

$$u_r = -\frac{K}{\mu_a} \times \frac{dP}{dr}, \tag{14.8}$$

where K is the intrinsic permeability of soil, which is independent of the fluid properties, μ_a is the viscosity of air, and dP/dr is the pressure gradient in the radial r direction.

Finally, the Ideal Gas Law can be used to describe the relationship between air density and pressure:

$$\rho_a = \frac{P \times \mathrm{MW}}{RT}, \tag{14.9}$$

where MW is the molecular weight of air, R is the Ideal Gas Law constant, and T is the absolute temperature.

Combining Equations 14.7–14.9, a differential equation, with pressure as the single variable, can be derived:

$$\theta_a \frac{\partial P}{\partial t} = \frac{K}{\mu_a} \times \frac{\partial\left[Pr(\partial P/\partial r)\right]}{\partial r}. \tag{14.10}$$

Under steady-state conditions, equation 14.10 has a simple analytical solution, which allows the calculation of the pressure P_r at several radial distances from the well:

$$P_r = \left[P_w^2 + (P_I^2 - P_w^2) \times \frac{\ln(r/R_w)}{\ln(R_I/R_w)}\right]^{1/2}, \tag{14.11}$$

where P_w is the pressure at the extraction well, R_w is the radius of the well, R_I is the radius of influence of the well, and P_I is the pressure at distance R_I.

14.2.2.3 Radius of Influence and Number of Wells

Equation 14.11 introduces the notion of radius of influence, which is one of the important design parameters of SVE systems. Theoretically, the maximum radius of influence of a well is the distance at which the pressure becomes equal to the ambient atmospheric pressure, i.e., $P_I = P_{atm}$. In practice, R_I is determined as the distance at which a sufficient level of vacuum still exists to induce airflow, e.g., 1% of the vacuum in the extraction well.[9,12] The extraction wells are usually constructed using pipes with a standard radius, e.g., $R_w = 5.1$ cm (2 in.) or 10.2 cm (4 in.), and the vacuum applied in the wells typically ranges from 0.05 to 0.15 atm, i.e., $P_w = 0.95$–0.85 atm.[9,12] If the vacuum required in the radius of influence is 1% of the vacuum in the extraction well, the

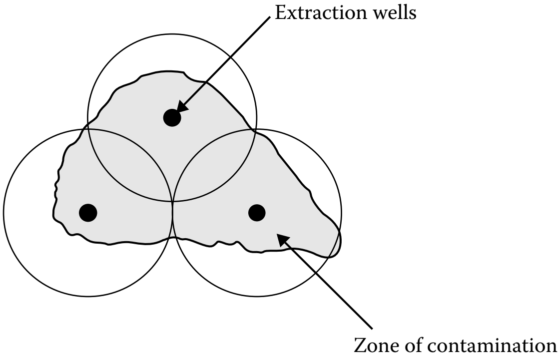


FIGURE 14.3 Determination of the required number of wells from the radius of influence.

corresponding P_I values will range from 0.9985 to 0.9995 atm. The radius of influence R_I is usually determined with preliminary field tests. Vacuum is applied in a test extraction well and the pressure P_r is measured in a monitoring well, installed at a distance r from the well. In practice, pressure drawdown is monitored at two or three points at varying radial distances from the well. Using the field-test data and Equation 14.11, it is possible to determine the radius of influence of the well R_I at various operating vacuum values P_w.

Once the radius of influence has been determined, the number of wells N_{wells} required to remediate the entire contaminated area can be calculated from Equation 14.12:

$$N_{\text{wells}} = 1.2 \times \frac{A_{\text{contam}}}{\pi R_I^2}, \tag{14.12}$$

where A_{contam} is the surface area corresponding to the contaminated zone. The factor 1.2 is arbitrarily chosen to account for the overlapping of the areas of influence between the wells and the fact that peripheral wells may reach outside the contaminated zone (Figure 14.3).[12]

14.2.2.4 Air Flow Rates

The flow rate of extracted air can be determined by considering the air velocity, as determined by Darcy's Law (Equation 14.8), and the radial distribution of pressure (Equation 14.11). The solution for air velocity as a function of the radial distance is given in Equation 14.13:

$$u_r = -\frac{K}{2 \times \mu_a} \frac{\left[\frac{P_w}{r \times \ln(R_w/R_I)}\right] \times \left[1 - \left(\frac{P_I}{P_w}\right)^2\right]}{\left[1 + \left(1 - \left(\frac{P_I}{P_w}\right)^2\right) \frac{\ln(r/R_w)}{\ln(R_w/R_I)}\right]^{1/2}}. \tag{14.13}$$

Using Equation 14.13, one can easily calculate the volumetric flow rate Q_w of the air extracted from the well:

$$Q_w = 2\pi R_w u_w H = \pi H \frac{K}{\mu_a} \frac{P_w\left[1 - (P_I/P_w)^2\right]}{\ln(R_w/R_I)}, \tag{14.14}$$

where u_w is the velocity at the wellbore and H is the thickness of the vadose zone though which air is removed. The volumetric flow rate Q_w corresponds to the pressure P_w of the well. To convert this flow rate to equivalent standard conditions, the following relationship can be applied:

$$Q_w^* = Q_w \frac{P_w}{P_{atm}}. \tag{14.15}$$

It is obvious from Equation 14.14 that the most important parameter determining the volumetric air flow rate Q_w is the intrinsic permeability K of soil. At this point it is important to stress the difference between water permeability (or hydraulic conductivity) k_w, air permeability k_a, and intrinsic permeability K. In most cases, when permeability data are provided for a type of soil or geological formation, these data are based on hydraulic conductivity measurements and describe how easily the water can flow through this formation. However, the flow characteristic of a fluid depends greatly on its properties, e.g., density ρ and viscosity μ. Equation 14.16 describes the relationship between permeability coefficient k and fluid properties ρ and μ:

$$k = K \times \frac{\rho \times g}{\mu}, \tag{14.16}$$

where K is the geometric or intrinsic permeability of the soil, which depends only on the geometric characteristics of the soil (e.g., particle size distribution), and g is the gravity acceleration constant (g = 9.81 m/s^2). Note that water and air permeability coefficients have units of velocity (cm/s), but K has units of surface (cm^2).

When the hydraulic conductivity k_w of a soil is known, one can easily estimate the corresponding values of intrinsic and air permeabilities, taking into consideration the properties of water and air under usual environmental conditions: e.g., $\rho_w = 1.0$ g/cm^3, $\mu_w = 1 \times 10^{-2}$ g/(cm·s), $\rho_a = 1.2 \times 10^{-3}$ g/cm^3, and $\mu_a = 1.83 \times 10^{-4}$ g/(cm·s) (T = 20°C, P = 1 atm). For instance, a soil with hydraulic conductivity $k_w = 1 \times 10^{-3}$ cm/s has an approximate intrinsic permeability of $K = 1 \times 10^{-8}$ cm^2, and its permeability to airflow under normal conditions will be $k_a = 6.6 \times 10^{-5}$ cm/s.

The airflow equations presented above are based on the assumption that the soil is a spatially homogeneous porous medium with constant intrinsic permeability. However, in most sites, the vadose zone is heterogeneous. For this reason, design calculations are rarely based on previous hydraulic conductivity measurements. One of the objectives of preliminary field testing is to collect data for the reliable estimation of permeability in the contaminated zone. The field tests include measurements of air flow rates at the extraction well, which are combined with the vacuum monitoring data at several distances to obtain a more accurate estimation of air permeability at the particular site.

14.2.2.5 Removal Rate of Contaminants and Required Cleanup Time

The contaminants removal rate R_{rem} can be calculated by multiplying the flow rate of air extracted from all the wells by the concentration of contaminant in the soil air C_a:

$$R_{rem} = N_{wells} \times Q_w^* \times C_a. \tag{14.17}$$

The required cleanup time T_{clean} is directly related to the removal rate:

$$T_{clean} = M_{spill}/R_{rem}, \tag{14.18}$$

where M_{spill} is the estimated total amount of spill.

Equations 14.17 and 14.18 are very simple, but the accuracy of the predictions depends greatly on the realistic estimation of C_a, which varies with time during the operation of the SVE system. For the start of the SVE project and considering that the free organic phase, NAPL, is present in the subsurface, a first approximation is to calculate C_a from the vapor pressure data of the contaminants (equation 2 in Table 14.3 or Equation 14.1). The actual concentration, however, will be lower than this value for two main reasons: (1) the extracted airstream does not pass only through the contaminated zone and (2) limitations on mass transfer exist. An effectiveness factor η should be considered to take into account the effect of these phenomena on removal rates. The value of this factor can be determined by comparing the calculated concentration with data obtained from the preliminary pilot tests at the site:

$$\eta = \frac{C_{\mathrm{a,field}}}{C_{\mathrm{a,equil}}}, \tag{14.19}$$

where $C_{\mathrm{a,field}}$ is the concentration in extracted air measured during the field tests and $C_{\mathrm{a,equil}}$ is the value calculated from the vapor pressure data.

Practical experience from the application of SVE at sites contaminated with a single type of contaminant (e.g., trichloroethylene, TCE) indicates that the removal of contaminants follows a trend in two distinct phases. During the initial phase, which covers the period from the project startup to the exhaustion of NAPL in the subsurface, the removal rate is almost linear. The second phase is characterized by a constant decrease in removal rates.

This trend can be explained with the following mechanism. In the presence of NAPL, the extracted vapor concentration depends mainly on the vapor pressure of the contaminant. After the disappearance of free NAPL, the extracted vapor concentration becomes dependent on the partitioning of contaminants among the three other phases (see Table 14.3). As the air passes through the pores, the dissolved contaminants volatilize from the soil moisture to the gas phase, causing the desorption of contaminants from the surface of soil particles into the aqueous phase. As a result, the concentration in all three phases decreases, with a consequent decrease in removal rates.

For the initial linear phase of remediation, the pilot test data and Equations 14.17 to 14.19 can provide relatively good predictions for the required cleanup time. For the second phase, it is necessary to use more sophisticated models combining airflow, equilibrium, and mass transfer Equations 14.13 to 14.16, in order to obtain sufficiently accurate predictions. To obtain a first rough estimation, the methodology proposed by Kuo[12] can be applied. Kuo's approach is based on the observation that the VOC concentrations of extracted air decrease exponentially with time during the second stage of remediation. To simulate the exponential decrease in removal rates, the following procedure is suggested:

1. The mass of contaminant that must be removed during the second stage is divided into two or three equal parts, corresponding to successive cleanup time intervals.
2. Initial $C_{\mathrm{a,i}}$ and final $C_{\mathrm{a,f}}$ vapor concentrations are calculated for each interval using the phase distribution equations in the absence of NAPL (see Table 14.3).
3. A mean vapor concentration $C_{\mathrm{a,m}}$ representing each time interval is determined from the geometric average of the two concentrations:

$$C_{\mathrm{a,m}} = \sqrt{C_{\mathrm{a,i}} \times C_{\mathrm{a,f}}}\,. \tag{14.20}$$

4. The successive cleanup time intervals are calculated using the mean concentration values, and they are summed to determine the total required time.

This procedure is illustrated in the practical example presented in Section 14.2.2.6.

Note that the initial linear phase is observed only in sites containing a single contaminant. For sites contaminated with mixtures of contaminants there is a decreasing rate of removal from the beginning of the project due to the different volatility of the components. The more volatile constituents are extracted with a higher rate from all the phases, and as a consequence the total VOC content of extracted air decreases constantly with time. This effect should be considered during the design phase.

14.2.2.6 A Practical Example

A tank containing 20 m^3 toluene ruptures, contaminating an area of 1250 m^2 in the vadose zone with an average depth of 4 m. The soil in the subsurface has the following characteristics: bulk density $\rho_b = 1.7$ g/cm^3, total porosity $\theta_t = 0.4$, moisture corresponding to porosity $\theta_w = 0.2$, and organic carbon content $f_{oc} = 0.01$.

Owing to the high volatility of toluene (vapor pressure $P^o = 22$ mmHg), the decision was to use SVE technology. Preliminary field tests were conducted in the area using an extraction well with $R_w = 5.1$ cm (2 in.) and total perforated length inside the contaminated zone $H = 4$ m. The tests were carried out applying a vacuum of 0.1 atm (i.e., $P_w = 0.9$ atm) in the well, and the pressure was measured at a distance of 6 m and found to be 0.99 atm after reaching steady-state conditions. The flow rate of extracted air, as measured in the exhaust of the vacuum pump, was $Q_w^* = 0.2$ m^3/min, and the air contained 78 mg/L toluene. The temperature of the subsurface was 25°C.

To determine some important design parameters for this SVE project, the following procedure could be used:

Step 1: *Obtain the physicochemical data of the compound of concern.* Important sources for this type of data are references 9, 10, and 24–27. From tables included in Reference 9, the following properties of toluene were obtained: MW = 92.14 g/mol, $P^o = 22$ mmHg = 0.0289 atm, $K_H = 0.276$ (dimensionless), $C_w^o = 490$ mg/L, log $K_{oc} = 2.06$, and $\rho_{or} = 0.866$ g/cm^3.

Step 2: *Calculate the initial distribution of toluene in the subsurface.* The initial distribution of toluene can be calculated using equations 1 to 5 from Table 14.3 and taking into consideration that the organic phase is a pure compound, i.e., $X = 1$, $m = 1$, and $\gamma = 1$. The total quantity of contaminant per unit soil C_t can be estimated from the known amount of spill M_{spill} and the volume of the contaminated zone:

$$C_t = \frac{M_{spill}}{A_{contam} \times H} = \frac{20{,}000\,\text{L} \times 0.866\,\text{kg/L}}{(1250 \times 4)\,\text{m}^3} = \frac{17{,}320\,\text{kg}}{5000\,\text{m}^3} = 3.464\,\text{kg/m}^3 = 3464\,\text{mg/L}.$$

The concentrations and the mass distribution of toluene in the four phases, as calculated from this set of equations, are presented in Table 14.4. As seen in the table, the major part of the toluene, i.e., 68.9%, remains in the vadose zone as free NAPL, 27.6% is adsorbed on the surfaces of solid particles, and only 3.5% is distributed between the aqueous and gas phases. Free NAPL occupies only a small part of the available pore volume, and it is not expected to disturb the movement of air through the contaminated zone.

Step 3: *Calculate from the field test data the radius of influence, the required number of wells, and the required capacity of the gas treatment facility.* The radius of influence R_I can be calculated from equation 14.11 using the pressure monitoring data at $r = 6$ m while considering that the minimum required vacuum at R_I should be 0.001 atm, i.e., $P_I = 0.999$ atm. With these values R_I is found to be 9.91 m. The number of wells is calculated from equation 14.12, $N_{wells} = 4.86$. This means that five wells must be installed to remediate the entire contaminated area. Once the number of wells has been determined, the required capacity of the gas treatment facility can be defined from the flow rate data obtained during the field tests. In this case, the gas treatment unit should be able to treat $N_{wells} \times Q_w^* = 5 \times 0.2 = 1.0$ m^3/min of toluene-laden air.

TABLE 14.4
Concentrations, Mass Distribution of Toluene, and Volume Occupied by the Four Phases in the Vadose Zone

	Total	Free NAPL	Aqueous	Gas	Solids
Toluene concentrations	3464 mg/L	866 × 10^3 mg/L	490 mg/L	109 mg/L	563 mg/kg
Toluene mass distribution	17.32 t	11.94 t	0.49 t	0.11 t	4.78 t
Volume of four phases	5000 m^3	14 m^3	1000 m^3	986 m^3	3000 m^3

The flow rate data can also be used to estimate the permeability of the subsurface. The required additional parameter is the value of air viscosity, i.e., $\mu_a = 1.83 \times 10^{-4}$ g/(cm·s). The intrinsic permeability of soil is calculated from equations 14.16 and 14.15 and is found to be $K = 1.34 \times 10^{-8}$ cm^2. Care should be taken to perform the appropriate unit conversions when using Equation 14.15.

Step 4: *Estimate the effectiveness factor* η *for the removal and the cleanup time required to obtain a residual toluene concentration of 150 mg/L.* The phase distribution calculations carried out in Step 2 indicate that the equilibrium concentration of toluene in the gas phase is $C_{a,equil} = 109$ mg/L (see Table 14.4). The concentration measured in the extracted air during the field tests is lower, at $C_{a,field} = 78$ mg/L, indicating that the removal effectiveness is limited either as a result of mass transfer phenomena or the existence of uncontaminated zones in the airflow pattern. The corresponding effectiveness factor is $\eta = 78/109 = 0.716$.

The amount of toluene that must be removed from the soil M_{rem} can be calculated by considering the initial total amount of spill M_{spill} and the residual acceptable quantity corresponding to the cleanup objectives M_{final}:

$$M_{rem} = M_{spill} - M_{final} = 17.32\text{ t} - (150\text{ g/m}^3) \times 5000\text{ m}^3 \times (10^{-6}\text{ t/g}) = (17.32 - 0.75)\text{ t} = 16.57\text{ t}.$$

The removal of toluene is assumed to take place in two stages. The first stage corresponds to the removal of free NAPL, which, according to the phase distribution calculations (Step 2; Table 14.4) represents a mass of $M_{rem1} = 11.94$ t. The second stage corresponds to the removal of toluene, which is distributed among the other three phases, and represents a mass of $M_{rem2} = 16.57 - 11.94 = 4.63$ t.

As this site is contaminated with a single compound, the removal of free NAPL is expected to follow a linear trend with constant removal rate. The required time can be calculated from Equations 14.17 and 14.18:

$$T_1 = \frac{M_{rem1}}{\eta \times N_{well} \times Q_w^* \times C_{a,equil}} = \frac{(11.94\,\text{t}) \times (10^6\,\text{g/t})}{0.716 \times 5 \times (0.2\,\text{m}^3/\text{min}) \times (109\,\text{g/m}^3) \times (1440\,\text{d/min})} = 106.5\text{ d}$$

The second stage of treatment is assumed to follow an exponential decrease in removal rates. Applying the approach of Kuo, this stage is divided into two time intervals, $T_{2\text{-}1}$ and $T_{2\text{-}2}$, representing the successive removal of equivalent amounts of toluene, $M_{rem2\text{-}1} = M_{rem2\text{-}2} = 2.315$ t. The initial theoretical concentration in the gas phase for the time interval $T_{2\text{-}1}$ is equal to the vapor pressure of toluene, $C_{a,i} = 109$ mg/L. The final vapor concentration for this interval $C_{a,f}$ can be calculated from the total residual concentration $C_{t,f}$ and the phase distribution equations 5 and 7–9 in Table 14.3:

$$C_{t,f} = \frac{(M_{spill} - M_{rem1} - M_{rem2-1})}{5000\,\text{m}^3} = \frac{(17.32 - 11.94 - 2.315)\text{t}}{5000\,\text{m}^3} = 0.613 \times 10^{-3}\,\text{t/m}^3 = 613\,\text{mg/L}$$

$$C_{\mathrm{a,f}} = \frac{C_{\mathrm{t,f}}}{\rho_{\mathrm{b}} K_{\mathrm{oc}} f_{\mathrm{oc}} / K_{\mathrm{H}} + \theta_{\mathrm{w}} / K_{\mathrm{H}} + \theta_{\mathrm{t}} - \theta_{\mathrm{w}}} = \frac{613\,\mathrm{mg/L}}{8.0} = 76.7\,\mathrm{mg/L}$$

The mean vapor concentration $C_{\mathrm{a,m}}$ for the time interval $T_{2\text{-}1}$ is calculated from the geometric average of $C_{\mathrm{a,i}}$ and $C_{\mathrm{a,f}}$ (Equation 14.20), i.e., $C_{\mathrm{a,m}} = 91.4$ mg/L, and the required treatment time from Equations 14.17 and 14.18:

$$T_{2\text{-}1} = \frac{M_{\mathrm{rem2-1}}}{\eta \times N_{\mathrm{well}} \times Q_{\mathrm{w}}^{*} \times C_{\mathrm{a,equil}}} = \frac{(2.315\,\mathrm{t}) \times (10^{6}\,\mathrm{g/t})}{0.714 \times 5 \times (0.2\,\mathrm{m^3/min}) \times (91.4\,\mathrm{g/m^3}) \times (1440\,\mathrm{d/min})} = 24.6\,\mathrm{d}$$

The same procedure is applied for the last time interval $T_{2\text{-}2}$, and the following values are calculated:

$$C_{\mathrm{a,i}} = 76.7\,\mathrm{mg/L},\ C_{\mathrm{a,f}} = 18.8\,\mathrm{mg/L},\ C_{\mathrm{a,m}} = 37.9\,\mathrm{mg/L},\ T_{2\text{-}2} = 59.4\,\mathrm{d}$$

The total cleanup time, as estimated with this approach, will be

$$T_{\mathrm{clean}} = T_1 + T_{2\text{-}1} + T_{2\text{-}2} = 106.5 + 24.6 + 59.4 = 190.5\,\mathrm{d}$$

As seen from these calculations, the removal of free NAPL, representing almost 70% of the total toluene spill, takes approximately 106 days. The operation of the SVE system should continue for an additional 84 days in order to achieve the cleanup objectives and remove the final 30% of the toluene spill.

14.3 BIOREMEDIATION

14.3.1 INTRODUCTION

The bioremediation techniques exploit the biological activity of microorganisms to degrade or detoxify environmentally hazardous compounds. Traditionally, biological treatment has been applied for the remediation of sites contaminated with organic contaminants. Most organic compounds can be degraded through the action of appropriate microbial communities towards more simple and less harmful inorganic or organic molecules. The degree of degradation determines whether mineralization or biotransformation has occurred. Mineralization is the complete degradation of organic compounds into inorganic final products, such as carbon dioxide and water, whereas biotransformation is the partial degradation of the compound to more simple organic molecules.

Bioremediation is not restricted only to biodegradable organic contaminants. New techniques are currently under development for the bioremediation of metal-contaminated sites. Microbial activity can alter the oxidation state of some elements, reducing or increasing their mobility, and this transformation can be used for remediation purposes.

Bioremediation systems in operation today rely on microorganisms indigenous to contaminated sites. The two main approaches, based on the actions of native microbial communities, are biostimulation and intrinsic bioremediation. In biostimulation, the activity of native microbes is encouraged, creating (*in situ* or *ex situ*) the optimum environmental conditions and supplying nutrients and other chemicals essential for their metabolism. The vast majority of bioremediation projects are based on this biostimulation approach. Intrinsic bioremediation is a remedial option that can be applied when there is strong evidence that biodegradation will occur naturally over time without any external stimulation; i.e., a capable microbial community exists at the site, the required nutrients are available, and the environmental conditions are favorable. An additional prerequisite is that the naturally occurring rate of biodegradation is faster than the rate of contaminant migration towards sensitive environmental receivers, e.g., a well used for abstraction of drinking water. In that case, and if sufficient supportive data are provided, the regulatory authorities may issue a permit to pursue the intrinsic bioremediation option for a particular site. This remediation strategy is not a "no action" alternative. It requires the design and implementation of a systematic monitoring procedure to follow closely the progress of this natural process and prevent any undesirable side effects, such as the generation of toxic bioproducts due to unexpected changes in redox conditions.

In some cases the indigenous microorganisms are not able to degrade or detoxify the specific contaminants to acceptable levels. The use of nonnative microbes or even genetically engineered microorganisms especially suited to degrading the contaminants of concern is another bioremediation option known as bioaugmentation, that is currently under development. An important research effort has been devoted since the mid-1990s to discover microbial species capable of destroying or detoxifying specific hazardous pollutants, and to isolate them in pure cultures in order to exploit their efficiency in bioremediation projects. Such pure specific degrading microbial populations have been successfully used for the treatment of contaminated soils under laboratory conditions, but to date there are no known cases of full-scale projects applying the bioaugmentation principle.

Regardless of whether the microbes are native or artificially introduced into the soil, it is important to understand the mechanisms by which they degrade or detoxify hazardous pollutants through their metabolic activity. Understanding these mechanisms is essential for the proper design of bioremediation systems that provide the optimum conditions and the required nutritional supplements for the specific microbial process.

14.3.2 PRINCIPLES OF BIOREMEDIATION

14.3.2.1 Basic Microbial Metabolism

The microbial degradation of organic contaminants occurs because the organisms can use the pollutants for their own growth and maintenance. A microbial cell operates two critical types of metabolic processes, referred to as anabolic (cell-building) and catabolic (energy-releasing) processes. Anabolic processes involve the production of new cells and require a source of carbon, which is the most important constituent of cellular mass. Catabolic processes are energy-producing chemical reactions and require a source of energy.

Organic contaminants are used by microorganisms both as a source of carbon and as a source of energy. The microbes gain energy from the contaminants through their oxidation, which involves the breaking of chemical bonds and transfer of electrons away from the contaminant. To complete the chemical reaction, another compound is needed to receive the electrons. The contaminant, which is oxidized, is called the electron donor and the chemical, which is reduced, is called the electron acceptor. The microorganisms use the energy produced from these electron transfers to build new cells or simply to maintain the existing cells. The electron donor and the electron acceptor are essential for cell growth and maintenance and are commonly called the primary substrates.

Depending on the type of electron acceptor, the metabolic modes are broadly classified into three main categories: aerobic respiration, anaerobic respiration, and fermentation. Aerobic respiration is the term used to describe the metabolism in which molecular oxygen (O_2) serves as the electron acceptor. Many microorganisms follow the mode of aerobic respiration, and most bioremediation projects exploit this particular type of metabolism. There is, however, a wide variety of microorganisms that are able to survive and grow under anaerobic conditions using several inorganic or organic compounds other than oxygen as electron acceptors. This form of metabolism is called anaerobic respiration. The most commonly used electron acceptors under anaerobic conditions are nitrates (NO_3^-) and sulfates (SO_4^{2-}), which are soluble constituents in the aqueous phase, and the oxidized forms of iron (Fe[III]) and manganese (Mn[IV]), which are common constituents of soil particles, mainly in the form of oxides. A type of metabolism that can play an important role under strictly

TABLE 14.5
Typical Benzene Biodegradation Reactions under Various Electron Acceptor and Redox Conditions

Indicative Redox Conditions, E_h	Electron Acceptors	Biodegradation Reactions	Refs.
$> +200$ mV	O_2	$C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O$	[28]
$< +200$ mV	NO_3^-	$C_6H_6 + 6\ NO_3^- + 6\ H^+ \rightarrow 6\ CO_2 + 3\ N_2 + 6\ H_2O$	[29]
< 0 mV	Fe(III)	$C_6H_6 + 30\ Fe^{3+} + 12\ H_2O \rightarrow 6\ CO_2 + 30\ Fe^{2+} + 30\ H^+$	[30]
< -100 mV	SO_4^{2-}	$C_6H_6 + 3.75\ SO_4^{2-} + 7.5\ H^+ \rightarrow 6\ CO_2 + 3.75\ H_2S + 3\ H_2O$	[31]
< -200 mV	C_6H_6	$C_6H_6 + 12\ H_2O \rightarrow 2.25\ CO_2 + 3.75\ CH_4$	[32]

anaerobic conditions is fermentation. During fermentation there is no need for an external electron acceptor, because the organic contaminant serves as both electron donor and electron acceptor.

The typical biodegradation reactions under various electron acceptor conditions are presented in Table 14.5 for the simple case of benzene. Which type of electron acceptor will be used is closely related to the prevailing redox conditions. Under aerobic conditions, with redox potential greater than 200 to 220 mV, biodegradation is mainly performed by aerobic microorganisms. When oxygen is depleted but the redox potential remains relatively high, biodegradation can proceed through the metabolic activity of nitrate-reducing bacteria. The Fe(III) oxides of soil can be used as electron acceptors over a wide range of redox values, depending upon their crystallinity. Finally, sulfate-reducing and methanogenic bacteria are active only under strongly reducing conditions.

14.3.2.2 Co-Metabolism

In some cases, microorganisms can transform a contaminant, but they are not able to use this compound as a source of energy or carbon. This biotransformation is often called co-metabolism. In co-metabolism, the transformation of the compound is an incidental reaction catalyzed by enzymes, which are involved in the normal microbial metabolism.[33] A well-known example of co-metabolism is the degradation of (TCE) by methanotrophic bacteria, a group of bacteria that use methane as their source of carbon and energy. When metabolizing methane, methanotrophs produce the enzyme methane monooxygenase, which catalyzes the oxidation of TCE and other chlorinated aliphatics under aerobic conditions.[34] In addition to methane, toluene and phenol have been used as primary substrates to stimulate the aerobic co-metabolism of chlorinated solvents.

Tetrachoroethylene (perchloroethylene, PCE) is the only chlorinated ethene that resists aerobic biodegradation. This compound can be dechlorinated to less- or nonchlorinated ethenes only under anaerobic conditions. This process, known as reductive dehalogenation, was initially thought to be a co-metabolic activity. Recently, however, it was shown that some bacteria species can use PCE as terminal electron acceptor in their basic metabolism; i.e., they couple their growth with the reductive dechlorination of PCE.[35] Reductive dehalogenation is a promising method for the remediation of PCE-contaminated sites, provided that the process is well controlled to prevent the buildup of even more toxic intermediates, such as the vinyl chloride, a proven carcinogen.

14.3.2.3 Microbial Transformation of Toxic Elements

It has long been known that certain microbes can alter the oxidation state of some toxic metals, mainly by reducing them to a lower oxidation state, and this chemical transformation can be used for the bioremediation of contaminated soils. Three main mechanisms are involved in the bioreduction of toxic elements: dissimilatory (respiratory) reduction, direct enzymatic reduction (not supporting growth), and indirect chemical reduction induced by metabolic byproducts. Dissimilatory reduction has been demonstrated for uranium, selenium, and arsenic.[36–38] Recently, many bacteria species able to couple their growth with the reduction of Ur(VI), Se(VI), and As(V) have been isolated and characterized.[37,38] Direct enzymatic reduction is a kind of co-metabolism, i.e., a reaction that is catalyzed by microbial enzymes but cannot support biomass growth. Enzymatic reduction is one of the mechanisms involved in the bioreduction of Cr(VI).[39] The third mechanism is the indirect chemical reduction by metabolic byproducts. The most characteristic case is the reduction of Cr(VI) by H_2S, which is the main byproduct of the basic metabolism of sulfate-reducing bacteria.

Biological activity can be used in two ways for the bioremediation of metal-contaminated soils: to immobilize the contaminants *in situ* or to remove them permanently from the soil matrix, depending on the properties of the reduced elements. Chromium and uranium are typical candidates for *in situ* immobilization processes. The bioreduction of Cr(VI) and Ur(VI) transforms highly soluble ions such as CrO_4^{2-} and UO_2^{2+} to insoluble solid compounds, such as $Cr(OH)_3$ and UO_2. The selenate anions SeO_4^{2-} are also reduced to insoluble elemental selenium Se^0. Bioprecipitation of heavy metals, such as Pb, Cd, and Zn, in the form of sulfides, is another *in situ* immobilization option that exploits the metabolic activity of sulfate-reducing bacteria without altering the valence state of metals. The removal of contaminants from the soil matrix is the most appropriate remediation strategy when bioreduction results in species that are more soluble compared to the initial oxidized element. This is the case for As(V) and Pu(IV), which are transformed to the more soluble As(III) and Pu(III) forms. This treatment option presupposes an installation for the efficient recovery and treatment of the aqueous phase containing the solubilized contaminants.

14.3.3 ENGINEERING FACTORS

Biological treatment consists of promoting and maintaining the metabolic activity of a microbial population, which then is able to degrade or detoxify the target contaminants. In order to properly design a bioremediation system, it is important to control a number of factors that are crucial for maintaining microbial activity at efficient levels. Some important engineering factors affecting the performance of bioremediation systems include the availability of electron acceptors and nutrients, and environmental conditions such as moisture content, temperature, pH, and redox conditions.

14.3.3.1 Electron Acceptor

The great majority of bioremediation projects involve the aerobic degradation of organic contaminants, and the limiting factor is often the availability of oxygen. The mass of oxygen required by aerobic systems can be calculated based on stoichiometric considerations or laboratory measurements. Both anabolic and catabolic reactions require an electron acceptor. The stoichiometry of catabolic reactions can be easily determined by considering the end products. For instance, the catabolic complete mineralization of toluene, C_7H_8, is described by the following reaction:

Catabolic reaction

$$C_7H_8 + 9\,O_2 \longrightarrow 7\,CO_2 + 4\,H_2O \tag{14.21}$$

For anabolic reactions, which result in the production of new cells, it is important to know the approximate chemical composition of the biomass. The bacterial protoplasm comprises 75 to 80% water. The solid material is composed of several complex organic molecules, such as proteins, carbohydrates, and DNA. The mean composition of these molecules can be approximated by a relatively simple empirical formula, $C_{60}H_{87}O_{23}N_{12}P$, or in an even more simple form as $C_5H_7O_2N_{10}$.Numerous other elements such as sulfur, sodium, potassium, calcium, magnesium,

TABLE 14.6
Calculation of the Requirements in Oxygen and Macronutrients (N, P) for the Aerobic Biodegradation of Toluene

			Oxygen Required		CO_2 Produced		Biomass Produced	Nitrogen Required	Phosphorus Required
Catabolic reaction (50%)	C_7H_8	+	9 O_2	→	7 CO_2				
Anabolic reaction (50%)	C_7H_8	+	4 O_2	→	2 CO_2	+	$C_5H_7O_2N$	(~1/12 $C_{60}H_{87}O_{23}N_{12}P$)	
Moles per mole of C_7H_8	1		6.5		4.5		0.5	0.5	0.042
Grams per mole of C_7H_8	92		208		198		56.5	7	1.3
Grams per gram of C_7H_8	1		2.26		2.15		0.61	0.076	0.014

Note: Calculations assume 50% degradation for energy production and 50% for biomass production.

chlorine, iron, and various trace metals are also contained in the biomass, but the sum of these elements represents approximately 5% of the total dry biomass. Using the simple formula for the composition of cellular mass, the assimilation of toluene to build new cells can be described by the following reaction:

Anabolic reaction

$$C_7H_8 + 4\,O_2 + NH_4^+ \longrightarrow C_5H_7O_2N + 2\,CO_2 + 2\,H_2O + H^+ \qquad (14.22)$$

Based on established experience with aerobic degradation of organic contaminants, environmental engineers customarily assume that half of the organic compound is converted to cellular mass and half oxidized for energy. With this assumption the amount of oxygen required to biodegrade 1 mol of toluene corresponds to 6.5 mol, i.e., 4.5 mol for energy production and 2 mol for biomass production. An example of these calculations is presented in Table 14.6.

14.3.3.2 Nutrients

As is evident from the empirical formulas describing the typical composition of the cellular mass, nitrogen and phosphorous are important components, often referred to as macronutrients. All other elements are characterized as micronutrients. Most soil and aquifer systems contain a sufficient amount of micronutrients, but very often nitrogen and phosphorus are in shortage and must be added, usually in the form of soluble ammonium and orthophosphate salts. The formula $C_{60}H_{87}O_{23}N_{12}P$ provides a basis for calculating the theoretical amount of nitrogen and phosphorous required to produce new cellular mass. The C : N : P molar ratio for anabolic reactions is 60 : 12 : 1, but the actual demand in N and P for the biodegradation of organic carbon is lower, as only part of the organic carbon is used for the production of new biomass. In the previous example for the biodegradation of toluene (see Table 14.6), only 2.5 of the 7 carbon atoms of one toluene molecule were assumed to be assimilated into the new biomass and the total C : N : P ratio for both anabolic and catabolic reactions is 168 : 12 : 1. A general rule-of-thumb[12] usually applied by environmental engineers to estimate N and P requirements is the molar ratio C : N : P = 120 : 10 : 1.

For bioremediation, an initial feasibility study is always recommended, and the determination of nutrient requirements should be part of this study. The actual requirements are very much dependent upon the type of contaminants, which are often a mixture of compounds of variable biodegradability, and on the availability of nutrients in the specific contaminated soil, and should be determined with appropriate laboratory tests. However, there are guidelines that provide a useful basis for initial economic evaluations and for calculating ranges to be tested during the laboratory tests.

14.3.3.3 Moisture

Moisture is necessary for biodegradation for two reasons:

1. For cellular growth, because water constitutes 75 to 80% of cellular tissue
2. As a medium for the movement of microorganisms to the organic contaminants and vice versa[10]

A moisture ranging between 25 and 85% of complete saturation is considered to be adequate for soil bioremediation.[12] In many cases, the soil moisture in the vadose zone is below or at the lower end of this range, so the addition of water is often needed to maintain good operating conditions.

14.3.3.4 Temperature

Temperature has a major influence on metabolic activity, and microorganisms are classified into three main categories based upon the optimum temperature for their growth. Psychrophiles are microorganisms that can grow at temperatures below 20°C, mesophiles are characterized as organisms with an optimum growth temperature between 25 and 40°C, and thermophiles are those preferring temperatures above 45°C. Very often, when the temperature increases a few degrees above the optimum value, growth declines precipitously; long exposure to the higher temperatures may even result in cell death. Lower temperatures, on the other hand, are not usually lethal—the cells remain dormant, but their activity can restart if the optimum temperature conditions are reestablished. Most soil bioremediation projects are based on the activity of mesophilic bacteria, which are the most common and abundant microorganisms in the subsurface.

14.3.3.5 pH

Another important factor affecting microbial activity is pH. Microorganisms that can grow under acidic ($\text{pH} < 4$) or alkaline ($\text{pH} > 10$) conditions are termed acidophiles or alkalophiles, respectively. Most bacteria, however, are neutrophiles. Neutrophiles can tolerate pH levels between 5 and 9, but their optimum growth is observed in a relatively narrow range around neutrality, i.e., between 6.5 and 7.5.

Microbial activity, which is often stimulated during bioremediation projects, can alter the external pH. For instance, the anaerobic degradation of chlorinated compounds produces organic acids and HCl and the pH may drop to acidic values if the soil has a low buffering capacity. In this case, control of the external pH will be required in order to maintain biodegradation activity at satisfactory levels.

14.3.3.6 Redox Potential

The most critical issue to be investigated during the initial biofeasibility study is the determination of which metabolic mode—aerobic or anaerobic—is more appropriate for the specific contaminants. As shown in Table 14.5, the redox potential is closely related to the metabolic mode, and careful control of this parameter is required to maintain the optimum metabolic mode during bioremediation. A general rule is that the redox potential should be above 50 mV to maintain the activity of aerobic and facultative anaerobic microorganisms and below that value for strictly anaerobic microorganisms.[12]

14.3.4 *IN SITU* METHODS FOR THE BIOLOGICAL TREATMENT OF ORGANIC CONTAMINANTS

Bioremediation methods may be applied either *in situ* or *ex situ*. In this section, the most important *in situ* treatment methods will be examined.

14.3.4.1 Bioremediation in the Vadose Zone

When contamination exists substantially above the water table, i.e., in the vadose zone, a very efficient *in situ* technique that may be used is bioventing, which is similar in many ways to SVE technology. In many SVE applications, it has been observed that air circulation through the porosity of the vadose zone stimulates the biodegradation of organic contaminants. Based on these observations, bioventing technology was developed using a system configuration similar to SVE but optimizing the design in order to promote the aerobic biodegradation of contaminants. In practice, SVE and bioventing are usually combined in an integrated treatment scheme, where the highly volatile compounds are removed by volatilization and the biodegradable constituents are biologically destroyed.

The main requirements for the design of a bioventing system are the following[9]:

1. An O_2 flow must be maintained through the contaminated zone at a level sufficient for the aerobic biodegradation of contaminants. Note that during bioventing the main aim is the maximum utilization of O_2 by the microbial cultures. For this reason, air flow rate is usually an order of magnitude lower than that applied in simple SVE systems. A simple empirical rule is that the mean residence time of air in the contaminated soil pore volume should be between 1 and 2 days.
2. The moisture of the soil should be maintained at an optimum value for microbial activity. As previously mentioned, a minimum level of soil moisture is necessary for successful biodegradation. The continuous circulation of air during bioventing results in the evaporation of soil moisture. For this reason, the design of these systems must include an appropriate installation for adding water to the contaminated zone. Care must be taken to avoid the addition of excess water. If soil moisture is significantly increased, e.g., above the limit of 85%, air circulation is no longer effective due to the decrease in free soil porosity.
3. Macro- and micronutrients should be provided as needed. Soils usually contain sufficient levels of micronutrients, but very often there is a lack of nitrogen and phosphorus. The addition of N and P is particularly important during the initial stages of treatment, in order to stimulate the growth of indigenous bacteria. After the initial development of a critical microbial mass, N and P are constantly recycled due to the lysis of dead microbial cells.[9]

A schematic of a bioventing installation, including a system for the addition of water and nutrients, is depicted in Figure 14.4. When the contaminated zone is near the surface and the soil is sufficiently permeable, the addition of water, together with dissolved nutrients, can be carried out using a simple surface irrigation system. When the contamination is located at lower horizons, an underground infiltration system or a network of wells may be more appropriate.

14.3.4.2 Bioremediation in the Water-Saturated Zone

When the contaminated zone is located below the water table, the availability of oxygen becomes a critical problem due to the low solubility of oxygen in water. In adding the required oxygen, two kinds of systems are usually applied:

1. Water circulation systems, where groundwater is pumped, oxygenated in surface installations and reinjected in the contaminated aquifer
2. Air sparging systems, involving the injection of air directly into the groundwater

Water circulation systems

A typical water circulation system is presented in Figure 14.5. Groundwater is pumped to the surface from a well, which is located downgradient of the contaminated zone, and directed to an

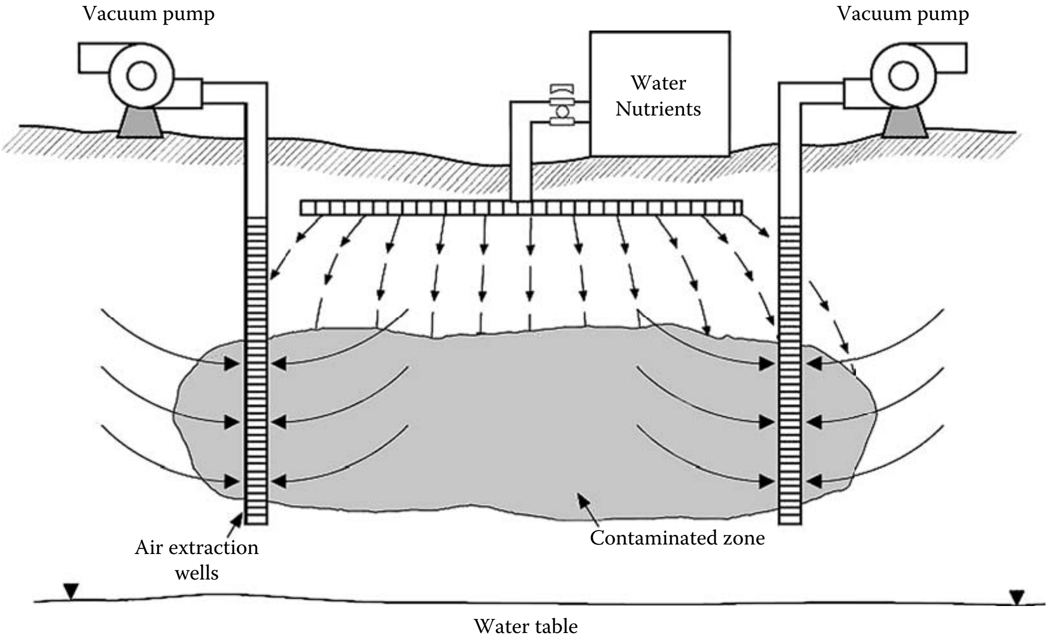


FIGURE 14.4 Schematic diagram of a bioventing system.

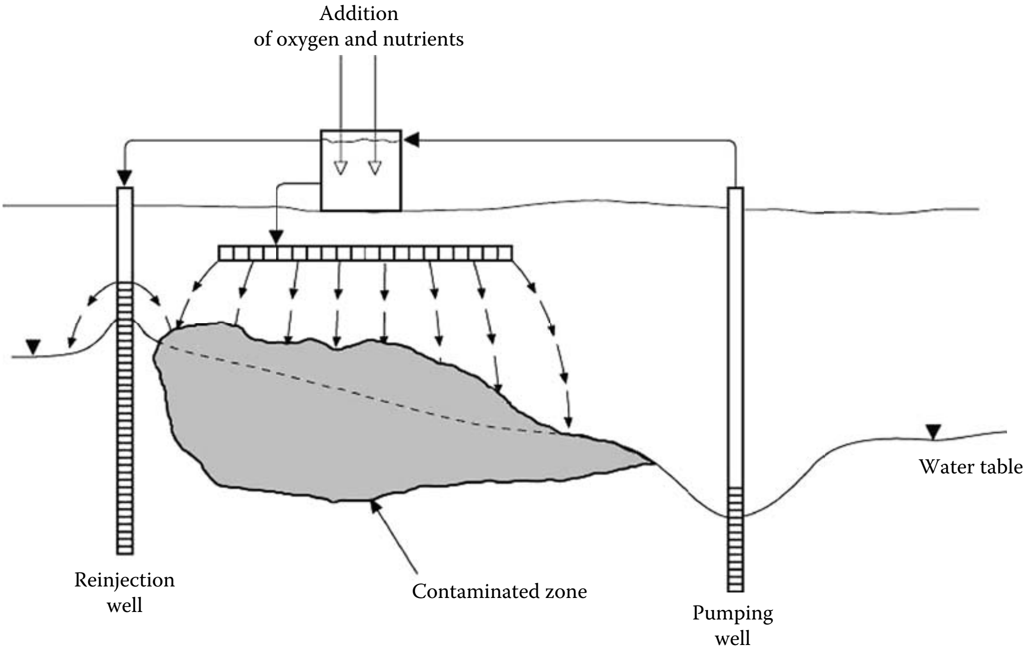


FIGURE 14.5 Representation of a water circulation bioremediation system.

installation where it is amended with nutrients and oxygen. Enriched groundwater is then reinjected into the aquifer using wells, trenches, or injection galleries, depending on the situation.

The addition of oxygen can be carried out by sparging the groundwater with air or pure oxygen or by adding hydrogen peroxide (H_2O_2). When the oxygenation is carried out by simple aeration, the concentration of dissolved oxygen may not exceed 8 to 12 mg/L, but with pure oxygen sparging, concentrations of up to 40 mg/L of dissolved oxygen can be attained. The H_2O_2 produces O_2 according to the following dissociation reaction:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 \tag{14.23}$$

As a result of this reaction, dissolved H_2O_2 serves as a continuous source of oxygen. Thus the amount of available oxygen is greater than the limit of 40 mg/L, corresponding to the solubility of pure O_2, and depends on the concentration of dissolved H_2O_2. It has been established, however, that H_2O_2 has a toxic effect on microorganisms at concentrations greater than 1000 mg/L. For this reason, concentrations between 100 and 500 mg/L are generally used.

Simple aeration of groundwater in surface installations cannot meet the demand for oxygen supply in most bioremediation projects. This is illustrated in the following example (adapted from Reference 10).

Example: Alternative modes of supplying oxygen in a water circulation system

Leakage from a toluene tank resulted in the contamination of an aquifer with approximately 5000 kg of toluene. *In situ* measurements and laboratory tests confirmed the existence of indigenous bacteria, able to biodegrade toluene in the presence of oxygen. It was decided to carry out bioremediation of the site using a water circulation system. Estimate the time required for the remediation of this site if the groundwater is pumped at a rate of 300 L/min and O_2 addition is carried out (1) with simple aeration (2) with pure oxygen sparging, and (3) by the addition of H_2O_2 at a concentration of 250 mg/L.

As shown in Table 14.6, 14.26 g O_2 are required for the mineralization of 1 g toluene. Consequently, 11,300 kg O_2 are required for the biodegradation of the 5000 kg of toluene.

1. In the case of simple aeration, the rate of oxygen supply in the aquifer will be

$$300\text{ L/min} \times 8\text{ g/L} \times 1440\text{ min/d} = 3.5\text{ kg/d}$$

With this mode of O_2 supply, almost 9 years are needed for the complete degradation of the toluene.

2. In the case of pure oxygen sparging, the rate of oxygen supply in the aquifer will be

$$300\text{ L/min} \times 40\text{ g/L} \times 1440\text{ min/d} = 17.3\text{ kg/d}$$

The duration of the treatment in this case is 1.8 years.

3. According to reaction 2.23, 2 mol H_2O_2 produces 1 mol O_2; i.e., $2 \times 34 = 68$ g H_2O_2 produces 32 g O_2. Assuming that 250 mg/L H_2O_2 is added in the pumped waters, the rate of oxygen supply will be

$$300\text{ L/min} \times (250 \times 32/68)\text{ mg/L} \times 1440\text{ min/d} = 50.8\text{ kg/d}$$

With the addition of H_2O_2, the required treatment time is 7.4 months.

It is obvious from the above calculations that realistic remediation times can be obtained using either pure oxygen or H_2O_2. The final selection will be based on the overall environmental and

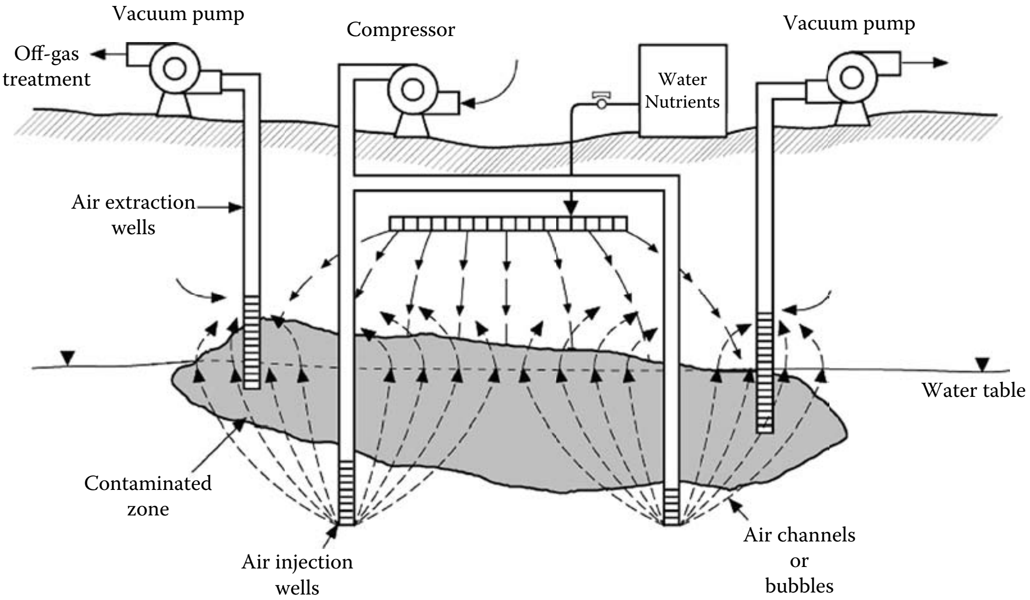


FIGURE 14.6 Air sparging system.

techno-economic evaluation of each alternative, taking into consideration the available timeframe and the financial resources available for the remediation of the area of concern.

Air sparging systems

An important innovation in bioremediation technology has been the use of air sparging to oxygenate groundwater. A typical system is presented in Figure 14.6. Using this technique, the removal of contaminants is achieved using two simultaneous mechanisms:

1. Volatilization of the dissolved volatile contaminants through the air–water interface
2. Biodegradation as a result of the enrichment of the groundwater with oxygen

A continuous oxygen supply is thus achieved, which is limited only by the mass transport phenomena between the gas and aqueous phases; this is the main advantage of air sparging over the alternative of water circulation systems.

Which mechanism will be dominant during air sparging (volatilization or biodegradation) depends on the relative volatility and biodegradability of the specific contaminants. The volatility of dissolved contaminants is usually characterized using the Henry's Law constant. In contrast with volatility, biodegradability cannot be estimated with a simple physical constant. Many data, however, have been published describing the biodegradation of organic contaminants under various laboratory and field conditions. In most cases, biodegradability is expressed in terms of half-life $t_{1/2}$, representing the time required to biodegrade half of the initial amount of contaminant under particular laboratory or field conditions. Available biodegradability data for a long list of contaminants are compiled in some environmental engineering textbooks and handbooks[9,40] and such compilations constitute a highly valuable information source for conducting initial biofeasibility studies. The Henry's Law constants K_H and aerobic biodegradation data for some characteristic organic compounds are presented in Table 14.7. The first four aromatic compounds, known as BTEX, are removed easily with both volatilization and biodegradation. Chlorinated hydrocarbons, such as trichloroethylene and trichloroethane, usually have low biodegradability and high volatility. These compounds are therefore removed mainly through volatilization. Some compounds are highly soluble in the aqueous

TABLE 14.7
Henry's Law Constants and Biodegradation Data for Some Characteristic Organic Compounds

Compound	Henry Constant (atm.m^3/mol)	Aerobic Biodegradation in Soils Half-Life (h)	
		From	To
Benzene	5.5×10^{-3}	120	384
Toluene	6.6×10^{-3}	96	528
m-Xylene	6.3×10^{-3}	168	672
Ethyl-benzene	8.7×10^{-3}	72	240
Trichloroethylene	9.1×10^{-3}	4320	8640
1,1,1-Trichloroethane	16.2×10^{-3}	3360	6552
Acetonitrile	3.5×10^{-6}	168	672
Phenol	4.0×10^{-7}	24	240

Source: Suthersan S.S., *Remediation Engineering: Design Concepts*, CRC Press, Boca Raton, FL, 1997. With permission.

phase, e.g., acetonitrile and phenol, and are easily biodegraded, but their volatility from the aqueous phase is low. In such cases, the main removal mechanism is biodegradation.

Design parameters

The main aim in the design of air sparging systems is to achieve the maximum possible interface between air and groundwater. A large interface is necessary not only for the volatilization of contaminants (transfer from the aqueous phase to the air), but also for the oxygenation of groundwater (oxygen transfer from the air to the aqueous phase). The dispersion and movement of air in the water-saturated zone are very complex phenomena that are not yet fully understood. For instance, two different approaches are used to describe the upward movement of air. The first approach suggests that air travels in the form of discrete air channels. In the second, the air travels in the form of air bubbles. Owing to the complexity of the process and the absence of simple and reliable mathematical models, the design of air sparging systems is based mainly on experience and *in situ* tests. The most important design parameters are the following[9]:

1. *Zone of influence*. Whereas in SVE systems the zone of influence around each extraction well can be described as a cylinder of a particular radius, in air sparging systems it is not possible to define a radius of influence. Air sparging is usually carried out through one or more injection wells that are installed in such a way that their end is located below the contaminated area. Air bubbles emerging from the end of each well are transferred upwards, in the shape of an inverted cone. The width of the cone depends mainly on the permeability and the homogeneity of the soil. Permeable and homogeneous soils usually form narrow cones. Low-permeability soils or soils containing low-permeability zones form broader cones. The zone of influence is usually determined with *in situ* tests.
2. *Depth of air injection*. The end of the well from which air sparging is conducted is usually located 30 to 60 cm below the contaminated area.
3. *Air injection pressure and flow rate*. Air pressure must be greater than the hydrostatic pressure of the overlying water column at the depth of injection. Additional overpressure is also required to overcome the capillary forces inhibiting the penetration of air into the porous medium. The required overpressure depends on the permeability of the aquifer. A high overpressure, in the range of 0.3 to 3 m of H_2O, is usually applied in fine-grained soils with

low permeability. For permeable coarse soils, an overpressure between 3 and 30 cm of H_2O is sufficient. The typical values of volumetric flow rates per well range from 25 to 400 L/min.

14.3.5 *Ex Situ* Biological Treatment

In cases where *in situ* biological treatment cannot be applied, the contaminated soil is excavated and transferred to specially prepared areas where bioremediation can be carried out under well-controlled conditions. Some common *ex situ* biological methods are the landfarming technique and the biopile or biopit treatment options.[32]

14.3.5.1 Landfarming

In this treatment method, the soil is spread on a wide flat surface, creating a layer of thickness between 45 and 60 cm. At regular time intervals, the soil is plowed using classical tilling equipment to obtain good aeration and provide the oxygen necessary for the biological actions. Water and nutrients are also added as required using garden-type sprinkling equipment, which must be easily moved so that tilling can be conducted without destroying it. A schematic diagram of the landfarming treatment system is presented in Figure 14.7. The underlying surface is constructed with a slight slope (0.5 to 1%) towards a drainage collection point and is covered with an impermeable liner to obtain efficient recovery of the drainage and prevent eventual contamination of the subsoil. A permeable layer of sand is placed over the liner to protect it from the tilling equipment and promote the drainage of excess water. The contaminated soil is placed on top of the sand layer. This method is easily carried out and presents no technical difficulties. The main prerequisite is the availability of a large amount of surface, because the thickness of the soil layer cannot exceed 60 cm. This limit corresponds to the maximum plow depth of the available tilling machines.

14.3.5.2 Treatment in Biopile or Biopit

When available land space is insufficient for land farming, soil treatment can be carried out in piles or pits. Typical biopile and biopit constructions are presented in Figure 14.8 and Figure 14.9, respectively. When the soil has relatively low permeability, the pile can be constructed with sequential "lifts" of soil, approximately 60 cm in thickness, separated by permeable sand layers. These layers are connected with a vacuum pump or blower that is used to produce airflow though the soil pile. Water and nutrients are sprinkled on the top of the pile.

Treatment in a pit (Figure 14.9) can be carried out in the same area from which the soil was excavated, following isolation of the area with an impermeable liner. In this case, the upper surface of the pit can be covered with asphalt and rendered for use before the completion of the bioremediation project. If the upper surface is covered, an appropriate venting system must be installed to

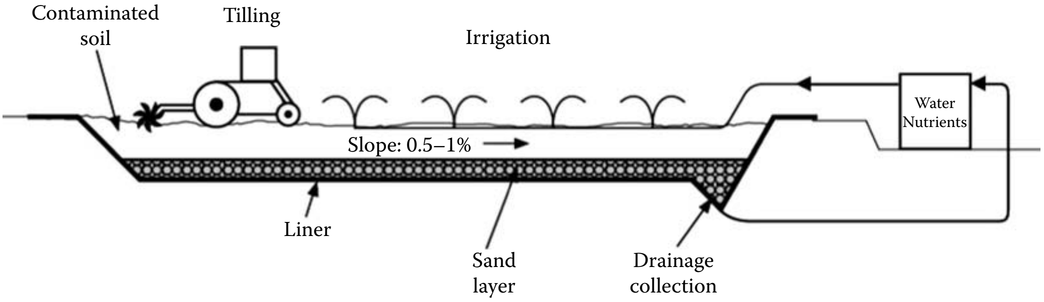


FIGURE 14.7 Landfarming treatment system.

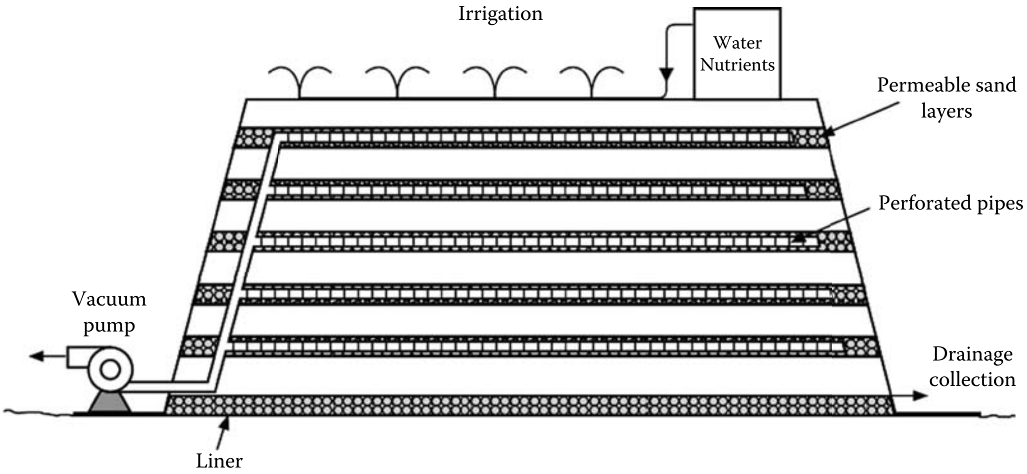


FIGURE 14.8 Treatment in a biopile.

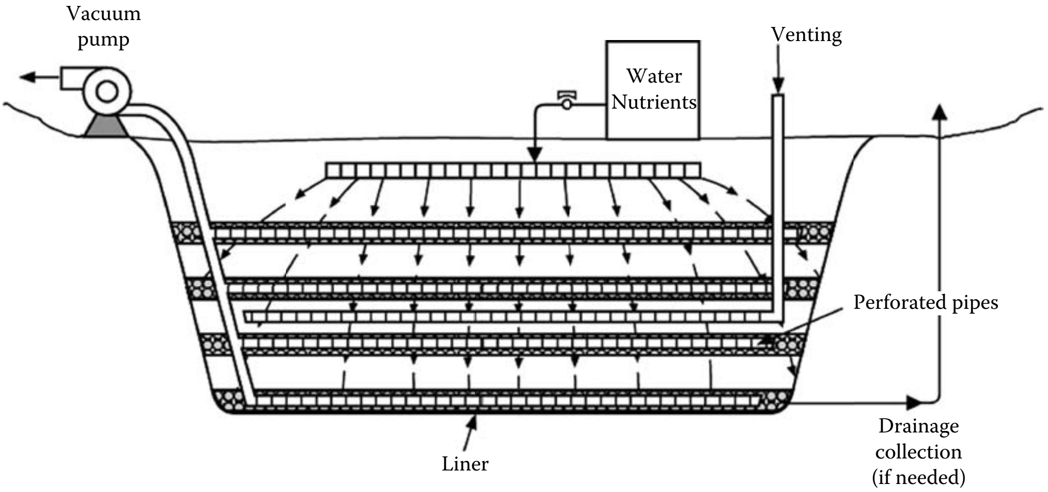


FIGURE 14.9 Treatment in a biopit.

allow the infiltration of fresh air inside the pit. Biopit is also a treatment option well adapted for anaerobic processes. With this configuration, the soil can be easily kept under water-saturated anaerobic conditions, and an impermeable cover on the surface will exclude any contact with atmospheric oxygen.

14.4 PHYTOREMEDIATION

14.4.1 General Description

Phytoremediation (also called green remediation, botano-remediation, agroremediation, and vegetative remediation) is the name given to a set of technologies that use living green plants and their associated microorganisms for *in situ* (in-place or on-site) partial or substantial remediation of contaminated soils, sludges, sediments, and groundwater. Both organic and inorganic contaminants can be addressed by applying phytoremediation technologies. Typical contaminants include petroleum hydrocarbons, crude oil, chlorinated compounds, pesticides, explosives, heavy metals, metalloids, and radioactive materials.

Plants aid remediation of polluted sites by means of several mechanisms. Some plants may withstand relatively high concentrations of organic chemicals without toxic effects, and in some cases can take up and quickly convert chemicals to less toxic metabolites. In addition, they stimulate the degradation of organic chemicals in the rhizosphere by releasing root exudates, enzymes and the buildup of organic carbon in the soil. Other plants, called hyperaccumulators, absorb unusually large amounts of metals. Growing these plants on contaminated soil and harvesting at certain times may result in decontamination of the soil. Still other plants may immobilize contaminants in the soil through absorption and accumulation into the roots, adsorption onto the roots, or precipitation or immobilization within the root zone. Therefore, based on the outcome for the contaminants, phytoremediation may be classified as a degradation, extraction, or containment technique. Another way of categorizing phytoremediation is based on the mechanisms involved. Such mechanisms include the following:

1. Extraction of contaminants from the soil and accumulation in the plant tissue for removal (phytoextraction)
2. Degradation of organic contaminants in the root zone by microorganisms (rhizodegradation)
3. Uptake of contaminants from the soil and metabolism above or below ground, within the root, stem, or leaves (phytodegradation)
4. Volatilization or transportation of volatile contaminants from the plants to the air (phytovolatilization)
5. Immobilization of contaminants in the root zone (phytostabilization)
6. Adsorption of contaminants on roots for containment or removal (rhizofiltration)

Phytoremediation is considered a low-cost remediation alternative for low-depth contamination, offering a permanent solution and improving the aesthetics of the polluted site. It is well-suited for use in the following situations:

1. At very large field sites where other methods of remediation are not cost-effective or practicable
2. At sites with low concentrations of contaminants where only a "polishing treatment" is required over long periods of time
3. In conjunction with other technologies where vegetation is applied as a final cap and closure of the site

Limitations need to be carefully considered before selecting this method for site remediation. These include the depth of contamination, the total length of time required for cleanup to below accepted limits, potential contamination of vegetation and the food chain, and difficulty in establishing and maintaining vegetation at some polluted sites.[8]

14.4.2 Phytoremediation Mechanisms

Phytoremediation takes advantage of the natural processes of plants (Figure 14.10). These processes include water and chemical uptake, metabolism within the plant, release of inorganic and organic compounds (exudates) into the soil, and the physical and biochemical impact of plant roots.[8,41] Plants require 13 essential inorganic plant nutrients (N, P, K, Ca, Mg, S, Fe, Cl, Zn, Mn, Cu, B, and Mo) for growth; these are taken up by the root system. In addition to these essential nutrients, other nonessential inorganics (such as various common contaminants like Pb, Cd, and As) or organics can be taken up. For uptake into a plant, a chemical must be in solution, either in the groundwater or in

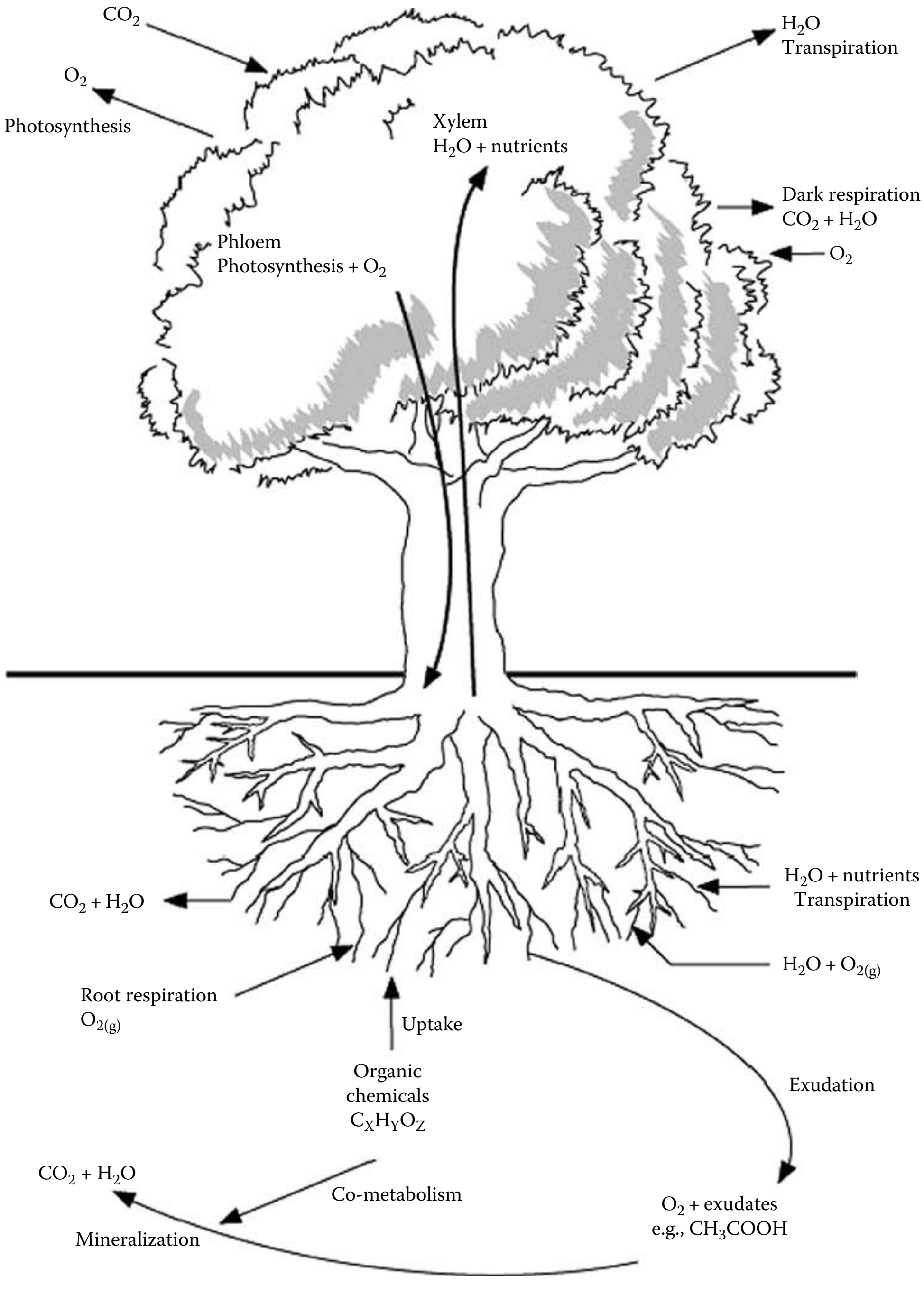


FIGURE 14.10 Oxygen, water, and chemical flows through a woody tree.

the soil solution. Water is absorbed from the soil solution into the outer tissue of the root and contaminants in the water can move to different parts of plants where they can be absorbed, bound, or metabolized.

Factors that affect the accessibility of chemicals to plant roots include hydrophobicity, polarity, sorption properties and solubility. In order to apply phytoremediation techniques to soils polluted by organic contaminants, the contaminant must come into contact with the plant roots and be dissolved in the soil water. One chemical characteristic that influences the uptake of organics into a plant is the octanol–water partition coefficient, log K_{ow}. Chemicals that are able to enter the plant have log K_{ow} values[8] between 1 and 3.5. Hydrophobic chemicals presenting log K_{ow} values greater than 3.5 are generally not sufficiently soluble in water or are bound so strongly to the surface of the roots that they cannot be easily translocated into the plant. On the other hand, chemicals that are highly polar and very water soluble (log $K_{ow} < 1.0$) are not sufficiently absorbed by the roots nor are they actively transported through plant membranes due to their high polarity.[42] Most benzene, toluene, ethylbenzene and xylene (BTEX) chemicals, chlorinated solvents, and short-chain aliphatic chemicals fall within the log K_{ow} range that allows them to be susceptible to phytoremediation.[8,41,42]

Plant roots cause changes at the soil–root interface as they release inorganic and organic compounds (root exudates) into the area of soil immediately surrounding the roots (the rhizosphere). Root exudates affect the number and activity of microorganisms, the aggregation and stability of the soil particles around the root, and the availability of elements. Root exudates can increase (mobilize) or decrease (immobilize), directly or indirectly, the availability of elements in the rhizosphere. Mobilization or immobilization of elements in the rhizosphere can be caused by changes in soil pH, the release of complexing substances such as metal-chelating molecules, changes in oxidation–reduction potential, and increases in microbial activity.

Different forms of phytoremediation may require different types of plants and be relevant for specific types of contaminants (Table 14.8). In the following section, each remediation form is presented separately.

14.4.2.1 Phytoextraction

Phytoextraction (also called phytoaccumulation, phytosequestration, phytoabsorption, and phytomining) refers to the use of certain plants to transport metals from the soil and concentrate them into the roots and aboveground shoots. One or a combination of these plants can be selected and planted at a site based on the type of metals present and other site conditions. After the plants have been allowed to grow for several weeks or months, they are harvested and either incinerated or recycled as metal ore. This procedure may be repeated as necessary to lower soil contaminant levels to allowable limits. Phytoextraction may be applied to metals (e.g., Ag, Cd, Co, Cr, Cu, Hg, Mn, No, Ni, Pb, and Zn), metalloids (e.g., As and Se), radionuclides (e.g., ^{90}Sr, ^{137}Cs, ^{234}U, and ^{238}U), and nonmetals (e.g., B). It has generally not been considered for organic or nutrient contaminants, as these can be metabolized, changed, or volatilized by the plant, thus preventing accumulation.

Phytoextraction is mainly carried out by certain plants called hyperaccumulators, which absorb unusually large amounts of metals compared to other plants. A hyperaccumulator is a plant species capable of accumulating 100 times more metal than a common nonaccumulating plant. Therefore, a hyperaccumulator will concentrate more than 1000 mg/kg or 0.1% (dry weight) of Co, Cu, Cr, or Pb, or 10,000 mg/kg (1%) of Zn and Ni (dry matter).[43,44] Similarly, halophytes are plants that can tolerate and, in many cases, accumulate large amounts of salt (typically sodium chloride but also Ca and Mg chlorides). Hyperaccumulators and halophytes may be selected and planted at a site based on the type of metals or salts present, the concentrations of these constituents, and other site conditions.

Almost all known metal-hyperaccumulating species were discovered on metal-rich soils and they are endemic to such soils, suggesting that hyperaccumulation is an important ecophysiological adaptation to metal stress and one of the manifestations of resistance to metals. These plants are generally rare and found only in localized areas around the world, with fewer than 400 identified species for eight heavy metals.[41] Phytoextraction occurs in the root zone of plants. The root zone typically may be relatively shallow, with the bulk of the roots at shallower rather than greater depths. This is a potential limitation of phytoextraction. One type of plant may take up different metals to different degrees. Experimental studies[45] have indicated that the phytoextraction coefficients (the ratio of the metal concentration in the shoot to the metal concentration in the soil) for different metals taken up by Indian mustard vary significantly (as shown in Table 14.9).

TABLE 14.8
Typical Plants Used in Various Phytoremediation Applications

Mechanism	Media	Typical Contaminants	Plant Types
Phytodegradation	Soils, groundwater, landfill leachate, land application of wastewater	Herbicides (atrazine, alachlor) Aromatics (BTEX) Chlorinated aliphatics (TCE) Nutrients (NO_3^-, NH_4^+, PO_4^{3-}) Ammunition wastes (TNT, RDX)	Phreatophyte trees (poplar, willow, cottonwood, aspen) Grasses (rye, Bermuda, sorghum, fescue) Legumes (clover, alfalfa, cowpeas)
Rhizodegradation	Soils, sediments, land application of wastewater	Organic compounds (TPH, PAHs, BTEX, pesticides, chlorinated solvents, PCBs)	Phenolics releasers (mulberry, apple, osage orange) Grasses with fibrous roots (rye, fescue, Bermuda) for contaminants 0–3 ft deep Phreatophyte trees for 0–10 ft Aquatic plants for sediments
Phytostabilization	Soils, sediments	Metals and metalloids (As, Cd, Cr, Cu, Pb, Zn, U, Se) Hydrophobic organics (PAHs, PCBs, dioxins, furans, pentachlorophenol, DDT, dieldrin)	Phreatophyte trees to transpire large amounts of water for hydraulic control Grasses with fibrous roots to stabilize soil erosion Dense root systems are needed to sorb/bind contaminants
Phytoextraction	Soils, sediments	Metals (Ag, Au, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn) Radionuclides (^{90}Sr, ^{137}Cs, ^{239}Pu, ^{234}U, ^{238}U)	Sunflowers Indian mustard Rape seed plants Barley, hops Crucifers Serpentine plants Nettles, dandelions
Phytovolatilization	Soils, sediments, sludges, groundwater	Chlorinated solvents, MTBE, some inorganics (Se, Hg, As)	Herbaceous species Trees Wetland species
Rhizofiltration	Groundwater, water and wastewater in lagoons or created wetlands	Metals (Pb, Cd, Zn, Ni, Cu) Radionuclides (^{137}Cs, ^{90}Sr, ^{234}U, ^{238}U) Hydrophobic organics	*Aquatic plants*: Emergents (bullrush, cattail, coontail, pondweed, arrowroot, duckweed) Submergents (algae, stonewort, parrotfeather, Eurasian water milfoil, Hydrilla)

Source: Schnoor, J.L., Phytoremediation. Technology Evaluation Report TE-98-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA, 1997; Interstate Technology and Regulatory Cooperation Work Group (ITRC), Phytotechnologies Work Team, Technical/Regulatory Guidelines. Phytotechnology Technical and Regulatory Guidance Document, 2001, www.itrcweb.org/Documents/PHYTO-2.pdf. With permission.

Higher phytoextraction coefficients indicate higher metal uptake. The effectiveness of phytoextraction can be limited by the sorption of metals to soil particles and the low solubility of the metals; however, metals can be solubilized through the addition of acids or chelating agents and so allow uptake of the contaminant by the plant. Ethylene diamine tetra-acetic acid (EDTA), citric acid, and ammonium nitrate have been reported to help in the solubilization of lead, uranium, and cesium

TABLE 14.9
Phytoextraction Coefficients

Metal	Phytoextraction Coefficient
Cr^{6+}	58
Cd^{2+}	52
Ni^{2+}	31
Cu^{2+}	7
Pb^{2+}	1.7
Cr^{3+}	0.1
Zn^{2+}	17

Source: Kumar, P.B.A.N., Dushenkov, V., Motto, H. and Raskin, I., Phytoextraction: The use of plants to remove heavy metals from soils, *Environ. Sci. Technol.*, 29, 1232–1238, 1995. With permission.

137, respectively.[46] However, the potential adverse impact of such chemicals on groundwater, plant growth, or other elements' solubility must be considered before use.

Phytoextraction has several advantages. The contaminants are permanently removed from the soil and the quantity of the waste material produced is substantially decreased. In some cases, the contaminant can be recycled from the contaminated biomass. However, the use of hyperaccumulating plants is limited by their slow growth, shallow root systems, and small biomass production. In order for this remediation scheme to be feasible, plants must tolerate high metal concentrations, extract large concentrations of heavy metals into their roots, translocate them into the surface biomass, and produce a large quantity of plant biomass.

14.4.2.2 Rhizodegradation

Rhizodegradation (also called phytostimulation, rhizosphere biodegradation, or plant-assisted bioremediation/degradation) is the breakdown of contaminants in the soil through the enhanced bioactivity existing in the rhizosphere. Typical compounds exuded by plant roots in the rhizosphere include sugars, amino acids, organic acids, fatty acids, sterols, growth factors, nucleotides, flavanones, and enzymes.[47] Root exudates provide sufficient carbon to support large numbers of microbes (approximately 1×10^8 to 1×10^9 vegetative microbes per gram of soil in the rhizosphere). Because of these exudates, microbial populations and activities between 5 and 100 times greater in the rhizosphere than in bulk soil. This plant-induced enhancement of the microbial population is referred to as the "rhizosphere effect."[48,49] The increased microbial populations and activity in the rhizosphere can increase contaminant biodegradation in the soil, and degradation of the exudates can stimulate co-metabolism of contaminants in the rhizosphere.

Organic contaminants such as petroleum hydrocarbons or chlorinated solvents can be directly metabolized by proteins and enzymes, leading to the degradation, metabolism, or mineralization of the contaminants. Furthermore, many of these contaminants can be broken down into harmless products or converted into a source of food and energy for the plants or soil organisms.[50]

Rhizodegradation is a symbiotic relationship that has evolved between plants and soil microbes. The plants provide the nutrients necessary for the microbes to thrive, and the microbes provide a healthier soil environment in which the plant roots can proliferate.

14.4.2.3 Phytodegradation

Phytodegradation (also known as phytotransformation) is the uptake, metabolizing, and degradation of contaminants within the plant, or the degradation of contaminants external to the plant through the effect of compounds such as enzymes produced and released by the plant. Phytodegradation is not dependent on the microorganisms associated with the rhizosphere. For the type of phytodegradation that occurs within a plant, the plant must be able to take up the contaminant. Therefore, only moderately hydrophobic compounds, with an octanol–water partition coeffiecient $\log K_{\mathrm{ow}}$ between 1 and 3.5, are susceptible to phytodegradation.[8] The direct uptake of a chemical into a plant through its roots depends on the uptake efficiency, transpiration rate, and the concentration of the contaminant in the soil water.[51] Once an organic chemical is translocated, the plant may store the chemical and its fragments into new plant structures through lignification (covalent bonding of chemical or its fragments into lignin of the plant), or it can volatilize, metabolize, or mineralize the chemical completely to carbon dioxide and water.

14.4.2.4 Phytovolatilization

Phytovolatilization involves using plants to take up volatile or nonvolatile contaminants from the soil, transforming them into volatile forms and transpiring them into the atmosphere. Phytovolatilization is primarily a contaminant extraction process. However, metabolic processes within the plant might alter the initial form of the contaminant, and in some cases transform it to less toxic forms. Phytovolatilization may be applied to both organic and inorganic contamination. An example of phytovolatilization of inorganic contaminants is the transformation of the highly toxic mercuric ion to the less toxic elemental mercury. A disadvantage of this technique is that mercury released to the atmosphere is likely to be recycled by precipitation. Because phytovolatilization involves the transfer of contaminants to the atmosphere, a risk analysis of the impact of this transfer on the ecosystem and human health may be necessary.

14.4.2.5 Phytostabilization

Phytostabilization (also known as in-place inactivation or phytoimmobilization) is the use of certain plant species to immobilize contaminants in the soil through absorption and accumulation by roots, adsorption onto roots, or precipitation, complexation, and metal valence reduction within the root zone. The following three mechanisms determine the fate of the contaminants within the phytostabilization process[46]:

1. *Phytoremediation in the root zone.* Proteins and enzymes produced by the plant can be exuded by the roots into the rhizosphere. These plant products target contaminants in the surrounding soil, leading to precipitation or immobilization in the root zone. This mechanism within phytostabilization may reduce the fraction of the contaminant in the soil that is bioavailable.
2. *Phytostabilization on the root membranes.* Proteins and enzymes directly associated with the root cell walls can bind and stabilize the contaminant on the exterior surfaces of the root membranes. This prevents the contaminant from entering the plant.
3. *Phytostabilization in the root cells.* Proteins and enzymes present on the root cell walls can facilitate the transport of contaminants across the root membranes. Upon uptake, these contaminants can be sequestered into the vacuole of the root cells, preventing further translocation to the shoots.

Phytostabilization has generally focused on metal contamination, with lead, chromium, and mercury being identified as the top potential candidates for phytostabilization.[44,52] However, there is potential for phytostabilization of organic pollutants, because some organic contaminants or metabolic byproducts of these contaminants can be attached to or incorporated into plant components.[41] Very hydrophobic organic compounds with $\log K_{\mathrm{ow}}$ values greater than 3.5 are candidates for phytostabilization.[8]

Effective phytostabilization requires a thorough understanding of the chemistry of the root zone, root exudates, contaminants, and fertilizers or soil amendments to avoid unintended effects that might increase contaminant solubility and leaching. It has been suggested that phytostabilization might be most appropriate for heavy-textured soils and soils with high organic matter contents.[53]

Phytostabilizing plants should be able to tolerate high levels of contamination (i.e., metal-tolerant plants for heavy-metal-contaminated soils), with roots growing into the zone of contamination, and should be able to alter the biological, chemical, and physical conditions in the soil. Furthermore, contaminants should not be accumulated in the plant tissues in order to eliminate the possibility that the harvested plants might themselves become hazardous wastes. Most research on phytostabilization deals with mining wastes or soils polluted by mining activities. Following field applications conducted in Liverpool, England, varieties of three grasses were made available for phytostabilization (*Agrostis tenuis, cv Parys* for copper wastes, *Agrosas tnuis, cv Coginan* for acid lead and zinc wastes, and *Festuca rubra, cv Merlin* for calcareous lead and zinc wastes.[54] Laboratory studies have indicated that other plants such as Indian mustard also have the potential for effective phytostabilization of Pb and Cr(VI).[55,56] Furthermore, poplar trees are being studied for possible use in phytostabilization, as they may be able to form roots up to the maximum depth of contamination.

Advantages associated with this technology include the fact that the disposal of hazardous material or biomass is not required, soil removal is unnecessary, the application cost is low, and the degree of disruption to site activities may be less than with other more vigorous remedial technologies. The technique is very effective when rapid immobilization is needed to preserve ground and surface waters. The presence of plants also reduces soil erosion and decreases the amount of water available in the system. The main disadvantage of phytostabilization is that the contaminants remain in the soil, and so the future release of contaminants should be prevented. Therefore, long-term maintenance of the vegetation or verification that the vegetation will be self-sustaining should be secured.

14.4.2.6 Rhizofiltration

Rhizofiltration (also known as phytofiltration) is adsorption or precipitation onto plant roots or absorption into the roots of contaminants that are in solution surrounding the root zone. The contaminant may remain on the root, within the root, or be taken up and translocated into other portions of the plant, depending on the contaminant, its concentration, and the plant species.[41] Applications of rhizofiltration are currently at the pilot-scale stage. It is intended to be generally applicable to the treatment of large volumes of water with low contaminant concentrations (in the ppb range). It is to be used in the treatment of metals, radionuclides, or mixed wastes, but it is also suitable for ammunition wastes. Rhizofiltration is effective in areas where wetlands can be created and all of the contaminated water may be allowed to come into contact with the roots.

14.4.3 DESIGN CONSIDERATIONS

The design of a phytoremediation system is determined by several factors associated with the contaminants (type, concentration, and depth), the conditions at the site, the plants, the level of cleanup required and the available time. Extraction techniques have different design requirements than immobilization or degradation methods. Nevertheless, it is possible to specify a few design factors that are a part of most phytoremediation efforts.

14.4.3.1 Root System

Remediation with plants requires that the contaminants be in contact with the root zone of the plants. Therefore, root morphology and depth directly affect the depth of soil that can be remediated or the depth of groundwater that can be influenced. A fibrous root system such as that found in grasses has numerous fine roots spread throughout the soil and provides maximum contact with the soil because of the high surface area of the roots. A tap root system (such as in alfalfa) is dominated

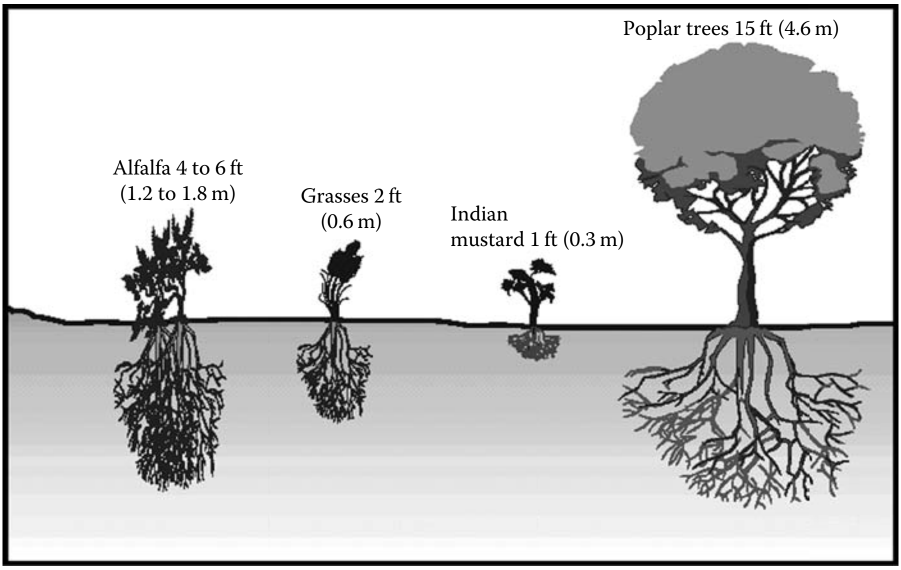


FIGURE 14.11 Root depths for different plants.

by one central root. Many hyperaccumulators have a tap root system, which limits root contact to relatively small volumes of soil. As shown in Figure 14.11, the effective root depth of plants varies by species and depends on soil and climate condition. The root depth ranges provided in the following represent maximum depths[57]:

1. *Legumes.* Alfalfa roots can extend down to about 9.1 m (30 ft), given the proper conditions.
2. *Grasses.* Some grass fibrous root systems can extend 2.4 to 3 m (8 to 10 ft) deep. The roots of major prairie grasses can extend to about 1.8 to 3 m (6 to 10 ft).
3. *Shrubs.* The roots of phreatophytic shrubs can extend to about 6 m (20 ft).
4. *Trees.* Phreatophyte roots will tend to extend deeper than other tree roots. Phreatophytic tree roots can reach as deep as 24 m (80 ft). Two examples are mesquite tap roots, which range from 12 to 30 m (40 to 100 ft), and river birch tap roots, which go to a depth of 27 to 30 m (90 to 100 ft).
5. *Other plants.* Indian mustard roots are generally about 15 to 22 cm (6 to 9 in.) deep.

These maximum depths are not likely to occur in most cases. The effective depth for phytoremediation using most nonwoody plant species is likely to be only 30 or 61 cm (1 or 2 ft). Most accumulators have root zones limited to the top foot of soil, which restricts the use of phytoextraction to shallow soils. The effective depth of tree roots is likely to be in the few tens of feet or less, with one optimistic estimate that trees will be useful for extraction of groundwater up to 9 m (30 ft) deep.[41,58]

14.4.3.2 Plant Growth Rate

The time required to clean up a site through phytoremediation may be longer than is acceptable for some redevelopment objectives. Phytoremediation is limited by the natural growth rate of plants and the length of the growing season. Several growing seasons may be required before phytoremediation systems become effective, and traditional methods may require a few weeks or months. Low removal rates may therefore prohibit the use of phytoremediation in cases where the time period available for cleanup is limited and is a key criterion in selecting a technology.[59] Growth rates can be defined differently for different forms of phytoremediation. For rhizodegradation, rhizofiltration, and phytostabilization, it is desirable to have fast growth in terms of root depth, density, volume, surface area, and lateral extension. For phytoextraction, a fast growth rate of aboveground plant mass is desirable.

A large root mass and large biomass are desired for an increased mass of accumulated contaminants, for greater transpiration of water, greater assimilation and metabolism of contaminants, or for production of a greater amount of exudates and enzymes. A fast growth rate will minimize the time required to reach a large biomass. For the phytoextraction of metals, the metals concentration in the biomass and the amount of biomass produced must both be considered. Metal hyperaccumulators are able to concentrate a very high level of some metals; however, their generally low biomass and slow growth rate means that the total mass of metals removed will tend to be low. A plant that extracts a lower concentration of metals, but that has a much greater biomass than many hyperaccumulators, is more desirable than the hyperaccumulator because the total mass of metals removed will be greater.[57]

The growth rate of a plant species will have a direct effect on its potential for use at a particular site. Fast-growing grasses will begin treating soil contamination more quickly than a tree, which must first establish deeper roots to treat target contaminants. As plants (particularly trees used in phytoremediation) mature their root structures deepen and their capacity to treat deeper levels of contamination improves. Phytoremediation can provide a number of benefits during the course of vegetation maturation. Plantings during initial stages can provide a cover that minimizes water infiltration. As the tree roots mature, phytoremediation processes take place to treat contaminants at increasing depths below the surface. Poplars, which have been widely used in phytoremediation applications, present high growth rates, varying between 2.7 and 4.6 m/yr (9 and 15 ft/yr).[57]

14.4.3.3 Plant Selection

Plant selection is probably one of the most important factors determining the success or failure of a phytotechnology project. Careful selection of the plant and plant variety is critical—first to ensure that the plant is appropriate for the climatic and soil conditions at the site, and second for the effectiveness of the phytoremediation. Once growing conditions at the site have been identified, the next goal of the plant selection process is to choose plants with appropriate characteristics for growth under site-specific conditions that also meet the objectives of the phytotechnology project. A screening test or knowledge from the literature of plant attributes will aid the design team in the selection of plants. Typical information needed for plant selection includes the species name (common and scientific), various tolerances (temperature, moisture, diseases, pests, etc.), growth habit (annual, perennial, biennial, evergreen vs. deciduous), climate zone, and general form (grass, leafy plant, shrub, tree, etc.). Another consideration in plant selection is the decision whether to use a monoculture or several plant species. In general, the use of a mixed variety of vegetation is preferred over monostands due to the following several advantages[46]:

1. Monostands can be susceptible to diseases that can destroy the entire phytotechnology system, while mixed stands may only lose one or two species.
2. Mixed stands support more diverse microbial communities (promoting potentially more complete rhizodegradation by further breaking down byproducts).
3. Synergistic effects such as nutrient cycling can be obtained in mixed stands.
4. Mixed stands have a more naturalized appearance.
5. Mixed stands promote biodiversity and potential habitat restoration qualities.

Plants are selected according to application needs and the contaminants concerned. For phytodegradation of organics, the design requirements are that vegetation is fast growing and hardy, easy to plant and maintain, utilizes a large quantity of water by evapotranspiration (if groundwater is an issue), and transforms the contaminants of concern to nontoxic or less toxic products. In temperate climates, phreatophytes (e.g., hybrid poplar, willow, cottonwood, aspen) are often selected because of their fast growth, deep rooting ability down to the surface of groundwater, large transpiration rates, and the fact that they are native throughout most of the U.S.[8] Indian mustard is a fast-growing accumulator plant with a relatively high biomass, which has the ability to take up and accumulate metals and radionuclides. Sunflower (*Helianthus annuus*) can accumulate metals and has about the same biomass as Indian mustard. Examples of metal hyperaccumulators that have been investigated include *Thlaspi caerulescens* (Alpine pennycress), but which is slow-growing and has a low biomass; *Thlaspi rotundifolium* spp. *cepaeifolium*, the only known hyperaccumulator of Pb; and other *Thlaspi* species that can hyperaccumulate cadmium, nickel, or zinc.[41]

Grasses are often planted in tandem with trees at sites with organic contaminants or even as the primary remediation method. They provide a tremendous amount of fine roots in the surface soil, which is effective at binding and transforming hydrophobic contaminants such as TPH, BTEX, and PAHs.[8] Grasses are often planted between rows of trees to provide for soil stabilization and protection against the wind-blown dust that can move contaminants off site. Some grasses, such as *Festuca ovina*, can take up metals but are not hyperaccumulators. Alfalfa has been investigated because of its deep root system, its ability to fix nitrogen, and the fact that there is a large knowledge base about this plant. These plants have been popular for research to date, but future screening studies will undoubtedly add many more candidates, some of which may prove to be much more effective for phytoremediation.

14.4.3.4 Treatability Studies

Treatability studies are recommended and may be required for all phytoremediation projects unless adequate site-specific information is available indicating a probable successful outcome. These studies may take the form of laboratory-scale germination tests, greenhouse-scale fate and transport studies and/or mass balances, or field-scale (up to 15 × 15 m) tests to examine site-specific survivability and treatment efficacy under existing site conditions.[8,46,57] Treatability tests should be carried out in real time, because plant growth cannot be accelerated and should continue for at least one growth cycle, including dormancy. Toxicity and transformation data are obtained in treatability studies. Regulators may require total mass balance information, which necessitates use of radiolabeled compounds in the laboratory-scale tests.

14.4.3.5 Plant Density and Patterns

Planting density depends on the application. For hybrid poplar trees, between 400 and 800 trees per hectare (1000 to 2000 trees per acre) are typically planted with a conventional tree planter at 30 to 46 cm (12 to 18 in.) depth or in trenched rows 0.30 to 1.8 m (1 to 6 ft) deep.[8] If a row conformation is used, the trees may be spaced with 0.6 m (2 ft) between trees and 3 m (10 ft) between rows. Several phreatophytes, such as willow and cottonwood, can be planted in a similar manner. Hardwood trees and evergreens may require a lower initial planting density. A high initial planting density assures a significant amount of evapotranspiration in the first year, which is normally desirable, but the trees will naturally thin themselves by competition to 240 to 320 trees per hectare (600 to 800 trees per acre) over the first six years. If desired, hybrid poplars can be harvested on a six-year rotation and sold for fuelwood or pulp and paper, and the trees will grow back from the cut-stump (coppicing trait). The dense, deep root system stays in place to sustain growth for the next year. The lifetime of hybrid poplars is on the order of 30 years, which is usually sufficient as the design life of the project. Grasses are usually drilled or broadcast for planting at contaminated sites. Biomass densities (above ground) of 200 to 600 g/m^2 are achieved by the second crop, with 1 to 3 crops per year depending on climate and water availability.[8]

14.4.3.6 Groundwater Capture and Transpiration

For the estimation of the contaminants' uptake rate and consequently the time required for the phytoremediation of a contaminated site, single mathematical models may be applied. In the following paragraphs, analysis as well as the examples given in *Groundwater Remediation Technologies Analysis Center Technology Evaluation Report on Phytoremediation*, by Schnoor, is presented without modification.[8]

A simple capture zone calculation[60] can be used to estimate whether the phytoremediation "pump" can be effective at entraining the plume of contaminants. Trees can be grouped for consideration as average withdrawal points. The goal of such a phytoremediation effort is to create a water table depression where contaminants will flow to the vegetation for uptake and treatment. Organic contaminants are not taken up at the same concentration as in the soil or groundwater; rather, there is a transpiration stream concentration factor (a fractional efficiency of uptake) that accounts for the partial uptake of the contaminant (due to membrane barriers at the root surface). The uptake rate is given by the following equation:

$$U = \text{TSCF} \times T \times C \tag{14.24}$$

where U = uptake rate of contaminant (mg/d), TSCF = transpiration stream concentration factor (dimensionless), T = transpiration rate of vegetation (L/d), and C = aqueous phase concentration in soil water or groundwater (mg/L).

If the plants do not take up the dissolved contaminant, the plume that emerges will be concentrated (i.e., the mass of contaminant in the plume will be the same, but the concentration remaining will actually be greater due to the reduction in water volume caused by the vegetation). This is a potential concern for phytoremediation of groundwater plumes or in created wetlands, where a relatively hydrophilic contaminant can be concentrated on the downstream side of the phytotechnology system.

A method for estimating the TSCF for equation 14.24 is given in Table 14.10. The root concentration factor is also defined in Table 14.10 as the ratio of the contaminant in the roots to the concentration dissolved in the soil water (μg/kg root per μg/L). This is important in estimating the mass of contaminant sorbed to roots in phytoremediation systems. The values of TSCF and RCF for metals depend on the metals' redox states and chemical speciation in soil and groundwater.

Mature phreatophyte trees (poplar, willow, cottonwood, aspen, ash, alder, eucalyptus, mesquite, bald cypress, birch, and river cedar) typically can transpire 3700 to 6167 m^3 (3 to 5 acre-ft) of water per year. This is equivalent to about 2 to 3.8 m^3 (600 to 1000 gal) of water per tree per year for a mature species planted at a density of 600 trees per hectare (1500 trees per acre). Transpiration rates in the first two years would be somewhat less, about 0.75 m^3 per tree per year (200 gal per tree per year), and hardwood trees would transpire about half the water of a phreatophyte. Two meters of water per year is a practical maximum for transpiration in a system with complete canopy coverage (a theoretical maximum would be 4 m/yr based on the solar energy supplied at latitude 40°N on a clear day).

If evapotranspiration of the system exceeds precipitation, it is possible to capture water that is moving vertically through soil. Areas that receive precipitation in the wintertime (the dormant season for deciduous trees) must be modeled to determine if the soil will be sufficiently dry to hold water for the next spring's growth period.

14.4.3.7 Contaminant Uptake Rate and Cleanup Time

From equation 14.24 it is possible to estimate the uptake rate of the contaminant(s). First-order kinetics can be assumed as an approximation for the time duration needed to achieve remediation goals. The uptake rate should be divided by the mass of contaminant remaining in the soil:

$$k = U/M_{\text{o}} \tag{14.25}$$

TABLE 14.10

Estimating the Transpiration Stream Concentration Factor (TSCF) and Root Concentration Factor (RCF) for Some Typical Contaminants (8)

Chemical	Log K_{ow}[a]	Solubility[a], $-\text{Log } C_w^{sat}$ @25°C (mol/L)	Henry's Constant[a] kH @25°C (dimensionless)	Vapor Pressure $-\text{Log } P_o$@ 25°C (atm)	TSCF[b]	RCF[c] (1/kg)
Benzene	2.13	1.64	0.2250	0.90	0.71	3.6
Toluene	2.69	2.25	0.2760	1.42	0.74	4.5
Ethylbenzene	3.15	2.80	0.3240	1.90	0.63	6.0
m-Xylene	3.20	2.77	0.2520	1.98	0.61	6.2
TCE	2.33	2.04	0.4370	1.01	0.74	3.9
Aniline	0.90	0.41	2.2×10^{-5}	2.89	0.26	3.1
Nitrobenzene	1.83	1.77	0.0025[d]	3.68	0.62	3.4
Phenol	1.45	0.20	$>1.0 \times 10^{-5}$	3.59	0.47	3.2
Pentachlorophenol	5.04	4.27	1.5×10^{-4}[d]	6.75[d]	0.07	54
Atrazine	2.69	3.81	1.0×10^{-7}[d]	9.40[d]	0.74	4.5
1,2,4-Trichlorobenzene	4.25	3.65	0.1130	3.21	0.21	19
RDX	0.87	4.57	—	—	0.25	3.1

[a] Physical chemical properties[61] unless otherwise noted.

[b] $\text{TSCF} = 0.75 \exp\{-[(\log K_{ow}-2.50)^2/2.4]\}$ (Ref. 62).

[c] $\text{RCF} = 3.0 + \exp(1.497 \log K_{ow}-3.615)$ (Ref. 62).

[d] *Source*: Schnoor, J.L., *Environmental Modeling—Fate and Transport of Pollutants in Water, Air, and Soil*, John Wiley & Sons, New York, 1996. With permission.

Vic, E.A. and Bardos, P., Remediation of Contaminated Land. Technology Implementation in Europe, Federal Environmental Agency, Austria. CLARINET Report, available at www.clarinet.at, 2002. With permission.

where k = the first-order rate constant for uptake (yr^{-1}), U = the contaminant uptake rate (kg/yr), And M_o = the initial mass of contaminant (kg). Then, an estimate for mass remaining at any time is expressed by Equation 14.26:

$$M = M_o e^{-kt} \tag{14.26}$$

where M = mass remaining (kg) and t = time (yr).

Solving for the time required to achieve cleanup of a known action level:

$$t = -(\ln M/M_o)/k \tag{14.27}$$

where t = time required for cleanup to action level (yr), M = mass allowed at action level (kg), and M_o = initial mass of contaminant (kg).

14.4.3.8 Examples

Equations 14.24 to 14.27 can be applied to most sites where soil cleanup regulations are known for metals or organic contaminants. Two examples follow, one for TCE treatment by phytotransformation and another for lead removal by phytoextraction, which demonstrate the use of the design equations.

Example 1: Organics

TCE residuals have been discovered in an unsaturated soil profile at a depth of 3 m. From lysimeter samples, the soil water concentration is approximately 100 mg/L. Long cuttings of hybrid poplar trees will be planted through the waste at a density of 600 trees per hectare (1500 trees per acre) for uptake and phytotransformation of the TCE waste. By the second or third year, the trees are expected to transpire 3700 m^3/yr (3 acre-ft/yr) of water or about 2.27 m^3/tree (600 gal/tree) per year. Estimate the time required for cleanup if the mass of TCE per hectare is estimated to be 400 kg/hectare (1000 kg/acre), and the cleanup standard has been set at 40 kg/hectare (100 kg/acre) (90% cleanup).

The uptake rate of TCE can be determined by Equation 14.24:

$$U = \text{TSCF} \times T \times C,$$

where TSCF = 0.74 (from Table 14.10), $T = (2.27\ \text{m}^3/\text{tree-yr})(600\ \text{tree/hectare})(1000\ \text{L/m}^3) = 1.362 \times 10^6$ L/hectare-yr, and $C = 100$ mg/L (given). Therefore,

$$\begin{aligned} U &= \text{TSCF} \times T \times C = 0.74 \times (1.362 \times 10^6\ \text{L/hectare-yr}) \times (100\ \text{mg/L}) \\ &= 1.00788 \times 10^8\ \text{mg/hectare-yr} = 100.788\ \text{kg/hectare-yr} \end{aligned}$$

The coefficient k can be determined from Equation 14.25:

$$k = U/M_o = (100.788\ \text{kg/hectare-yr})/(400\ \text{kg/hectare}) = 0.259\ \text{yr}^{-1}$$

Therefore, the time required to achieve the remediation goal is calculated from Equation 14.27:

$$t = -(\ln M/M_o)/k = -(\ln 40/400)/(0.259\ \text{yr}^{-1}) = 8.9\ \text{yr}$$

Most of the TCE that is taken up by the poplars is expected to volatilize slowly to the atmosphere. A portion will be metabolized by the leaves and woody tissue of the trees.

Example 2: Metals

Lead at a lightly contaminated brownfield site has a concentration in soil of 600 mg/kg to a depth of 1 ft. The cleanup standard has been set at 400 mg/kg. Indian mustard, *Brassica juncea*, will be planted, fertilized, and harvested three times each year for phytoextraction. Using small doses of EDTA, it is possible to achieve concentrations in the plant of 5000 mg/kg (dry weight basis), and harvestable densities of 2.72 t (3 short tons) dry matter per crop. Estimate the time required for cleanup:

$$\begin{aligned} U &= \text{uptake rate} = (5000\ \text{mg/kg}) \times (3 \times 2.72\ \text{t/hectare-yr}) \times (1000\ \text{kg/t}) \\ &= 4.09 \times 10^7\ \text{mg/hectare-yr} = 40.9\ \text{kg/hectare-yr} \\ M_o &= \text{mass of Pb in soil at a dry bulk density of 1.5 kg/L} \\ M_o &= (600\ \text{mg/kg}) \times (1.5\ \text{kg/L}) \times (1233\ \text{m}^3) \times (1000\ \text{L/m}^3) \times (10^{-6}\ \text{mg/kg}) \\ M_o &= 1110\ \text{kg/hectare (initial mass in soil)} \\ M &= 740\ \text{kg/hectare (cleanup standard of 400 mg/kg)} \end{aligned}$$

Zero-order kinetics is assumed (constant rate of Pb uptake each year), because EDTA will make the lead continue to be bioavailable to the sunflowers, so

$$t = (M - M_o)/U = 9.0\ \text{yr}$$

The time to cleanup may actually be somewhat less than 9 years if Pb migrates down in the soil profile with the addition of EDTA, or if tillage practices serve to "smooth out" the hot spots. Regulatory cleanup levels are usually based on a limit that cannot be exceeded, such as 400 mg/kg, and soil concentrations would need to be analyzed to ensure compliance at the end of each year.

14.5 SOIL WASHING

14.5.1 General Description

Soil washing is a physical and/or chemical separation technology in which excavated soil is washed with fluids to remove contaminants. It is considered feasible for the treatment of a wide range of inorganic and organic contaminants including heavy metals, radionuclides, cyanides, polynuclear aromatic compounds, pesticides, and PCBs. Soil washing removes contaminants from soils by (1) concentrating them into a smaller volume of soil through mineral-processing techniques and (2) by dissolving or suspending them in the wash solution.

In the first technique, clean and contaminated soil particles are separated by taking advantage of their physical properties, such as selective adsorption of contaminants onto fine clay particles of soil,[64,65] variations in specific gravity, magnetic,[66] and surface properties of clean and contaminated soil particles.[67,68,84] Research studies have shown that a large percentage of soil contamination, especially organic, is sometimes associated with, or bound to, very small (silt and clay) soil particles. In these situations, a physical separation of the large soil particles (sand and gravel) from the silt, clay, and humic material effectively concentrates the contaminants in the fine fraction.

The second soil-washing technique involves chemical treatment using water or chemical agents and aims at the selective leaching of contaminants from soil particles, or the total dissolution of contaminated particles. Chemical treatment is mainly applied for the removal of heavy metals using leaching reagents such as inorganic acids (hydrochloric acid, sulfuric acid, $\text{pH} < 2$), organic acids (acetic, lactic, citric acid, $\text{pH} \geq 4$), complexing reagents such as EDTA, and nitrilotriacetic acid (NTA), and combinations of these reagents.[69–72] In the case of organic contaminants the use of surfactants (surface active agents) or co-solvents may be considered in order to increase their solubility in aqueous solutions.

The procedure of soil washing involves three main operations:

1. Intensive mixing of contaminated soil with washing fluid
2. Separation of clean soil particles
3. Treatment of the supernatant solution containing the dissolved or suspended contaminants[73–76]

A general flow diagram of a soil-washing treatment is shown in Figure 14.12. Initially, the contaminated soil is sieved to remove large objects such as pieces of wood, plant roots, stones, etc. The maximum size of particles allowed in the feedstock varies with the equipment used, ranging from 10 to 50 mm.[77]

The main soil-washing stage involves mixing, washing, rinsing, and size separation steps. In the soil-washing stage, two main mechanisms are involved. The first is the dispersion of fine contaminated particles, which either occur as aggregates or cover the surface of soil particles. For better dispersion, sodium hydroxide and surface active reagents such as lye are used. The second mechanism is the dissolution of contaminants in the aqueous solution; this can be enhanced by the addition of appropriate chemical reagents such as inorganic or organic acids, complexing agents, and surfactants or co-solvents, depending on the types of contaminants. Intensive contact between the soil grains and the wash fluid causes the soil contaminants to be dissolved and dispersed into the water. Energy is introduced into the mixture by high-pressure water jets, vibration devices, and other means.

After mixing for an appropriate time, clean soil particles and wash water containing the dissolved and suspended contaminants are separated. Separation techniques in soil-washing systems are similar to those applied in the mineral-processing industry.[78] The most common separation techniques are as follows:

1. *Hydrocyclones.* Particle separation in hydrocyclones uses the centrifugal force as the means of separation. The slurry, consisting of clean soil and contaminated particles, is separated

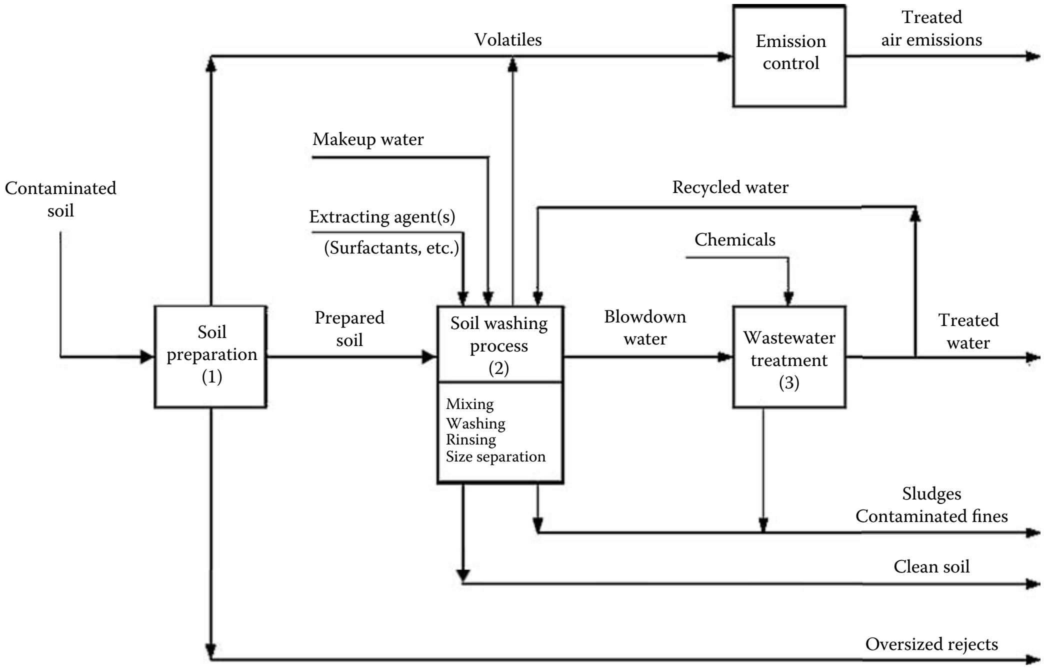


FIGURE 14.12 Typical soil-wash flow diagram for the treatment of contaminated soils.

into an underflow stream (where coarse particles are collected) and an overflow stream (containing the fine particles). To make operation more effective, multiple hydrocyclones may be placed in series. Selective separation is possible for particles with grain sizes greater than 10 to 20 μm.

2. *Fluidized bed separation system.* This separation system is based on the difference in gravimetric settling velocity of fine contaminated particles and coarse clean soil particles. The pulp containing the contaminated and clean soil particles is fed from the upper part of a vertical column countercurrent to the leaching solution. The rate of solution injection inside the column is adjusted so that sinking of the coarse soil particles is possible. The wash fluid containing the contaminated particles is removed from the upper part of the column. With this system, a selective separation of particles with grain size greater than 50 μm is achieved.
3. *Gravimetric separation systems.* These include jigs, shaking tables, Humphrey-type spiral concentrators, and so on.
4. *Flotation.* In many cases, contaminants adsorbed on the surface of clay particles, or contaminants occurring in soil as discriminate particles, have different surface properties to clean soil particles. By adding special chemical substances, the formation of a hydrophobic surface on the contaminated particles is possible. Pulp aeration results in the attachment of hydrophobic contaminated particles to the surface of the small bubbles that are formed. In this way, selective flotation of these particles is achieved. Contrary to the gravimetric separation methods, flotation offers the possibility to separate contaminated and noncontaminated particles of the same grain size and density but with different surface properties.

After the separation stage, the coarse soil fraction is rinsed with clean water to remove residual contaminants and any fine soil particles that may adhere to the coarse particles. Soil washing is not usually a stand-alone technology. Typically, both the fine soil fraction (silts and clays) recovered after washing and the spent wash water are subject to further specific treatment and disposal techniques, as appropriate, to complete cleanup. For the stripping of the washing solution, which contains dissolved contaminants and fine contaminated soil particles, a large number of physical and chemical systems are available. Dissolved contaminants can be removed by applying chemical methods such as neutralization, precipitation, ion exchange, and so on, whereas suspended particles originating either from the contaminated soil or produced during solution treatment can be removed by applying physical techniques such as flocculation, thickening, and filtering. Part or all of the purified washing solution is recycled back to the soil-washing stage.

The sludge produced from the wash water stripping stage can be dewatered with a centrifuge, filter press, or sieve belt press. The amount of sludge is a determinant factor for the cost-effectiveness of the soil-washing technique. This sludge mainly consists of clay soil particles. Although the fraction of contaminated compounds is relatively small, total contaminants concentration is rather high, so the sludge is usually characterized as a hazardous waste. Its final management may involve either disposal in a hazardous waste landfill or further treatment using thermal as well as stabilization techniques.

The soil-washing method already described may generate sidestreams, such as air emissions, spent solvents, and exhausted resins, which must also be properly managed.

14.5.2 DESIGN CONSIDERATIONS

The main parameters that affect the cost-effectiveness of soil washing include the physicochemical parameters of the soil (grain size distribution, cation exchange capacity, percentage of silt, clay, or organic matter), and the type and concentration of contaminants.

Soils with relatively high percentages of sand and gravel respond better to soil washing than fine-grained soils. High percentages of clay and silt (i.e., fine particles with size <0.25 mm) reduce the efficiency of contaminant removal. Practically, soil washing is most appropriate for soils that contain at least 50% sand or gravel, i.e., coastal sandy soils and soils with glacial deposits. Soils rich in clay and silt tend to be poor candidates for soil washing. Modifications of soil washing with a view to being applied to predominantly silt and clay soils have been investigated at the laboratory scale, but it is not known whether they have yet been applied on an industrial scale. Figure 14.13 presents different difficulty levels in the application of soil-washing techniques for different particle size distributions of contaminated soil according to the evaluation of U.S. EPA.[77]

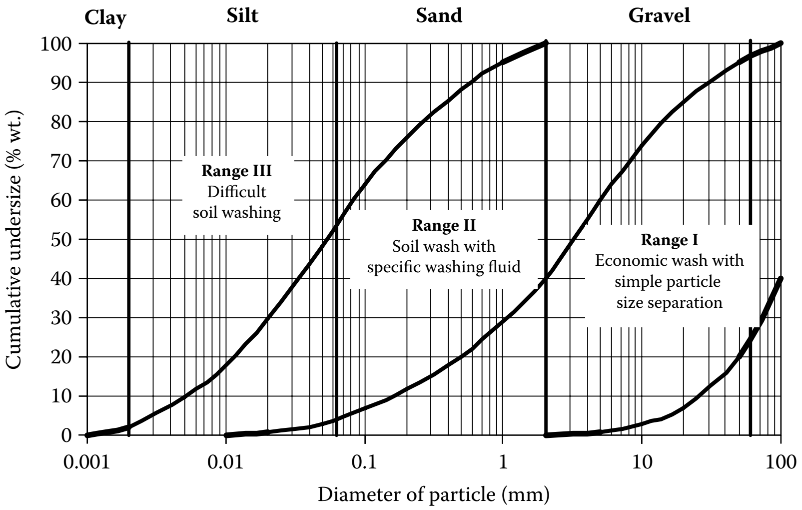


FIGURE 14.13 Ranges of soil-washing difficulty, based on the particle size distribution in the soil.

Cation exchange capacity (CEC) measures the tendency of the soil to exchange weakly held cations in the soil particles for cations in the wash solution. Soils with relatively low CEC values (<50 to 100 meq/kg) respond better to soil washing than soils with higher CEC values. Furthermore, high humic content in the soil makes separation of contaminants very difficult. Humus consists of decomposed plant and animal residues and offers binding sites for the accumulation of both organics and metals. Early characterization of these parameters and their variability throughout the site provides valuable information for the initial screening of soil washing as an alternative treatment technology.

Chemical and physical properties of the contaminant should also be investigated. Solubility in water (or other washing fluids) is one of the most important physical characteristics. Hydrophobic contaminants can be difficult to separate from the soil particles and into the aqueous washing fluid. Reactivity with wash fluids may, in some cases, be another important characteristic to consider. Other contaminant characteristics such as volatility and density may be important for the design of remedy screening studies and related residuals treatment systems. Speciation is important in metal-contaminated sites.

Complex mixtures of contaminants in the soil, such as a mixture of metals, nonvolatile organics, semivolatile organics, and so on, make it difficult to formulate a single suitable washing fluid that will remove all the different types of contaminants from the soil. Sequential washing steps, using different additives, may be needed. In fact, each type of contaminated soil requires a special treatment procedure, which is determined through laboratory or pre-industrial tests, so that system modifications and optimum operative conditions are specified.

Frequent changes in contaminant type and concentration in the feed soil can disrupt the efficiency of the soil-washing process. To accommodate changes in the chemical or physical composition of the feed soil, modifications to the wash fluid formulation and the operating settings may be required. Alternatively, additional feedstock preparation steps, such as blending soils to provide a consistent feedstock may be appropriate.[77,83]

Additives such as surfactants may be required to improve removal efficiencies. However, larger volumes of washing fluid may be needed when additives are used. Chelating agents, surfactants, solvents, and other additives are often difficult and expensive to recover from the spent washing fluid and recycle in the soil-washing process. The presence of additives may make the spent washing fluid difficult to treat by conventional treatment processes such as settling, chemical precipitation, or activated carbon. Furthermore, the presence of additives in the contaminated soil and treatment sludge residuals may increase difficulty in disposing of these residuals.

14.6 *IN SITU* SOIL FLUSHING

14.6.1 General Description

In situ flushing is the injection or infiltration of an aqueous solution into a contaminated zone, followed by downgradient extraction of groundwater and elutriate (flushing solution mixed with the contaminants) and aboveground treatment and discharge or reinjection. A schematic representation of *in situ* soil flushing is given in Figure 14.14. The goal of *in situ* flushing is to enhance conventional pump and treat methods of remediation by enhancing the solubility or mobility of contaminants, thus accelerating the remediation process.

Introduction of the flushing solution may occur within the vadose zone, the saturated zone, or both. Flushing solutions may consist of plain water, or surfactants, co-solvents, acids, bases, oxidants, chelants, and solvents. The infiltrating flushing solution percolates through the soil and soluble compounds present in the soil are dissolved. The elutriate is pumped from the bottom of the contaminated zone into a water treatment system to remove pollutants. The process is carried out until the residual concentrations of contaminants in the soil satisfy given limits.

Any variety of configurations of injection wells, horizontal wells, trenches, infiltration galleries, aboveground sprayers or leach fields, and extraction wells, open ditches, or subsurface collection

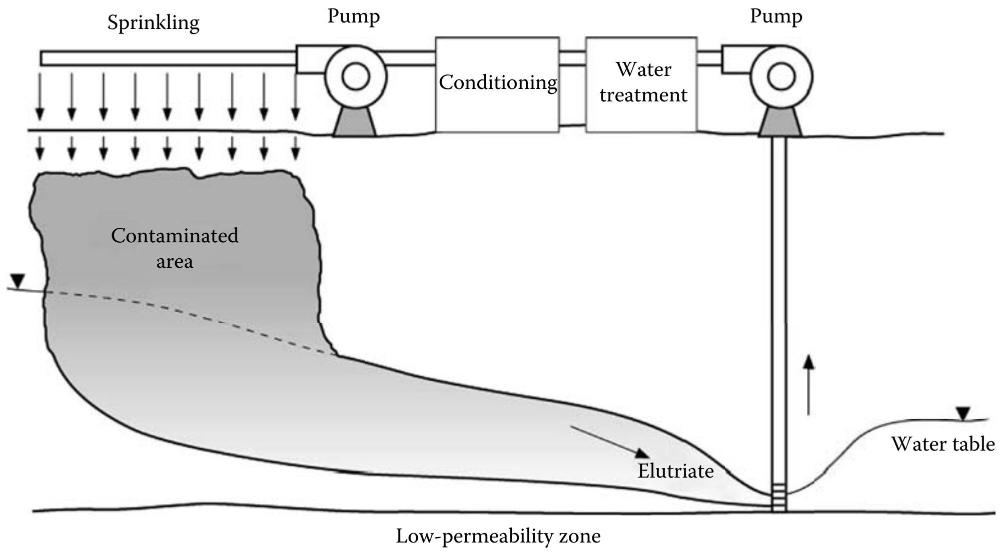


FIGURE 14.14 Typical soil-flushing system.

drains or trenches can be used to put the flushing solution in contact with the contaminated zone and collect elutriate.[76,79–81]

The *in situ* flashing technique is applicable to a variety of organic and inorganic contaminants. Organics, such as nonaqueous phase liquid (NAPL), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), halogenated pesticides, dioxins/furans, and corrosives, and inorganics including volatile and nonvolatile metals, cyanides, and radioactive contaminants may potentially be removed using *in situ* flushing. Removal efficiencies of contaminants depend on the contaminant as well as the soil type. Halogenated volatiles, nonhalogenated semivolatiles and nonvolatile metals are amongst the classes of chemical compounds treated successfully by *in situ* flashing.[80]

14.6.2 DESIGN CONSIDERATIONS

There are a number of critical parameters to be considered for the application of *in situ* soil flushing, including the hydrogeological conditions of the contaminated site, the type and properties of contaminants, the properties of the additives, and the treatability of the flushing solution.[76,80]

14.6.2.1 Site Conditions

Regarding the hydraulic properties of contaminated soil, high permeability is a prerequisite for the application of this method. Hydraulic conductivity values should ideally be greater than 1.0×10^{-3} cm/s to allow flushing solutions to pass through the geologic matrix in a reasonable period of time. This means that contaminated sandy soils are susceptible to *in situ* flushing. Less permeable materials, with hydraulic conductivity values ranging from 1×10^{-5} to 1×10^{-3} cm/s may also be considered for *in situ* flushing. The presence of impermeable clay layers does not exclude the application of *in situ* soil flushing providing that special techniques for the effective injection of the flashing agent through the impermeable layer are applied. It is also important to ensure the percolation of the flushing agent through the entire area of contamination. Therefore, as well as vertical variability, lateral variability of permeability should also be taken into account. Hydraulic conductivity should be measured at several locations within the potential treatment zone, and the total number of measurements should be consistent with the size of the potential treatment area and the potential for heterogeneity.

Containment of the flushed contaminants and spent flushing solutions is essential to successful application of *in situ* flushing. This happens when the treatment zone is bounded geologically by materials with relative low hydraulic conductivity. Depth to the contaminated zone is a limiting factor because of the higher injection and extraction costs that are required compared with more shallow contaminated zones. Contaminants can be easily removed when the flushing solution follows the same channels as the pollutant. Also, possible mechanical disturbance of the surface layer of the contaminated area may render the contaminants inaccessible.

14.6.2.2 Flushing Solution

Flushing with plain water is effective only in cases where contaminants are soluble inorganic salts or hydrophilic organics, i.e., those presenting log K_{ow} values <1, such as lower molecular weight alcohols, phenols, and carboxylic acids. For medium- or low-solubility contaminants, additives should be introduced into the flushing solution to enhance mobilization of the contaminants. Surfactants such as detergents or emulsifiers may be used for low-solubility (hydrophobic) organics, such as chlorinated pesticides, PCBs, SVOCs (chlorinated benzenes and PAHs), petroleum products, aromatic solvents (BTEX), and chlorinated solvents (such as TCE). Co-solvents consisting of reagents such as alcohol may assist in enhancing the solubility of hydrophobic contaminants.[80]

The application of the *in situ* soil flushing technique for the removal of heavy metals is possible only when their solubility in the leaching solution is relatively high. It is possible to increase heavy metals extraction rates by adding appropriate chemical reagents that favor desorption or dissolution of these metals. The following reagents have been evaluated at the laboratory scale as additives to flushing solutions: inorganic and organic acids, sodium hydroxide, complexing reagents such as EDTA and NTA, chloride solutions, as well as oxidative or reductive media.[70–72,82]

14.6.2.3 Injection and Extraction Systems

The selection of a soil flushing solution delivery technique depends mainly on the hydraulic properties of the treatment zone, which can generally be classified as gravity-driven and pressure-driven. In gravity-driven delivery systems, sprinklers, trenches, or infiltration galleries are used, and the flushing solution infiltrates into the treatment zone as a result of natural hydraulic gradients. In pressure-driven delivery systems, the flushing solution is injected into the treatment zone through vertical or horizontal injection wells.

NOMENCLATURE

A_{contam}	Surface area corresponding to the contaminated zone (m^2)
C_a	Vapor concentration in pore air (mg/L)
$C_{a,equil}$	Concentration calculated from the vapor pressure data (mg/L)
C_{or}	Concentration of the contaminant in the organic phase (mg/L)
C_s	Adsorbed concentration of contaminant in the soil particle (mg/kg)
C_t	Total quantity of contaminant per unit soil volume (mg/L)
C_w	Dissolved concentration in pore water (mg/L)
C_w^o	Water solubility (mg/L)
f_{oc}	Fraction of organic carbon in soil
g	Gravity acceleration constant (981 cm/s^2)
H	Thickness of the vadose zone (m)
K	Intrinsic permeability of soil (cm^2)
k_a	Air permeability (cm/s)

k	First-order rate constant for contaminant uptake (yr^{-1})
K_H	Henry's constant (dimensionless)
K_oc	Organic carbon partitioning coefficient (L/kg)
k_w	Hydraulic conductivity (cm/s)
m	Mass fraction of contaminant in NAPL mixture
M	Mass of contaminant remaining (kg)
M_o	Initial mass of contaminant (kg)
M_final	Residual acceptable quantity according to the cleanup objectives (t)
M_rem	Amount of contaminant that must be removed from the soil (t)
M_spill	Initial total amount of spill (t)
MW	Molecular weight (g/mol)
N_wells	Number of extraction wells
P_atm	Ambient atmospheric pressure (atm)
P^o	Vapor pressure (mmHg, atm)
P_I	Pressure in the subsurface at a distance corresponding to the radius of influence R_I of the SVE well (atm)
P_r	Pressure in the subsurface at a radial distance r from the SVE well (atm)
P_w	Pressure in the SVE well (atm)
Q_w	Volumetric flow rate (m^3/min)
Q_w^*	Volumetric flow rate in standard conditions (m^3/min)
r	Radial distance from SVE well (m)
R	Ideal Gas Law constant (L·atm/mol·K)
R_I	Radius of influence of SVE well (m)
R_rem	Contaminants removal rate (g/min)
R_w	Radius of SVE well
T	Absolute temperature (K)
T_clean	Required cleanup time (min)
TSCF	Transpiration stream concentration factor (dimensionless)
u	Air velocity (m/s)
u_r	Air velocity in the radial r direction (m/s)
u_w	Air velocity at the wellbore (m/s)
U	Uptake rate of contaminant (mg/d)
X_i	Mol fraction of constituent i in the NAPL mixture

GREEK

γ_i	Activity coefficient of contaminant i in the NAPL mixture
η	Removal effectiveness factor
θ_a	Pore volume occupied by the gas phase (L/L)
θ_or	Pore volume occupied by NAPL (L/L)
θ_t	Total porosity of the soil (L/L)
θ_w	Pore volume occupied by water (L/L)
λ	Molar heat of vaporization (L·atm/mol)
μ	Viscosity (g/cm·s)
μ_a	Air viscosity (g/cm·s)
μ_w	Water viscosity (g/cm·s)
ρ	Density (kg/L)
ρ_a	Air density (kg/L)
ρ_b	Soil bulk density (kg/L)
ρ_or	Density of the NAPL mixture (kg/L)
ρ_w	Water density (kg/L)

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15 Leachate Treatment Using Bioremediation

Azni Idris, Katayon Saed, and Yung-Tse Hung

CONTENTS

15.1 INTRODUCTION

More than 90% of municipal solid waste is directly disposed of on land, the vast majority of it in an unsatisfactory manner. Open and burning dumps are common in many developing countries; these contribute to water and air pollution and provide food and breeding grounds for birds, rats, insects, and other carriers of disease. The presence of these dumps often reduces the property value of nearby land and residences.

Sanitary landfilling is an acceptable and recommended method for ultimately disposing of solid wastes. This method has sometimes been confused with waste disposal on open and burning dump sites, but this is a misconception. The sanitary landfill is an engineered landfill that requires sound and detailed planning and specification, careful construction, and efficient operation. In essence, modern landfilling involves spreading the wastes in thin layers, compacting them to the smallest practical volume, and covering them with daily earth cover in a manner that minimizes adverse environmental pollution.

The sanitary landfill, the most acceptable alternative to the present poor practices of land disposal, involves the long-term planning and application of sound engineering principles and construction techniques. By definition, no burning of solid waste will ever occur at a sanitary landfill. A sanitary landfill is not only an acceptable and economic method of solid waste disposal, it is also an excellent way to make otherwise unsuitable or marginal land valuable.[1]

All landfills produce a liquid stream called leachate, which is a highly complex and polluted wastewater. Leachate pollution is a concern for many local authorities as it directly degrades river water quality. Many researchers continue to search for ways to treat leachate effectively using different biological processes. To secure long-term dewatering of landfills and reduce the increasing treatment costs, it is therefore necessary to control leachate quantity and quality. This is often difficult, as increasing water quality standards make the requirements on leachate treatment ever more stringent.

Treatment procedures must consider the highly varying flow and complex composition of the leachate; this often results in special operational problems. The following chapters give an overview of leachate generation and the development of leachate control and treatment applicable to many landfills.

15.2 SANITARY LANDFILL

A sanitary landfill is defined as a land disposal site that applies an engineered method of disposing of solid wastes on land in a manner that minimizes environmental hazards by spreading the solid wastes to the smallest practical volume, and applying and compacting cover material at the end of each day.[2]

Landfills are the physical facilities used for the ultimate disposal of residual solid wastes in the ground. In the past, the term sanitary landfill was used to denote a landfill in which the wastes were placed in the landfill and then covered at the end of daily operation. Today, sanitary landfill refers to an engineered facility for the disposal of municipal solid waste (MSW), designed and operated to minimize public health and environmental impact.

Solid wastes deposited in a landfill undergo slow degradation to produce residual solid, liquid, and gaseous products. Ferrous and other metals are oxidized and organic and inorganic wastes are utilized by microorganisms through aerobic and anaerobic processes. Organic acids, which are produced as a result of microbial degradation, increase chemical activity within the fill. Food wastes degrade quite readily, but other materials, such as plastics, rubber, glass, and some demolition wastes, are highly resistant to decomposition.

The degree of degradation of organic waste in landfills is very much dependent on the organic content of the waste. Wastes in Asian countries are reported to have a larger organic fraction, which leads to more problems in leachate generation. Waste data from Indonesia and China show that the organic fraction comprised 70.2% and 67.3%, respectively.[3]

Landfill methods are considered the most economical and environmentally acceptable way of disposing of solid wastes throughout the world. Even with the implementation of waste reduction, recycling, and transformation technologies, disposal of residual solid waste in landfill will still remain an important component of an integrated solid waste management strategy.[4]

In engineering terms, a sanitary landfill is also sometimes identified as a bioreactor due to the presence of anaerobic activities in the wastes. As such, landfilling sites need the incoming waste stream top be monitored, as well as placement and compaction of the waste, and installation of landfill environmental monitoring and control facilities. Gas vent and leachate collection pipes are important features of a modern landfill.

15.3 LEACHATE

The harmful liquid that collects at the bottom of a landfill is known as leachate. The generation of leachate is a result of uncontrolled runoff, and percolation of precipitation and irrigation water into the landfill. Leachate can also include the moisture content initially contained in the waste, as well as infiltrating groundwater. Leachate contains a variety of chemical constituents derived from the solubilization of the materials deposited in the landfill and from the products of the chemical and biochemical reactions occurring within the landfill under the anaerobic conditions.

An estimation of leachate generation in a landfill can be carried out by calculating the infiltration through a landfill cover using a water budget model such as the Hydrologic Evaluation of Landfill Performance (HELP).[5] The model uses conservation of mass to predict water movement, which enables the volumetric flux of water infiltrating into the waste to be calculated on a time-varying basis.

The generated leachate can cause significant environmental damage, becoming a major pollution hazard when it comes into contact with the surrounding soil, ground, or surface waters. One such problem is caused by infiltrating rainwater and the subsequent movement of liquid or leachate out of the fill into the surrounding soil. This leachate often contains a high concentration of organic matter and inorganic ions, including ammoniacal nitrogen and heavy metals. Therefore, in order to avoid environmental damage, landfill leachate must be collected and appropriately treated before being discharged into any water body.

15.4 COMPOSITION AND CHARACTERISTICS OF LEACHATE

Leachate tends to percolate downward through solid waste, continuing to extract dissolved or suspended materials. In most landfills, leachate seeps through the landfill from external sources, such as surface drainage, rainfall, groundwater, and water from underground springs, as well as from the liquid produced from the decomposition of the wastes, if any.[3]

Many factors influence the production and composition of leachate. One major factor is the climate of the landfill. For example, where the climate is prone to higher levels of precipitation, there will be more water entering the landfill and therefore more leachate generated. Another factor is the site topography of the landfill, which influences the runoff patterns and again the water balance within the site.

The composition of leachate is important in determining its potential effects on the quality of nearby surface water and groundwater. Contaminants carried in leachate are dependent on solid waste composition and on the simultaneously occurring physical, chemical, and biological activities within the landfill. The quantity of contaminants in leachate from a completed landfill where no more waste is being disposed of can be expected to decrease with time, but it will take several years to stabilize.

15.4.1 Leachate of Different Age

The decomposition of solid urban waste in landfills is essentially a result of microbiological processes and, therefore, the production of biogas and leachate are both directly related to the activity of microorganisms. It has been demonstrated that large variations in leachate quality exist for different landfills, but also at different locations within the same landfill.[6]

New landfills generate more organic pollutants than older landfills. The BOD : COD (biochemical oxygen demand : chemical oxygen demand) ratio in young leachate is typically in the range of 0.5 to 0.7, which indicates higher biodegradability than that of mature landfills, which produce leachate with a BOD : COD ratio of less than 0.4.

15.4.2 Leachate in Different Countries

It is expected that leachate characteristics will vary by country. This is because the soil under a landfill site, the composition of disposed waste, the climate, sampling and landfill management vary among countries.[7,8]

15.5 LEACHATE TREATMENT

Many landfills pollute water bodies by discharging untreated leachate. When leachate percolates through the ground, it entrains landfill components such as decaying organic matter, microorganisms, metals, and inorganic compounds into the underlying groundwater, causing serious contamination.

Landfill leachates are commonly classified as a high-strength wastewater containing dissolved and entrained landfill components.[9] Freshly produced landfill leachates are characterized by low pH values, high BOD_5 and COD values, as well as by the presence of several other toxic/hazardous compounds.[10] Several treatment options have been utilized for leachate treatment, with varying degrees of efficiency. The main applicable methods are biological, chemical, membrane separation, and thermal treatment processes.[11]

Physico-chemical processes are generally considered to incur high operating costs and sometimes lower effectiveness. A biological process is normally preferred, such as a conventional activated sludge process, which has been proven to be effective for the removal of organic carbon and nutrient content. Nevertheless, the problem of poor sludge settleability has usually been encountered, as well as the need for longer aeration times, for settling tanks of larger volume, and for total biomass recycling.

Some landfills practice leachate recycling in the fill area, where leachate percolates through the waste cell and undergoes further degradation. The treatment process or processes selected will depend to a large extent on the contaminants to be removed.[4]

Biological processes have been increasingly used in the treatment of leachate in combination with physical and chemical processes. Selected microorganisms are introduced in the aerobic treatment to achieve a better process efficiency. However, because of the variation in leachate composition from site to site, the remedial process train will generally be tailored to the site and consist of several unit operations. The following section discusses applications of bioremediation processes to landfill leachates. It is important to remember that characterization of leachate plumes through groundwater modeling, analysis of leachate physical and chemical characteristics, and development of leachate recovery systems are all important in selecting a leachate treatment system.[12]

15.6 BIOREMEDIATION METHODS

Bioremediation is defined as the use of microorganisms or microbial processes to degrade environmental contaminants. Bioremediation has numerous applications, including cleanup of groundwater, soils, lagoons, sludge, and process waste streams.

In general terms, bioremediation involves multiphase but heterogeneous environments, such as soils in which the contaminant is present in association with the soil particles, dissolved in soil liquids, and in the soil atmosphere. Because of these complexities, successful bioremediation depends on an interdisciplinary approach involving microbiology, biochemistry, and engineering.

For leachate treatment, the bioremediation method may be carried out either on or off site. Both methods have their advantages and disadvantages, depending on the site condition. Two factors favor the treatment of leachates on site: the expense of off-site transportation and the reluctance of communities nationwide to permit transportation routes or treatment facilities within their jurisdictions. The desirability of on-site leachate treatment should encourage the development of small-scale technology requiring low capital investment. Biological processes are well suited to on-site leachate treatment for the removal of organic compounds.[9]

15.6.1 *In Situ* and *Ex Situ* Methods

Depending on the situation, a bioremediation method can be either *ex situ* or *in situ*. *Ex situ* treatments are treatments that involve the physical removal of the contaminated material in order to undergo the treatment process. *In situ* techniques involve treatment of the contaminated material in place. Examples of *in situ* and *ex situ* bioremediation are listed in the following:

1. *Land farming.* This is a solid-phase treatment system for contaminated soils; it may be carried out *in situ* or *ex situ*.
2. *Bioreactors.* Biodegradation is carried out in a container or reactor; it may be used to treat liquids or slurries.
3. *Composting.* This is an aerobic, thermophilic treatment process in which contaminated material is mixed with a bulking agent; it can be carried out using static piles or aerated piles.
4. *Bioventing.* This is a method of treating contaminated soils by drawing air or oxygen through the soil to stimulate microbial activity.
5. *Biofilters.* Microbial stripping columns are used to treat air or liquid emissions.
6. *Bioaugmentation.* Bacterial cultures are added to a contaminated medium; this is frequently used in both *in situ* and *ex situ* systems.
7. *Biostimulation.* Indigenous microbial populations in soils or groundwater are stimulated by providing the necessary nutrients.
8. *Intrinsic bioremediation.* This is the unassisted bioremediation of the contaminant; the only process carried out is regular monitoring.

15.6.2 ADVANTAGES AND DISADVANTAGES OF BIOREMEDIATION

Successful bioremediation requires microbes and suitable environmental factors for degradation to occur. The most suitable microbes are bacteria or fungi that have the physiological and metabolic capabilities to degrade the pollutants.

Bioremediation offers several advantages over conventional methods of waste treatment such as landfilling or incineration. Bioremediation can be done on site, it is often less expensive, involves minimal site disruption, eliminates waste permanently, eliminates long-term liability, has greater public acceptance with regulatory encouragement, and can be coupled with other physical or chemical treatment methods.

Bioremediation also has its limitations. Some chemicals are not amenable to biodegradation, for instance, heavy metals, radionuclides, and some chlorinated compounds. In some cases, the microbial metabolism of the contaminants may produce toxic metabolites. Bioremediation is a scientifically intensive procedure that must be tailored to site-specific conditions, and usually requires treatability studies to be conducted on a small scale before the actual cleanup of a site.[13] The treatability procedure is important, as it establishes the extent of degradation and evaluates the potential use of a selected microorganism for bioremediation. A precise estimate on vessel size or area involved, speed of reaction, and economics can therefore be determined at the laboratory stage.

15.6.3 PHYSIOLOGY OF BIODEGRADATIVE MICROBES

Bioremediation is based on the activities of aerobic or anaerobic heterotrophic microorganisms. Microbial activity is affected by a number of physicochemical environmental parameters. Factors that directly affect bioremediation are energy sources (electron donors), electron acceptors, nutrients, pH, temperature, and inhibitory substrates or metabolites. One of the primary distinctions between surface soils, subsurface soils, and groundwater sediments is the organic material content. Surface soils, which typically receive regular inputs of organic material from plants, will undoubtedly have higher organic matter content.

High organic matter content is typically associated with high microbial numbers and a great diversity of microbial populations. Organic matter serves as a wardrobe of carbon and energy as well as a source of other macronutrients such as nitrogen, phosphorous, and sulfur. Subsurface soils and groundwater sediments have lower levels of organic matter and thus lower microbial numbers and population diversity than surface soils.[14] Bacteria become more dominant in the microbial community with increasing depth in the soil profile, because the numbers of other organisms such as fungi or actinomycetes decrease. This is attributed to the ability of bacteria to use alternative electron acceptors to oxygen. Other factors that control microbial populations are moisture content, dissolved oxygen, nutrient, and temperature.[13]

15.6.4 METABOLIC PROCESSES

The primary metabolism of an organic compound uses a substrate as a source of carbon and energy. For the microorganism, this substrate serves as an electron donor, which results in the growth of the microbial cell. The application of co-metabolism for bioremediation of a xenobiotic is necessary because the compound cannot serve as a source of carbon and energy due to the nature of the molecular structure, which does not induce the required catabolic enzymes. Co-metabolism has been defined as the metabolism of a compound that does not serve as a source of carbon and energy or as an essential nutrient, and can be achieved only in the presence of a primary (enzyme-inducing) substrate.

Two conditions favor metabolic activities: aerobic and anaerobic environments. Aerobic processes are characterized by metabolic activities involving oxygen as a reactant. Dioxygenases and monooxygenases are two primary enzymes used by aerobic organisms during the transformation and mineralization of xenobiotics. Anaerobic microbes take advantage of a range of electron acceptors, including, depending on their availability and the prevailing redox conditions, nitrate, iron, manganese, sulfate, and carbon dioxide.

15.6.5 FACTORS AFFECTING BIOREMEDIATION

15.6.5.1 Energy Sources

The primary factor that affects the activity of bacteria is the ability and availability of reduced organic material to serve as an energy source. Whether a contaminant will serve as an effective energy source for an aerobic heterotrophic organism is a function of the average oxidation state of the carbon in the material. Each degradation process depends on microbial (biomass concentration, population diversity, and enzyme activities), substrate (physico-chemical characteristics, molecular structure, and concentration), and a range of environmental (pH, temperature, moisture content, availability of electron acceptors, and carbon and energy sources) factors. These parameters affect the acclimation period of the microbes to the substrate. Molecular structure and contaminant concentration have been shown to strongly affect the feasibility of bioremediation and the type of microbial transformation occurring, as well as whether the compound will serve as a primary, secondary, or co-metabolic substrate.

15.6.5.2 Bioavailability

The rate at which microbial cells can convert contaminants during bioremediation depends on the rate of contaminant uptake and metabolism and the rate of transfer to the cell (mass transfer). Increased microbial conversion capacities do not lead to higher biotransformation rates when mass transfer is a limiting factor.[15] This appears to be the case in most contaminated soils and sediments. For example, contaminating explosives in soil did not undergo biodegradation even after 50 years. Treatments involving rigorous mixing of the soil and breaking up of the larger soil particles stimulated biodegradation drastically.[16] The bioavailability of a contaminant is controlled by a number of physico-chemical processes such as sorption and desorption, diffusion, and dissolution. Slow mass transfer causes a reduced bioavailability of the contaminants in the soil to the degrading microbes. Contaminants become unavailable when the rate of mass transfer is zero. The decrease of bioavailability over the course of time is often referred to as aging or weathering. It may result from the following:

1. Chemical oxidation reactions incorporating contaminants into natural organic matter
2. Slow diffusion into very small pores and absorption into organic matter
3. The formation of semirigid films around nonaqueous-phase liquids (NAPL) with a high resistance to NAPL–water mass transfer

These bioavailability problems may be overcome by the use of food-grade surfactants,[17] which increase the availability of contaminants for microbial degradation.

15.6.5.3 Bioactivity

Bioactivity refers to the operating state of microbiological processes. Improving bioactivity implies that system conditions are adjusted to optimize biodegradation.[18] For example, if the use of bioremediation requires meeting a certain minimum rate, adjusting the conditions to improve biodegradation becomes important and a bioremediation configuration that makes this control possible has an advantage over one that does not.

In nature, the ability of organisms to convert contaminants to both simpler and more complex molecules is very diverse. In light of our current limited ability to measure and control biochemical pathways in complex environments, favorable or unfavorable biochemical conversions are evaluated in terms of whether individual or groups of parent compounds are removed, whether increased toxicity is a result of the bioremediation process, and sometimes whether the elements in the parent compound are converted to measurable metabolites. These biochemical activities can be controlled in an *in situ* operation when one can control and optimize the conditions to achieve a desirable result.

15.7 BIOREMEDIATION OF LANDFILL LEACHATE

Bioremediation is the treatment of choice for mineralizing most organic compounds in landfill leachate.[19] Mineralization is carried out by microorganisms, which can degrade organic compounds to carbon dioxide under aerobic conditions and to a mixture of carbon dioxide and methane under anaerobic conditions. Microorganisms are also capable of changing the oxidation state of metals and inorganic compounds and can concentrate heavy metals and hydrophobic compounds through ingestion or adsorption. Microorganisms are ubiquitous, self-replicating, adaptable to a variety of leachate compositions, and active at moderate reaction conditions. In addition, biodegradation benefits from a long process history in the treatment of domestic sewage.

Leachate that comes from mixed landfills, that is, those with municipal waste combined with industrial wastes, may contain a host of xenobiotics (synthetic or unnatural) compounds. A number of these xenobiotics are normally classified as hazardous waste. A vast majority of organic hazardous wastes can be degraded if the proper microbial communities are established, maintained, and controlled.[20] Degradation is not necessarily growth-associated,[21] as organic compounds may be transformed to microbial storage polysaccharides under nitrogen-limiting conditions rather than being mineralized to carbon dioxide. Research regarding the mechanisms controlling xenobiotic degradation is important in understanding the capabilities and limitations of biological leachate treatment.[22]

An important element in xenobiotic biodegradation is the broad specificity of some microbial enzymes, which permits an enzyme-catalyzed reaction to occur without providing energy or carbon for cell replication. This phenomenon is divided into two categories: fortuitous metabolism, in which a growth co-substrate is not obligate, and co-metabolism, in which the growth co-substrate is obligate.[23] One of the most thoroughly characterized examples of broad enzyme specificity is the ability of the methane mono-oxygenase enzyme (MMO) to oxygenate hydrocarbons other than methane, its natural substrate. The oxygenated hydrocarbons then accumulate stoichiometrically in the reactor.[24] MMO-catalyzed reactions are co-metabolic, because energy from a co-substrate is required to supply reducing power for the reaction.

Fortuitous or co-metabolic biodegradation may account for a significant portion of the removal of xenobiotics in the environment.[24] Numerous examples of co-metabolic activity have been described for pure substrates,[22] but co-metabolism has been very difficult to demonstrate in mixed-substrate, mixed-culture systems, because products of the co-metabolic reactions of one species may be degraded by another.[24] To encourage co-metabolism, easily degradable co-substrates should be included in the leachate prior to biological treatment. Fatty acids, which often occur in landfill leachates, may fulfill this requirement.

In the case of industrial landfill leachate, it is unlikely that the microbial enzymatic machinery would be sufficient to degrade all the compounds present,[25] especially if a single microbial species is used. Furthermore, the adaptability of a single microbial species is limited and the mutation rate is too slow to make single-species adaptation practical. In order to increase the diversity of degradative enzymes it is common to use a mixed microbial population, also known as a microbial consortium or mixed culture. Mixed cultures have two advantages over pure cultures in the degradation of complex substrates. First, the product of an incomplete mineralization by one microbe, such as from a co-metabolic transformation, may serve as a substrate for another microbe. Second, the transfer of genetic information between species may enhance the degradability of the culture.[26] It has been demonstrated that DDT (dichloro diphenyl trichloroethane) can be co-metabolized to pentachlorophenol-induced periplasmic protein (PCPA) by one species and that PCPA can be mineralized by another species. A combined culture of the two species results in the complete mineralization of DDT.[27] Stable mixed cultures degrading xenobiotics have been isolated in which the microbial consortia can degrade a substrate better than the individual species.[22]

Many strains of microorganism have been isolated that can degrade xenobiotics or families of xenobiotics.[28] For example, a white rot fungus studied for its lignin-degrading potential has been shown in laboratory studies to mineralize a number of recalcitrant organics, such as a tetrachlorodibenzo-paradioxin (TCDD) and DDT.[29] Degradation is carried out by extracellular enzymes whose production is stimulated by nitrogen limitation. Because of the requirements of nitrogen limitation and an acidic environment, the fungus is incompatible with many activated-sludge-derived organisms. Whether such organisms will be useful for degrading mixtures of compounds or will be active in a full-scale process has yet to be demonstrated.

Gross genetic changes brought about by the interspecies transfer of genetic material may be important in the microbial degradation of xenobiotics. Although there are several mechanisms for such transfers, the most important is thought to be conjugation. In this process, loops of extrachromosomal DNA mediate their own replication from host to recipient microorganisms. Conjugative plasmids, as these DNA loops are known, carry coding for a variety of proteins, which, although not required for reproduction, may confer a selective environmental advantage such as heavy metal resistance or extended substrate range.[30] In some cases, nonconjugative plasmids can link to conjugative plasmids and “piggy-back” from organism to organism.[23] Once a plasmid is transferred, DNA sequences called transposons may play a role in the integration of portions of the plasmid DNA into the genome of the new host. The rapid spread of antibiotic resistance among various classes of microorganisms is an example of the transfer of plasmid-born information.

The key issues in developing an effective biological landfill leachate treatment process are the following:

1. Process configuration
2. Microbial culture selection and development
3. Substrate modification
4. Process control

Due to the complex and varying nature of landfill leachate, these factors must be evaluated for each site. Chemical species thought to be biologically recalcitrant may be biodegradable given the proper acclimation. The principal mechanisms of acclimation are macromolecule modification, population selection, and genetic transfer. Modification of cellular components, for example, enzyme induction or increased membrane permeability, occurs when a substrate interacts with biological molecules of the cell. The time frame for such interactions ranges from minutes to hours.[30] Population selection, or shifts in the representation of preexisting species, occurs because some species or mutants within a species may be better adapted to a new environment. The time frame depends on growth rates and may range from hours to days for aerobic cultures and from days to weeks for anaerobic cultures.[31] Favorable genetic adaptation, alteration of the microbial DNA, may occur over periods ranging from months or years.[32]

Carbon limiting is also used to encourage enzyme induction, place the population under selective pressure for degradation of recalcitrant substrates, and favor the simultaneous rather than sequential metabolism of a mixed carbon source.[33] Carbon-limiting conditions can be achieved either through continuous culture (chemostat) or through a fed batch reaction.

To facilitate biodegradation, the leachate may require modification through pH adjustment, removal or addition of oxygen, amendment with nutrients, or dilution or removal of toxic species. Microbial nutrition is complex and is better understood for aerobes than for anaerobes.[34] Biological processes typically favor a pH near 7. Pretreatment processes to remove inhibitory components include coagulation and precipitation, carbon adsorption, and possibly ozonation.

A variety of biological processes options may be used to treat leachate.[35] The basic decision is whether to treat a particular leachate aerobically or anaerobically. Both aerobic and anaerobic processes can degrade a wide range of xenobiotics.[36] Aerobic processes are generally superior in mineralizing aromatic compounds; anaerobic processes are superior for short-chain aliphatic groups.[27] Aerobic processes have the advantage of speed and ease of control and acclimation. However, aerobic processes accumulate large quantities of microbial sludge that may contain adsorbed organics and heavy metals, and may strip volatile compounds. Anaerobic processes produce less sludge and can provide energy through methane production. They also reduce sulfate to sulfide, which is a powerful precipitator of heavy metals. However, because of their low reproduction rates, anaerobes require a long start-up time and are sensitive to toxic shocks.[37] Both aerobic and anaerobic processes have been shown to be capable of degrading landfill leachate.[38] However, many landfill leachate treatments have been found to be insufficient if the anaerobic process is used alone without the aerobic. Systems comprising combined anaerobic–aerobic treatment are therefore recommended to achieve effective treatment at landfill.

The rate of mineralization of organic carbon in a biological process depends on the concentration of active cell mass. The maximum cell growth in a process will depend on nutrient availability, gas transfer, and toxicity of the leachate. In aerobic and anaerobic treatment lagoons, no provision is made for concentrating the suspended cells. Therefore, lagoons must have a large surface area to facilitate effective organic destruction. The advantage of lagoons is that very low maintenance is needed except for a periodic desludging of the microbial sludge.[20]

The reduction in organic carbon achievable by microorganisms is limited to some extent by the minimum concentration required to maintain cellular metabolic processes.[39] Microbial species known as oligotrophs can operate at low substrate concentrations, but they may not be able to reduce contaminant concentrations below water quality standards. There are methods to circumvent the biological maintenance barrier to leachate degradation. A well-known approach involves the use of activated carbon to enhance the biodegradation reaction.[40] There are three known beneficial effects of adsorbent addition: organic carbon is concentrated for microbial attack in the microenvironment around the adsorbent particle; the concentration of potentially inhibitory organic compounds in the bulk solution is lowered; and the carbon particles serve as a surface for microbial growth.[41]

Leachate can also be degraded biologically *in situ* at the landfill site. Conditions within the landfill are controlled to encourage microbial activity, and leachate is recirculated through the landfill. Recirculated leachate may require nutrient amendment, neutralization, or heavy metal removal. Aerobic microbial activity occurs at the landfill surface, and anaerobic activity occurs in the landfill interior. Recirculation, combined with anaerobic activity, may stabilize heavy metals through the precipitation of heavy metal sulfides.[42] Aerobic biodegradation is faster and better understood, and methods for encouraging aerobic activity within a landfill by the addition of hydrogen peroxide or air microbubbles have been investigated.[43] Subsurface aeration wells have also been used to encourage *in situ* degradation.

Biodegradation is considered the first option for the primary removal of organic compounds from landfill leachate. However, some organic compounds are resistant to biological attack. In addition, biological sludge resulting from biological processes may become a disposal problem, particularly because of its capacity to store adsorbed undegraded hydrophobic organic species and heavy metals. No biological leachate treatment processes have yet to take advantage of microbial transformations, nor has adsorption of heavy metals though suitable microorganisms been studied in the laboratory.[44,48] Bioremediation processes are still relatively unsophisticated and the potential exists for combining various types of microbial process schemes for selective component removal.[9]

15.8 CASE STUDIES

15.8.1 CASE 1: ANAEROBIC/AEROBIC TREATMENT OF MUNICIPAL LANDFILL LEACHATE IN SEQUENTIAL TWO-STAGE UP-FLOW ANAEROBIC SLUDGE BLANKET REACTOR (UASB)/AEROBIC COMPLETELY STIRRED TANK REACTOR (CSTR) SYSTEMS

A project was conducted to study the treatability of leachate produced from a laboratory-scale simulated reactor treating food wastes using a two-stage sequential up-flow anaerobic sludge blanket reactor (UASB)/aerobic completely stirred tank reactor (CSTR).[45] Experiments were performed in two UASB reactors and a CSTR reactor having effective volumes of 2.5 and 9 L, respectively. The hydraulic retention times in the anaerobic and aerobic stages were 1.25 and 4.5 d, respectively. Following the startup period, the COD concentration of the leachate steadily increased from 5400 to 20,000 mg/L. The organic loading rate (OLR) was increased from 4.3 to 16 kg/m^3/d by increasing the COD concentrations from 5400 to 20,000 mg/L.

As reported, the effluent of the first anaerobic UASB reactor (Run1) was used as the influent of the second UASB reactor (Run2), and the effluent of the second UASB reactor was used for the influent of the aerobic CSTR reactor (Run3). COD removal efficiencies for the first UASB reactor and in the whole system (two-step UASB + CSTR) were 58%, 62%, 65%, 72%, 74%, 79%, and 96%, 96.8%, 97.3%, 98%, 98%, and 98%, respectively. As the OLR increased from 4.3 to 16 kg/m^3/d, the COD removal efficiency reached a maximum of 80%. NH_4–N removal efficiency was ca. 99.6% after the aerobic stage. The maximum methane percentages of the first and second UASB reactors were 64% and 43%, respectively.

The study used two continuously fed stainless steel anaerobic UASB (2.5 L) reactors and an aerobic CSTR reactor (9 L). The UASB was operated at 37 to 42°C using an electronic heater located in the central part of the reactor. The system was provided with a settling compartment (with an effective volume of 1.32 L). The dissolved oxygen concentration was maintained above 2 mg/L in the CSTR reactor. Partially granulated anaerobic sludge taken from the methanogenic reactor of the Pakmaya Yeast Baker Factory in Izmir was used as seed in the UASB reactor. The activated sludge culture was obtained from the DYO Dye Industry in Izmir and was used as seed for the aerobic CSTR reactor.

In this study, anaerobic and aerobic processes using sequential two-step UASB/CSTR reactors were found to form a feasible process for treating the leachate from food solid waste. COD removal efficiencies for the first and second anaerobic, aerobic and total system processes were 79%, 42%, 89%, and 98%, respectively. The COD loading rate used ranged from 4.3 to 16 kg/m^3/d.

The methane content of the first UASB reactor was ca. 60%. The NH_4-N removal efficiency of the total system was 99.6%. Ammonium nitrogen was converted to nitrate in the aerobic system via nitrification. The BOD_5/COD value obtained at the final stage was in the range 0.12 to 0.15.

15.8.2 Case 2: Comparison of Two Biological Treatment Processes Using Attached-Growth Biomass for Sanitary Landfill Leachate Treatment

Two biological systems were compared using attached-growth biomass for the treatment of leachate generated from a municipal waste sanitary landfill. A moving-bed biofilm process, which is a relatively new type of biological treatment system, was used.[46] The process was based on the use of small, free-floating polymeric (polyurethane) elements, and biomass was grown and attached as biofilm on the surface of these porous carriers. For comparison, a granular activated carbon (GAC) moving-bed biofilm process was also tested. This method offered the advantages of combining both physico-chemical and biological removal mechanisms for the removal of pollutants. The presence of GAC in the reaction tank provided a porous surface able to adsorb both organic matter and ammonia, as well as to provide an appropriate surface onto which biomass could grow. A laboratory-scale sequencing batch reactor (SBR) was used for examination of both carriers. The effects of different operation strategies on the efficiency of these biological treatment processes were studied in order to optimize their performance, especially for the removal of nitrogen compounds and biodegradable organic matter. It was found that these processes were able to remove nitrogen content almost completely, and the removal of organic matter such as BOD_5 and COD was acceptable.

The SBR reactor used was constructed from cylindrical Plexiglas® with a working capacity of 8 L (as shown in Figure 15.1).[47] The contents of the reactor were mixed with a magnetic stirrer, and

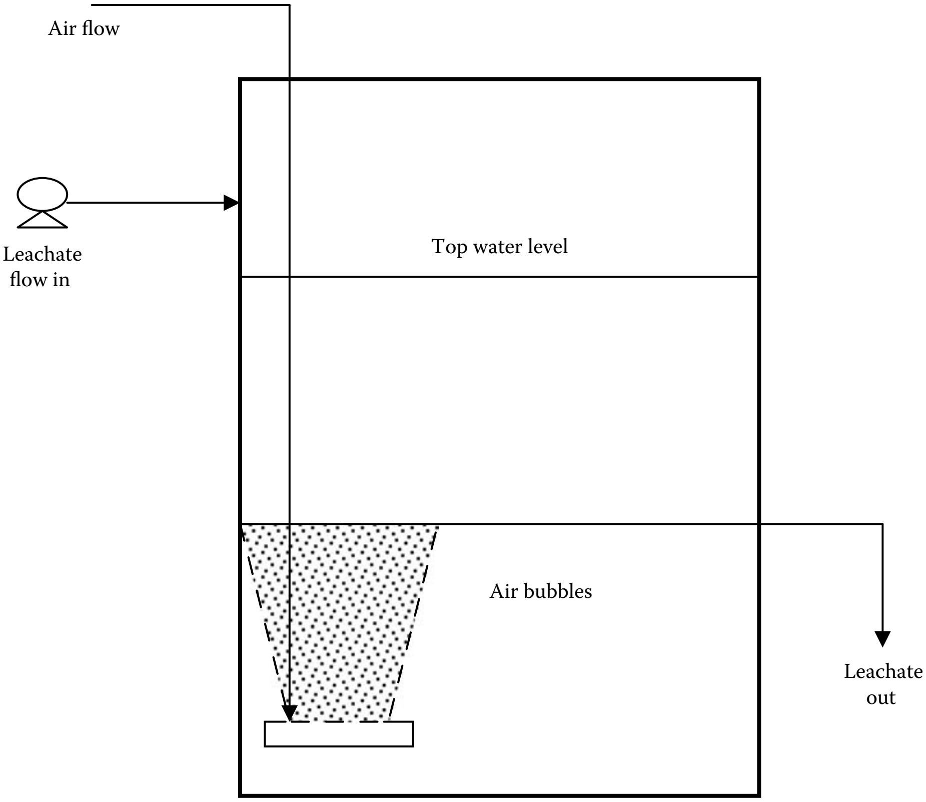

FIGURE 15.1 Schematic diagram of a laboratory-scale, sequencing batch (bio) reactor (SBR).

a ceramic diffuser was used for aeration. A peristaltic pump was used to feed leachate directly into the SBR, as well as to remove the treated effluent.

The study consisted of two separate treatment cycles using a suspended-carrier attached-biofilm process. During the first cycle, the SBR was filled up to 50% of its empty volume with cube-shaped waste polyurethane particles (total dry weight 30 g). The density of the carrier media was slightly below 1 g/cm^3, so the waste particles could easily follow the water flow pattern, circulating in the filled reactor. The continuous motion eliminated problems with clogging and dead space, which can often decrease the efficiency of fixed-bed biofilm systems. The cubes (having an approximate dimension of 1 cm) present high porosity (20 to 40 pores/cm^2). During the second operational cycle, GAC (type F400, supplied by Chemviron Co., Belgium) was added to the reactor (90 g total), with a specific surface area of 1100 m^2/g and density of 1.2 g/cm^3. The main parameters studied during this investigation included the following:

1. The addition of alkalinity, phosphorus, and methanol (different concentrations and rates were evaluated)
2. An increase in the hydraulic retention time
3. A replacement sequence for used carrier media
4. The application of intermittent aeration, i.e., operation with alternate aerobic and anoxic conditions

Table 15.1 summarizes process efficiency during the first operation cycle of the SBR, and Table 15.2 shows the treatment results for the second operation cycle (GAC).

This study demonstrated that the suspended carrier–biofilm treatment method can offer an alternative option to the conventional activated sludge process for the effective removal of carbon and nitrogen in sanitary landfill leachates. Although raw leachate is very difficult to treat, complete nitrification and a high degree of organic carbon removal were achieved using the moving-bed biofilm SBR process.

The study reported some problems regarding the data for the biofilm from the media after 3 weeks of operation, and also sludge accumulation at the bottom of the bioreactor. It was also found that an external carbon source, such as methanol, was necessary for controlling the denitrification stage.

An alternative moving-bed biofilm SBR process using GAC has also been proven to be an effective treatment method for the removal of nitrogen from landfill leachates. This method can remove biodegradable organic carbon (BOD$_5$) and COD. However, the main disadvantage of this process is the buildup of a large amount of residual suspended solids, hence increasing sludge disposal costs. An overall comparison between the two attached biomass biological treatment processes showed an advantage for the process that used porous polyurethane as its carrier material.[46]

TABLE 15.1

Average Treatment Results during First Operation Cycle (SBR)

Parameters	Influent Concentrations	Effluent Concentrations	Total Removal (%)
Ortho-P (mg/L)	3.2	1.1	66
Total-P (mg/L)	8.3	3.2	62
Cl^{-1} (mg/L)	4,640	3,062	34
Alkalinity (mg/L $CaCO_3$)	7,800	2,890	63
Conductivity (mS/cm)	24	14.3	40
TDS (mg/L)	14,000	7,000	50

SBR, sequencing batch reactor; TDS, total dissolved solids.

TABLE 15.2
Treatment Results for the Second Operation Cycle (GAC)

Parameters	Influent	Effluent	Total (%)
BOD_5 (mg/L)	1,292	114	91
Ortho-P (mg/L)	3.8	0.5	88
Total-P (mg/L)	9.3	2.2	73
Cl^{-1} (mg/L)	5,050	3,396	32.8
Alkalinity (mg/L $CaCO_3$)	733	1,395	81
Turbidity (NTU)	142	173	—
Conductivity (mS/cm)	25.4	12.5	50.7
TDS (mg/L)	14,900	6,900	54

BOD_5, 5d-biochemical oxygen demand; GAC, granular activated carbon; TDS, total dissolved solids; NTU, normal turbidity units.

15.8.3 CASE 3: LEACHATE TREATMENT USING AN AEROBIC BIOFILM REACTOR

In this project, leachate was treated using an innovative aerobic biofilter utilizing special plastic media. Aerobic biofilters have been shown to be very effective in many treatments for removing organic pollutants and also their nutrient content. This study focused on leachate treatment using an attached growth biofilm reactor, which contains a packing of 80 mm diameter plastic media called "Cosmo balls."[47] Figure 15.2 shows how the experiment was set up. The selected parameters for the study include COD, ammonia nitrogen, pH, and BOD. The results showed that the COD removal percentages were above 90% for COD but declined to 70% at very high loading. The ammonia nitrogen removal achieved in the study was above 85%.

The use of an attached growth aerobic biofilm reactor to treat leachate is relatively new. Past studies on anaerobic biofilters showed excellent organic removal up to 90%, and the retention time needed to treat high-strength effluent was between 3 and 5 d. The use of aerobic biofilters using

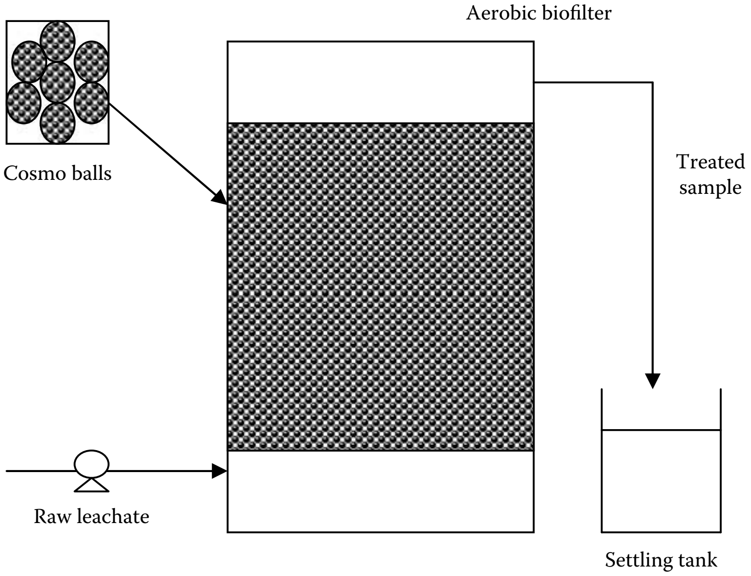

FIGURE 15.2 Schematic diagram of leachate treatment using an attached growth biofilm reactor.

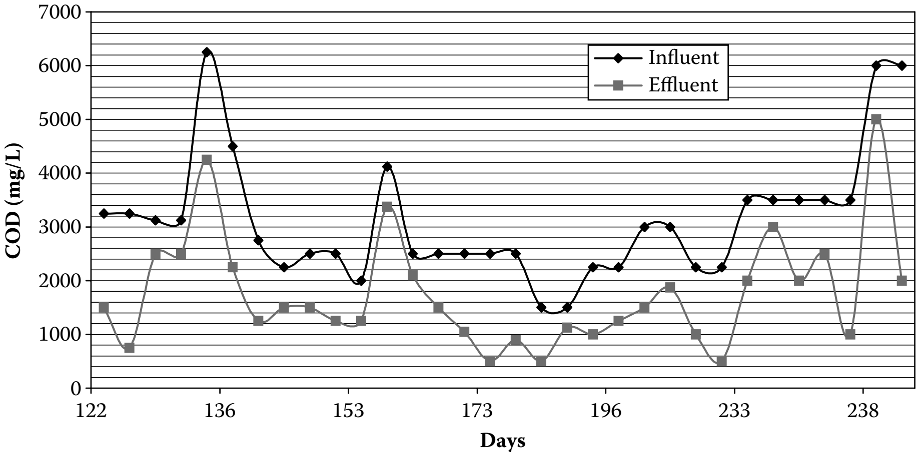

FIGURE 15.3 Relationship of COD content (mg/L) of influent and effluent over time (d).

Cosmo balls has been successful in treating sewage effluent with a short hydraulic retention time of only 4 h. This study was carried out to evaluate process efficiency using Cosmo balls with a hydraulic retention time of 5 d.

The aerobic biofilter used in the study had a capacity of 10 L. The reactor was packed to 60% of the empty bed volume with Cosmo ball media. The biofilter was seeded with active innoculum taken from an active aerated lagoon of a nearby landfill leachate treatment. Fresh raw leachate was used as feed to the reactor at a rate of 5 L/d over 24 h. The loading rates applied to the bioreactor were between 1.6 and 22.2 kg COD/m^3 d. Initial studies were conducted as a batch process lasting for a period of 24 d. Thereafter, the biofilter was fed continuously for a total period of 240 d.

Figure 15.3 shows that percentages of COD removed in the biofilter decreased with increasing feed COD concentration. The value of the influent fluctuated, indicating that leachate characteristics were never uniform. The aerobic bioreactor was shown to be capable of treating leachate with about 80% COD removal using the designed hydraulic retention time of 5 d. Figure 15.4 shows that the ammonia nitrogen levels in the treated effluent were fluctuating and that the percentage of ammonia nitrogen removed declined very slightly at increased ammonia loading. Ammonia nitrogen removal showed very good results, with more than 80% destruction achieved in this study.

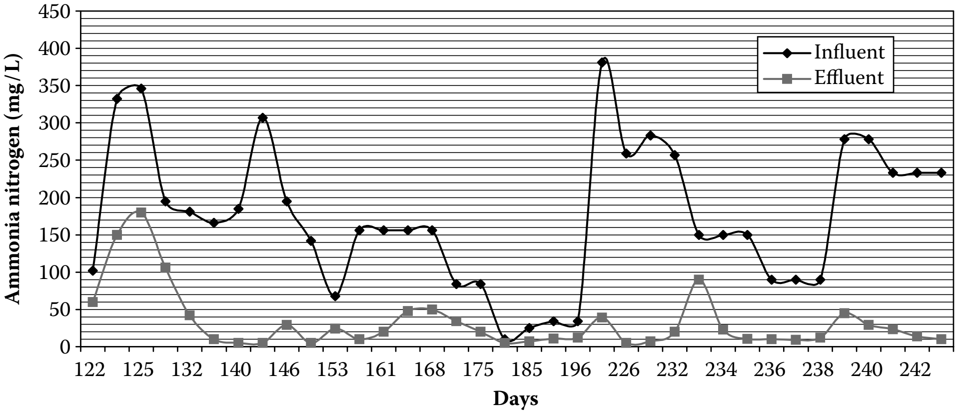

FIGURE 15.4 Relationship of ammonia nitrogen level (mg/L) in the influent and effluent over time (d).

It was observed that the factors contributing to the variation of leachate data are solid waste characteristics, for example, the composition and size of the waste and degree of compaction, the moisture content and degree of rainwater infiltration, temperature, sampling, and analytical methods.[47]

NOMENCLATURE

BOD	Bochemical oxygen demand
BOD_5	Five-day biochemical oxygen demand
COD	Chemical oxygen demand
CSTR	Completely stirred tank reactor
DDT	Dichloro diphenyl trichloroethane
DNA	Deoxyribonucleic acid
GAC	Granular activated carbon
MBAS	Methyl blue active substances
MMO	Methane mono-oxygenase enzyme
MSW	Municipal solid waste
OLR	Organic loading rate
PCPA	Pentachlorophenol-induced periplasmic protein
SBR	Sequencing batch reactor
TCDD	Tetrachlorodibenzo-paradioxin
TOC	Total organic carbon
TDS	Total dissolved solids
UASB	Up-flow anaerobic sludge blanket reactor
VDS	Volatile dissolved solids
VSS	Volatile suspended solids

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16 Remediation of Sites Contaminated by Hazardous Wastes

Lawrence K. Wang, Nazih K. Shammas, Ping Wang, and Robert LaFleur

CONTENTS

16.1 INTRODUCTION

Site contamination generally results from leakage, spillage, or disposal of industrial wastes, and can arise from the past uncontrolled disposal of chemical wastes or any recent negligence. Contaminated sites are a threat to human beings by the following means of contamination:

1. Contact with contaminated soil
2. Inhalation of evaporated toxic gases
3. Drinking of contaminated groundwater
4. Consumption/intake of a secondary contaminant, for example, by eating contaminated crops or livestocks fed in the contaminated area

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)[1–3] and the Superfund Amendments and Reauthorization Act (SARA)[4] protect the public from the risks created by past and recent chemical disposal practices. Cleanup of contaminated sites is needed in order to protect human and natural resources, as defined by the Clean Air Act,[5] the Clean Water Act,[6] the Safe Drinking Water Act,[7] and the Resource Conservation and Recovery Act (RCRA).[8,9]

This chapter presents a regulatory overview of on-site remediation, remedial investigations (RI), feasibility studies (FS), remedial technologies, and a simulated case study. The discussion of remedial investigations and feasibility studies also includes the development and selection of remedial technologies. The case study outlines a remedial investigation and feasibility study, as well as the selection of remedial technologies.

16.2 LEGISLATIVE AND REGULATORY OVERVIEW

16.2.1 COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT

In 1980, the U.S. Congress enacted the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), the first comprehensive federal law addressing the protection of the environment from the threat of hazardous substances. The primary goal of CERCLA is to establish an organized cost-effective mechanism for response to abandoned or uncontrolled hazardous waste sites that pose a serious threat to human health and the environment.[8,9] To accomplish this goal, two types of response capabilities are mandated by CERCLA[1–3]:

1. An emergency response action for handling major chemical spills or incidents requiring immediate action, usually only at the surface of a site (e.g., to avert an explosion, to clean up a hazardous waste spill, or to stabilize a site until a permanent remedy can be found); these action are limited to 12 months or USD 2 million in expenditure, although in certain cases these limits may be extended.
2. A remedial response capability for undertaking the long-term cleanup of abandoned hazardous waste disposal sites. These remedial actions represent the final remedy for a site and are generally more expensive and of a longer duration than emergency removals. The U.S. Environmental Protection Agency (U.S. EPA) deals only with remedial actions for hazardous waste sites that are on the National Priorities List (NPL).

Both removal and remedial actions may be carried out at the same site. To accomplish these tasks, CERCLA has given cleanup authority to U.S. EPA, has established the Hazardous Substance Response Trust Fund (Superfund) to finance the remedial actions at CERCLA sites, has initiated a procedure for the emergency response to accidental spills, and has imposed cleanup liability on those responsible. The National Contingency Plan (NCP) was developed in 1982 and in 1985 as the regulatory framework to guide these responses.

Preliminary assessments have been conducted at more than 31,000 sites reported as possible sources of contamination. In 1990 there were over 1100 sites (presenting the greatest health risk and hence eligible for Superfund reimbursement) on the NPL.[8,9] The NCP has outlined the level of cleanup necessary at Superfund sites and established the basic procedures that have to be followed for the discovery, notification, response, and remediation of the hazardous waste sites.[10]

16.2.2 Superfund Amendments and Reauthorization Act (SARA)

SARA has added several important new dimensions to CERCLA, including an increased emphasis on health assessments and the consideration of air releases.[11]

It should be noted that early remedial actions for contaminated soil consisted primarily of excavation and removal of the contaminated soil from the site and its disposal at a landfill. SARA strongly recommends on-site treatment that permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, and utilizes cost-effective permanent solutions. The legislation prohibits land disposal of hazardous wastes unless U.S. EPA determines otherwise (as in the Hazardous and Solid Waste Amendments, HSWA).

SARA requires that remedial actions meet all applicable or relevant federal standards or any more stringent state standards. Nine criteria that need to be met are set by CERCLA as amended by SARA for a complete assessment of treatment alternatives applicable for a site remedial action[12]:

1. The overall protection of human health and the environment by permanently and significantly reducing the volume, toxicity, or mobility of hazardous substance, pollutants, and contaminants
2. Compliance with applicable, relevant, and appropriate requirements (ARARs)
3. Long-term effectiveness and permanence
4. Reduction of toxicity, mobility, or volume
5. Short-term effectiveness
6. Implementability
7. Cost
8. State acceptance
9. Community acceptance

The CERCLA reauthorization regards off-site transport and disposal without treatment as the least favored alternative where practicable treatment technologies are available. It also favors the use of permanent solutions and alternative treatment technologies or resource recovery technologies and using them to the maximum extent practicable.

16.2.3 Resource Conservation and Recovery Act (RCRA)

RCRA has a regularity focus (in contrast to CERCLA, which has a response focus), and authorizes control over the management of wastes from the moment of generation until final disposal, including transportation, storage, and other processes.

16.3 OVERVIEW OF REMEDIAL STRATEGIES AND PHASES

The remedial strategies include the following:

1. Site selection from the NPL
2. Scoping

3. Remedial investigation including site characterization and a treatability study
4. Feasibility study including analysis and selection of alternatives
5. Remedial design and action (see Figure 16.1)[12]

The remedial strategies of concern focus on how to select a remedial method and how to complete the remediation at the most effective cost.

16.3.1 SCOPING

Scoping is the prework for RI and FS study. The task of scoping consists mainly of site data collection. As this is required for the RI phase, some investigators have regarded scoping as an early subphase of RI. However, scoping also involves project planning and other prework for FS, so it is to be regarded as a separate phase that precedes both RI and FS.

16.3.2 REMEDIAL INVESTIGATION/FEASIBILITY STUDY (RI/FS)

In accordance with §105 of CERCLA, U.S. EPA has established a process for locating releases, evaluating remedies, determining the appropriate extent of response, and ensuring that the remedies selected are cost-effective. This process is commonly referred to as the RI/PS process. The overall purpose of the RI/PS process represents the methodology that the Superfund program has established for characterizing the nature and extent of the risks posed by uncontrolled hazardous waste sites and for evaluating their potential remedial options.

The NCP requires that a detailed RI/PS be conducted for every site that is targeted for remedial response action under §104 of CERCLA.

Figure 16.2 outlines the major tasks carried out in the RI/FS process under CERCLA guidance.[13] The components of RI comprise the following:

1. Collecting data to characterize site conditions
2. Determining the nature of the waste

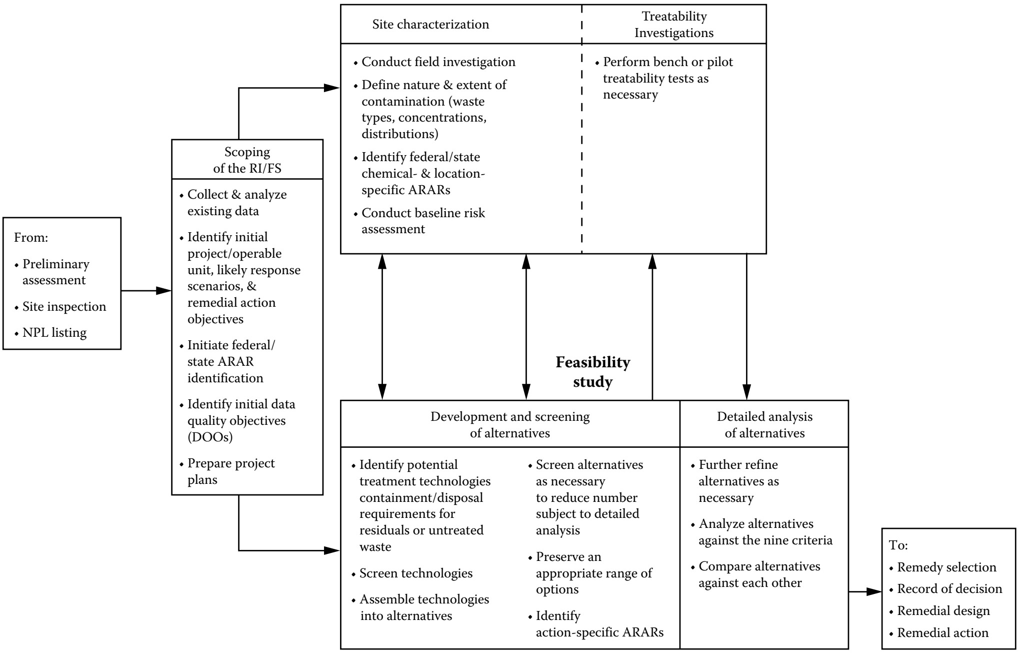


FIGURE 16.1 Phased remedial investigation process.

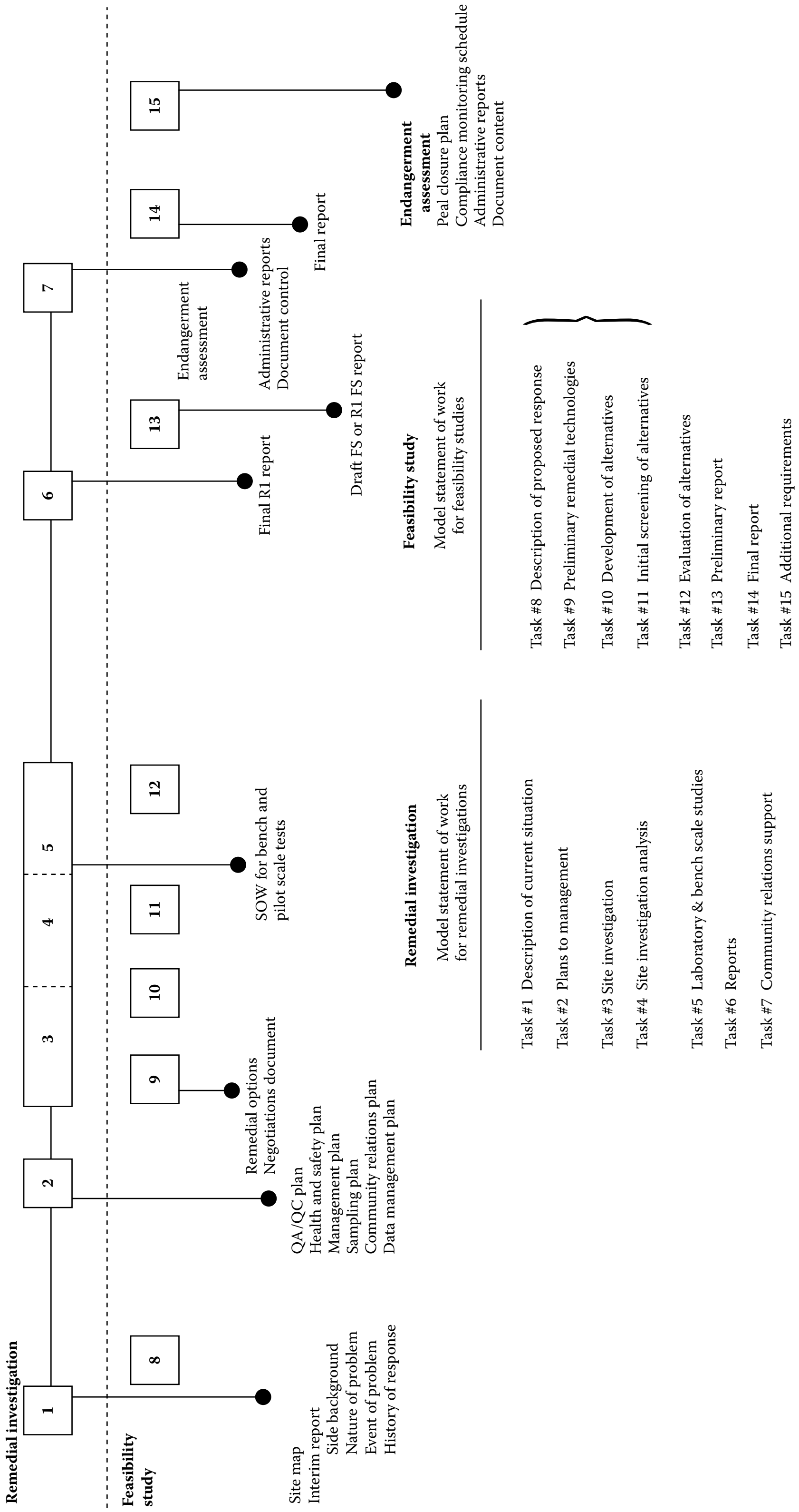


FIGURE 16.2 RI/FS process.

3. Assessing risk to human health and the environment
4. Conducting treatability testing as necessary to evaluate the potential performance and cost of the treatment technologies that are being considered[12,13]

The components of FS comprise developing, screening, and evaluating alternative remedial actions.

RI and FS are interdependent processes and are generally performed concurrently rather than sequentially, although the FS uses the data provided by the RI. This approach should be viewed as a dynamic, flexible process that can and should be tailored to specific circumstances of individual sites. It is not a rigid step-by-step approach that must be conducted identically at every site. Figure 16.3 illustrates a generic timeline of the phasing of RI/PS activities.

16.4 SCOPING THE REMEDIAL INVESTIGATION AND FEASIBILITY STUDY

Scoping is the initial planning phase of site remediation and is a part of the funding allocation and planning process.[12] Scoping of the RI/FS comprises the following steps:

1. Evaluating existing data
2. Developing the conceptual site model
3. Identifying the initial project/operable unit, likely response scenarios, and remedial action objects
4. Initiating potential federal/state ARARs identification
5. Identifying initial data quality objectives
6. Preparing project plans

16.4.1 PROJECT PLANNING

There are 12 tasks involved in project planning:

1. *Conducting project meetings.* This includes meeting with the lead agency, the support agency, and contractor personnel to discuss site issues and assign responsibilities for RI/FS activities.
2. *Collecting and analyzing existing data.* Existing data (Table 16.1) are collected and analyzed to develop a conceptual site model that can be used to assess both the nature and the extent of contamination and to identify potential exposure pathways and potential human health or environmental receptors.
3. *Describing the current situation.*
4. *Developing a conceptual site model.* An example of this is presented in Figure 16.4.[12]
5. *Developing preliminary remedial action alternatives.* This involves initiating limited field investigations if available data are inadequate to develop a conceptual site model and adequately scope the project, and identifying preliminary remedial action objectives and likely response actions for the specific project.
6. *Evaluating the need for a treatability study.* The requirement and schedule for treatability studies so as to better evaluate potential remedial alternatives are identified. If remedial actions involving treatment have been identified for a site, then the need for treatability studies should be evaluated as early as possible in the RI/FS process. This is because many treatability studies may take several months or longer to complete.
7. *Beginning preliminary identification of ARARs and "to be considered" (TBC) information.* This preliminarily identifies the ARARs that are expected to apply to site characterization and site remediation activities.
8. *Identifying data needs.* Data requirements and the level of analytical and sampling certainty required for additional data if currently available data are inadequate to conduct the FS is

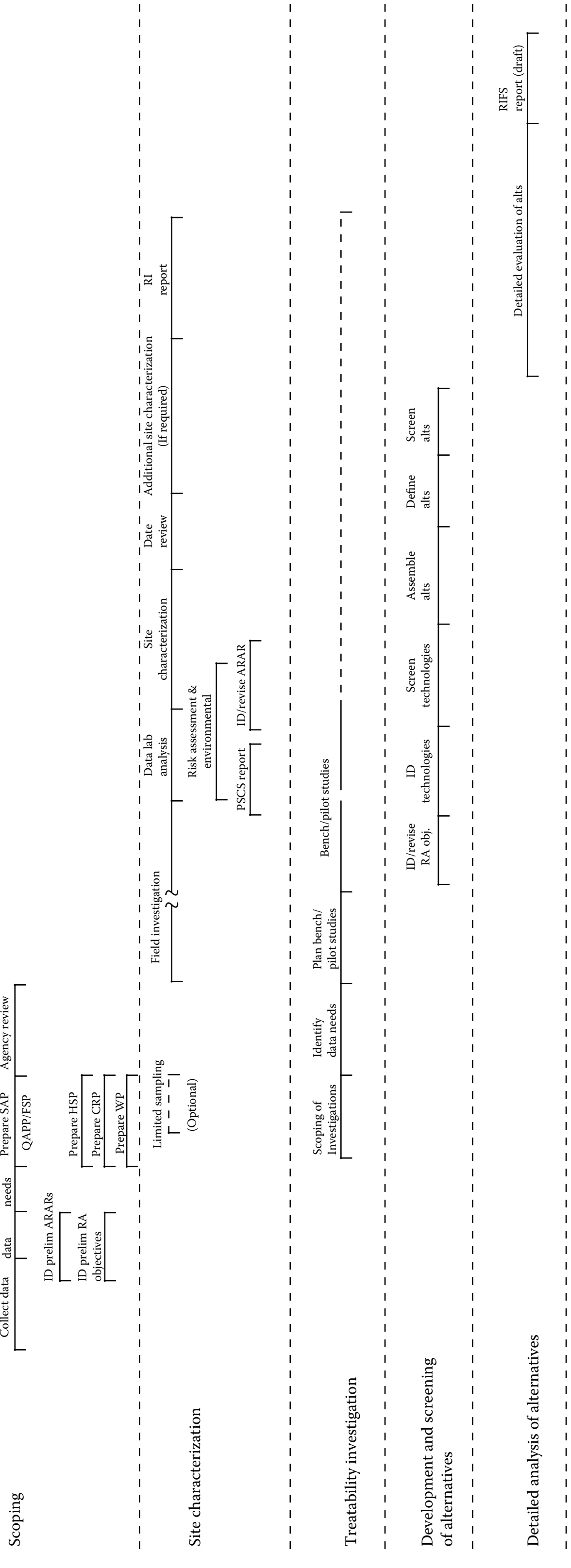


FIGURE 16.3 Generic phased RI/FS timeline.

TABLE 16.1
Data Collection Information

	Hazardous Waste	Migration Pathways			
Information Source	**Sources**	**Subsurface**	**Surface**	**Air**	**Receptors**
U.S. EPA files	×	×	×	×	×
U.S. Geological Survey		×	×		
U.S. DOA, Soil Conservation Service		×	×		
U.S. DOA, Agricultural Stabilization and Conservation Service		×	×		
U.S. DOA, Forest Service			×		×
U.S. DOI, Fish and Wildlife Agencies					×
U.S. DOI, Bureau of Reclamation	×	×	×		
U.S. Army Corps of Engineers	×				
Federal Emergency Management Agency			×		
U.S. Census Bureau					×
National Oceanic and Atmospheric Administration				×	
State Environmental Protection or Public Health Agencies	×	×	×	×	×
State Geological Survey		×	×		
State Fish and Wildlife Agencies					×
Local Planning Boards		×	×	×	×
County or City Health Departments	×	×	×	×	×
Town Engineer or Town Hall	×				×
Local Chamber of Commerce	×				×
Local airport				×	
Local library		×			×
Local well drillers		×			
Sewage treatment plants	×	×	×		
Local water authorities		×			×
City fire departments	×	×	×	×	
Regional geologic and hydrologic publications		×	×		
Court records of legal action	×				
Department of Justice files	×				
State Attorney General files	×				
Facility records	×				
Facility owners and employees	×	×			×
Citizens residing near site	×	×	×	×	×
Waste haulers and generators	×		×		
Site visit reports	×		×	×	×
Photographs	×		×		×
Preliminary assessment report	×	×	×	×	×
Field investigation analytical data	×	×	×	×	
FIT/TAT reports	×	×	×	×	×
Site inspection report	×	×	×	×	×
HRS scoring package	×	×	×	×	×
EMSL/EPIC	×		×		×

Source: From U.S. EPA, Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA, EPA/540/G-89/004, October, U.S. EPA, Washington, DC, 1988.

EMSL, Environmental Monitoring Support Laboratory; EPIC, Environmental Photographic Information Center; DOA, Department of Agriculture; DOI, Department of Interior; FIT, Field Investigation Team; TAT, Technical Assistance Team.

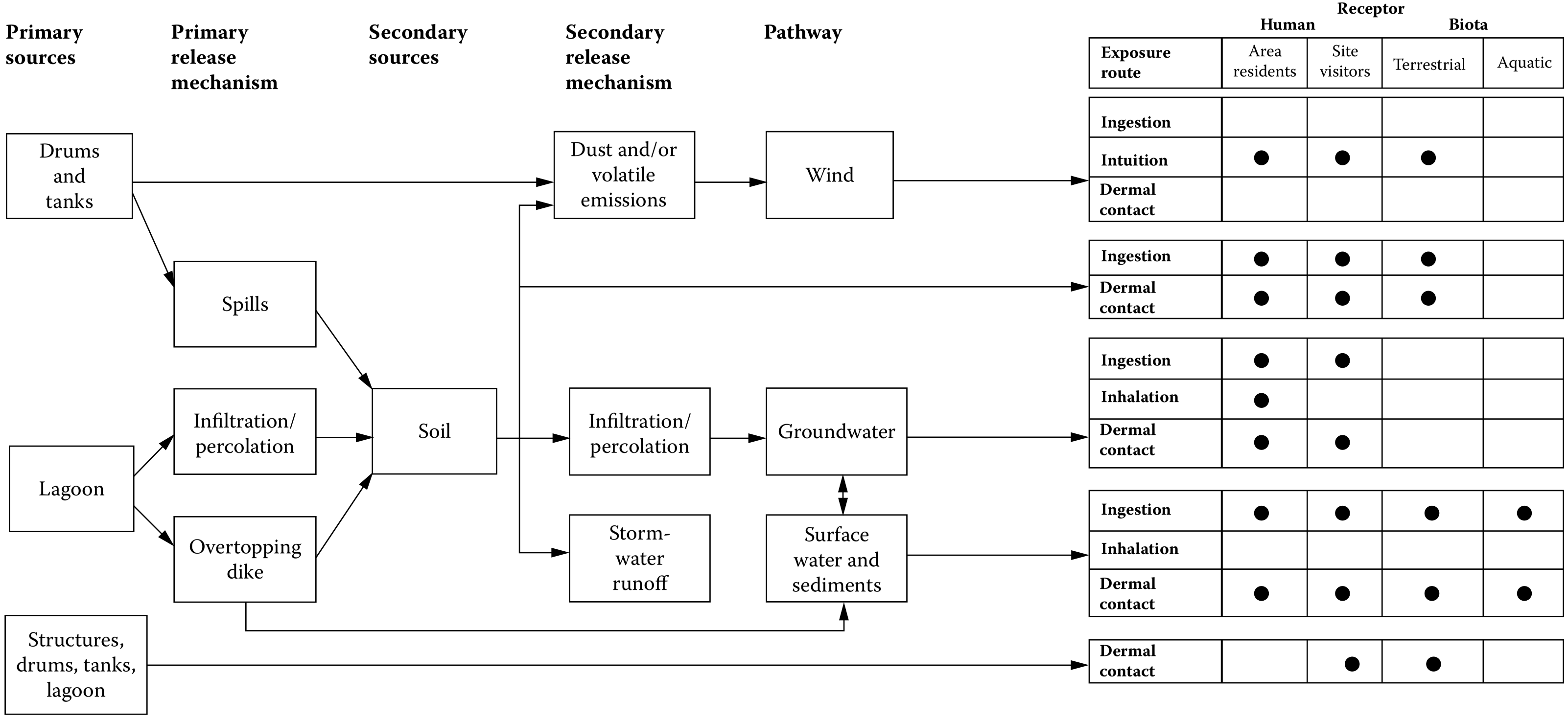


FIGURE 16.4 Example of a conceptual site model. (From U.S. EPA, Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA, EPA/540/G-89/004, U.S. EPA, Washington, October 1988.)

identified, as well as possible uses of the data, including monitoring during implementation, health and safety planning, site characterization, risk assessment, evaluating alternatives, determining the potential responsible party (PRP), and the design of alternatives.

9. *Designing a data collection program.* A data collection program is designed to describe the selection of sampling approaches and analytic options, to establish the level of confidence required for the data, and to develop strategies for sampling and analysis.
10. *Developing a work plan.* A work plan is established that documents the scoping process and presents anticipated future tasks.
11. *Identifying health and safety protocols.* In this stage, health and safety protocols required during field investigations are identified and documented, and a site health and safety plan is prepared to support the field effort and conform to the firm's or agency's health and safety program.
12. *Conducting community interviews.* Community interviews are carried out to obtain information that can be used to develop a site-specific community relations plan that documents the objectives and approaches of the community relations program.

The identification of sampling requirements involves specifying the sampling design, the sampling method, sample numbers, types, and locations, and the level of sampling quality control. Data quality requirements include precision, accuracy, representativeness, completeness, and comparability.

The purpose of a sampling and analysis plan (SAP) is to ensure that sampling data collection activities will be comparable to and compatible with previous data collection activities performed at the site, while providing a mechanism for planning and approving field activities. The plan also serves as a basis for estimating costs of field efforts for inclusion in the work plan.

The SAP consists of the field sampling plan (FSP) and the quality assurance project plan (QAPP) elements. The QAPP describes the policy, organization, functional activities, and quality assurance and quality control protocols necessary to achieve data quality objects dictated by the intended use of the data. The FSP provides guidance for all fieldwork by defining in detail the sampling and data-gathering methods to be used on a project, including plan preparation and responsibilities (timing, preparation and review, field sampling plan, and so on). Table 16.2 lists the format for the FSP and QAPP.

16.4.2 Deliverables and Communications

There are several points during the scoping process when communication is required between the lead agency and its contractor or the support agency (Table 16.3). It is especially important that discussion and information exchange occur if interim actions or limited field investigations are considered necessary.

Deliverables required for all RI/FSs in which field investigations are planned consist of a work plan, an SAP, a health and safety plan (HSP), and a community relations plan (CRP).

16.5 REMEDIAL INVESTIGATION

16.5.1 Site Characterization

Site characterization is necessary in order to determine to what extent a site poses a threat to human health or the environment.[12] Site characterization is the core of RI, and includes the following stages:

1. Conducting field investigations as appropriate
2. Analyzing field samples in the laboratory

TABLE 16.2
Suggested Format for the Sampling and Analysis Plan (Comprising the Field Sampling Plan and Quality Assurance Project Plan)

FSP
Site background
Sampling objectives
Sample location and frequency
Sample designation
Sampling equipment and procedures
Sample handling and analysis

QAPP
Title page
Table of contents
Project description
Project organization and responsibilities
QA objectives for measurement
Sampling procedures
Sample custody
Calibration procedures
Analytical procedures
Data reduction, validation, and reporting
Internal quality control
Performance and systems audits
Preventative maintenance
Data assessment procedures
Corrective actions
Quality assurance reports

Source: U.S. EPA, Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA, EPA/540/G-89/004, U.S. EPA, Washington, DC, October 1988.

3. Evaluating the results of data analysis to characterize the site and develop a baseline risk assessment
4. Determining if data are sufficient for developing and evaluating potential remedial alternatives

16.5.1.1 Field Investigation

The major components of field investigation are air, biota, close support laboratories, RI-derived waste disposal, soil, gas, support, well logging, mapping and survey, geophysical characteristics, well installation, groundwater, source testing, and surface water. A complete field investigation includes at least prefield work, site physical characteristics investigation, contamination sources identification, and contamination determination.

Prefield work

The following prefield work is often needed before beginning an official field work:

1. Analyzing the collected existing data, including site characteristics, history of site (including disposal practices, disposal locations, disposed waste condition, waste degradations, storage of raw materials)

TABLE 16.3
Communications and Deliverables during Scoping

Information Needed	Purpose	Potential Methods of Information Exchange
Interim actions (if necessary)	For lead agency and contractor to identify actions that will abate immediate threat to public health or prevent further degradation of the environment; to obtain concurrence of support agency	Meeting Tech memo Other
Limited field investigations (if necessary)	For lead agency and contractor to improve focus of RI and reduce time and cost; to obtain concurrence of support agency	Meeting Tech memo Other
Summary of existing data; field studies conducted prior to FS; identification of preliminary remedial action alternatives	For lead agency and contractor to confirm need for FS; for lead agency and contractor to plan data collection; to obtain support agency review and concurrence	Meeting Tech memo Other
Documentation of QA and field sampling procedures	For contractor to obtain lead agency review and approval; for lead agency to obtain support agency review and comment	SAP (FSP, QAPP)
Documentation of health and safety procedures	For contractor to obtain lead agency agreement that OSHA safety requirements are met	Health and safety plan
Documentation of all RI/FS tasks	For contractor to obtain lead agency review and approval; for lead agency to obtain support agency concurrence	Work plan

Source: U.S. EPA, Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA, EPA/540/G-89/004, U.S. EPA, Washington, DC, October 1988.

QA, quality assurance; RI, remedial investigation; FS, feasibility study; SAP, sampling and analysis plan; FSP, field sampling plan; QAPP, quality assurance project plan; OSHA, Occupational Safety and Health Administration.

2. Ensuring that access to the site and any other areas to be investigated has been obtained
3. Procuring equipment protective ensembles, air monitoring devices, sampling equipment, decontamination apparatus, and supplies (disposables, tape, notebook, and so on)
4. Coordinating with analytical laboratories, including sample scheduling, sample bottle acquisition reporting, chain-of-custody records, and procurement of close support laboratories or other in-field analytical capabilities
5. Procuring on-site facilities for office and laboratory space, decontamination equipment, and vehicle maintenance and repair, and sample storage, as well as on-site water, electric, telephone, and sanitary utilities
6. Providing for storage or disposal of contaminated materials (e.g., decontamination solutions, disposable equipment, drilling muds and cuttings, well-development fluids, well-purging water, and spill-contaminated materials)
7. Preparing field work, including time table, health, instrument, container, RCRA, equipment, and sample aspects

Site physical characteristics investigation

A site physical characteristics investigation examines the following[12]:

1. Surface features, including facility dimensions and locations, surface disposal areas, fencing, property lines and utility lines, roadways and railways, drainage ditches, leachate

springs, surface water bodies, vegetation, topography, and residence and commercial buildings

2. Geology information, including the geology of unconsolidated overburden and soil deposits (thickness and areal extent of units, petrology, mineralogy, particle size and sorting, and porosity) and the geology of the bedrock (type of bedrock, petrology, structure and texture, discontinuities such as joints, fractures, and foliation, and unusual features such as dikes, lavas, and karsts)
3. Soils and vadose zone information, including soil characteristics (type, holding capacity, temperature, biological activity, and engineering properties), soil chemical characteristics (solubility, ion specification, adsorption, leachability, cation exchange capacity, mineral partition coefficient, and chemical and sorptive properties), and vadose zone characteristics (permeability, variability, porosity, moisture content, chemical characteristics, and extent of contamination)
4. Surface water information, including drainage patterns (overland flow, topography, channel flow pattern, tributary relationships, soil erosion, and sediment transport and deposition), surface water bodies (flow, stream widths and depths, channel elevations, flooding tendencies, and physical dimensions of surface water impoundments; structures; surface water/groundwater relationships), and surface water quality (pH, temperature, total suspended solid, salinity, and specific contaminant concentrations)
5. Hydrogeology information, including geologic aspects (type of water-bearing unit or aquifer; thickness, areal extent of water-bearing units and aquifers; type of porosity; presence or absence of impermeable units or confining layers; depths to water table; thickness of vadose zone), hydraulic aspects (hydraulic properties of water-bearing unit or aquifer, such as hydraulic transmissivity, storativity, porosity, and dispersivity; pressure conditions such as confined, unconfined, or leaky confined), groundwater flow directions (hydraulic gradients horizontally and vertically, specific discharge, rate; recharge and discharge area; groundwater or surface water interactions; areas of groundwater discharge to surface water; seasonal variations of groundwater conditions), and groundwater use aspects (existing or potential aquifers; determination of existing near-site use of groundwater)
6. Atmospheric information, including local climate (precipitation, temperature, wind speed and direction, presence of inversion layers), weather extremes (storms, floods, winds), release characteristics (direction and speed of plume movement, rate, amount, and temperature of release, relative densities), and types of atmospheric hazards and hazards assessment
7. Human populations and land use
8. Ecological information, including information needed for public health evaluation (land use characteristics, water use characteristics) and information needed for environmental evaluation (ecosystem components and characteristics, critical habitats and biocontamination)

Contamination sources identification

The sources of contamination are usually those hazardous materials that are contained in drums, tanks, surface impoundments, waste piles, and landfills, as well as heavily contaminated media (such as soil) affected by the original leaking or spilling source. The purpose of defining sources of contamination is to help to identify the source location, potential releases, and engineering characteristics that are important in the evaluation of remedial actions, as well as waste characteristics, such as the type and quantity of contaminants that may be contained in or released to the environment, and the physical or chemical characteristics of the hazardous wastes present in the source.

Contamination determination

The targets for the determination of the nature and extent of contamination are groundwater, soil, surface water, sediments, and air.

16.5.1.2 Laboratory Analysis

Laboratory analysis provides data that will be used as the basis for decision-making. The data require that the analysis of samples in laboratories meets specific quality assurance and quality control (QA/QC) requirements.

16.5.1.3 Data Analysis

Data analysis should focus on the development or refinement of the conceptual site model by analyzing data on source characteristics, the nature and extent of contamination, the contaminants transport pathways and fate, and the effects on human health and the environment. All field activities, sample management and tracking, and document control and inventory should be well managed and documented to ensure their quality, validity, and consistency.

16.5.1.4 Community Relations Activities

Community relations should be properly maintained throughout the RI, including site characterization.

16.5.1.5 Reporting and Communication

During site characterization, communication is required between the lead and support agencies. The information is mainly on identifying ARARs, and includes a description of the contaminants of concern, the affected media, and any physical features. This information may be supplied by the preliminary site characterization summary or by a letter or other document.

A draft RI report should be produced for review by the support agency and submitted to the Agency for Toxic Substances and Disease Registry (ATSDR) for its use in preparing a health assessment and also to serve as documentation of data collection and analysis in support of the FS. The draft RI report can be prepared any time between the completion of the baseline risk assessment and the completion of the draft FS. Therefore, the draft RI report should not delay the initiation or execution of the FS.

16.5.2 TREATABILITY STUDY

The objectives of the treatability study are primarily to achieve the following:

1. To provide sufficient data to allow treatment alternatives to be fully developed and evaluated during the detailed analyses, and to support the remedial design of a selected alternative
2. To reduce cost and performance uncertainties for treatment alternatives to acceptable levels so that a remedy can be selected

Figure 16.5 shows a decision process for treatability studies.[12]

Certain technologies have been sufficiently demonstrated so that the site-specific information collected during site characterization is adequate to evaluate and cost those technologies without conducting treatability testing.

A treatability study performed during an RI/FS is used to adequately evaluate a specific technology, including evaluating performance, determining process sizing, and estimating costs in sufficient detail to support the remedy selection processes. In general, treatability studies include the following steps:

1. Preparing a work plan (or modifying the existing work plan) for the bench or pilot studies
2. Performing field sampling, and/or bench testing, and/or pilot testing

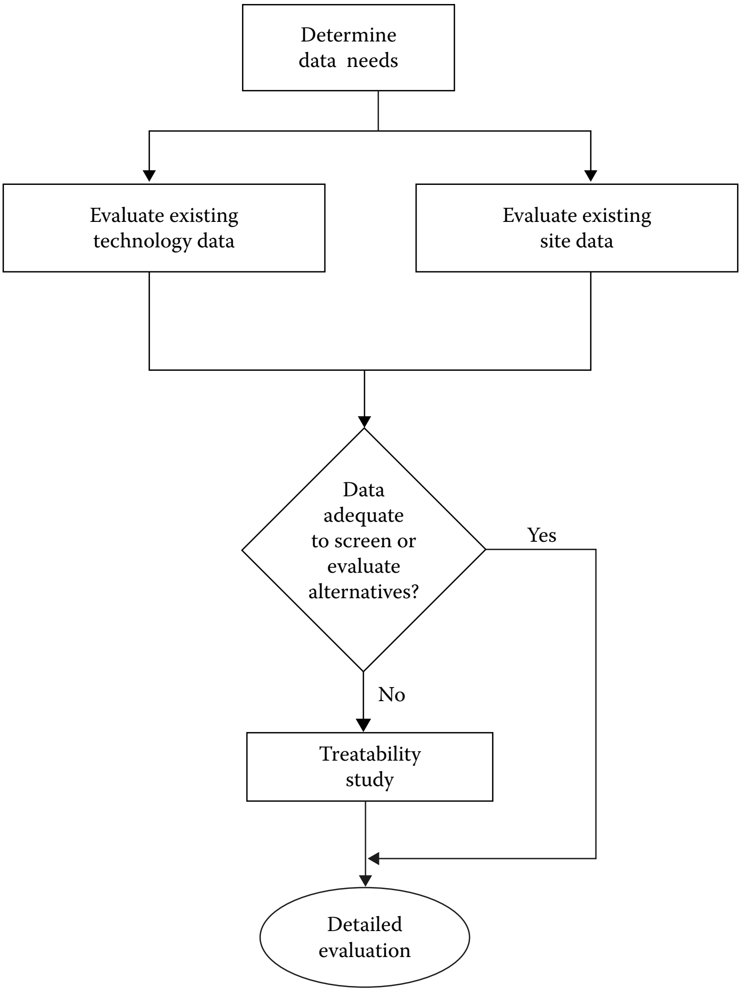


FIGURE 16.5 Treatability investigations.

3. Evaluating data from field studies, and/or bench testing, and/or pilot testing
4. Preparing a brief report documenting the results of testing

A treatability study can be performed by using bench-scale or pilot-scale techniques. Bench study is usually performed in a laboratory, in which comparatively small volumes of waste are tested for the individual parameters of a treatment technology to determine effectiveness of the treatment alternative on the waste, differences in performance between competing manufacturers, differences in performance between alternative chemicals, sizing requirements for pilot-scale studies, feasible technologies to be pilot tested, sizing of those treatment units that would sufficiently affect the cost of implementing the technology, and compatibility of materials with the waste.

Pilot testing is intended to simulate the physical, biological, and chemical parameters of a full-scale process; therefore, the treatment unit size and the volume of waste to be processed in pilot systems greatly increase over those of bench-scale testing. As such, pilot tests are intended to bridge the gap between bench-level analyses and full-scale operation, and are intended to more accurately simulate the performance of a selected full-scale process.

Once a decision is made to perform treatability studies, the type of treatability testing (bench or pilot scale) should be decided. The choice of bench versus pilot testing is affected by the level of development of the technology. For a technology that is well developed and tested, bench studies are often sufficient to evaluate performance on new wastes. For innovative technologies, however, pilot tests may be required as information necessary to conduct full-scale test is either limited or nonexistent.

16.6 FEASIBILITY STUDY

The feasibility study (FS) utilizes the data on site characterization and remedial technology screening to establish remedial alternatives, in turn, to select the cost-effective remedial actions. The FS may be viewed as occurring in three phases:

1. The development of alternatives
2. The screening of alternatives
3. The detailed analysis of alternatives

In practice, the specific point at which the first phase ends and the second phase begins is not so distinct. Therefore, the development and screening of alternatives are discussed together to better reflect the interrelation of these efforts. Furthermore, in many instances, there is only a limited number of available options and it may not be necessary to screen alternatives prior to detailed analysis.

16.6.1 Development and Screening of Alternatives

The primary objective is to develop an appropriate range of waste management options to be analyzed more fully in the detailed analysis phase of the FS.[12] Appropriate waste management ensures the protection of human health and the environment. It may involve, depending on site-specific circumstances, complete elimination or destruction of hazardous substances at the site, significant reduction of concentrations of hazardous substances to acceptable health-based levels, and prevention of exposure to hazardous substances via engineering or institutional controls, or some combination of the above.

Alternatives are typically developed concurrently with the RI site characterization, with the results of one influencing the other in a methodology of iteration. Alternatives for remediation are developed by assembling combinations of technologies, including the media to which they would be applied, into alternatives that address contamination on a site-wide basis or for an identified operable unit. The methodology of development and screening of alternatives consists of six general steps[12]:

1. Developing remedial action objectives specifying the contaminant and media of interest, exposure pathways, and preliminarily remediation goals that permit a range of treatment and containment alternatives to be developed on the basis of chemical-specific ARARs when available, other available information, and site-specific, risk-related factors
2. Developing general response actions for each medium of interest defining containment, treatment, excavation, pumping, or other actions, singly or in combination, that may be taken to satisfy the remedial action objectives for the site
3. Identifying volumes or areas of media to which general response actions might be applied, taking into account the requirements for protectiveness as identified in the remedial action objectives and the chemical and physical characterization of the site
4. Identifying and screening the technologies applicable for each general response action to eliminate those that cannot be implemented technically at the site and to specify remedial technology types

5. Identifying and evaluating technology process options to select a representative process for each technology type retained for consideration, alternative development and evaluation, with an intention to represent the broader range of process options within a general technology type
6. Assembling the selected representative technologies into alternatives representing a range of treatment and containment combinations, as appropriate

16.6.2 DETAILED ANALYSIS OF ALTERNATIVES

Analysis and presentation of the relevant information are needed to allow decision-makers to select a site remedy.

16.6.2.1 Overview of Detailed Analysis of Alternatives

A detailed analysis of alternatives consists of the following:

1. Further definition of each alternative, if necessary, with respect to the volumes or areas of contaminated media to be addressed, the technologies to be used, and any performance requirements associated with those technologies
2. An assessment and a summary profile of each alternative against the evaluation criteria
3. A comparative analysis among the alternatives to assess the relative performance of each alternative with respect to each evaluation criterion

16.6.2.2 Criteria for Detailed Analysis of Alternatives

During the detailed analysis, each alternative is assessed against the evaluation criteria. The results provide decision-makers with sufficient information to adequately compare the alternatives, select an appropriate remedy for a site, and demonstrate satisfaction of the CERCLA remedy selection requirements in the record of decision:

1. *Overall protection of human health and the environment.* This is the overall aim of the process.
2. *Compliance with ARARs.* It is considered how each alternative will comply with ARARs, or if a waiver is required and how it is justified.
3. *Long-term effectiveness.* The long-term effectiveness of alternatives in maintaining protection of human health and the environment after response objectives have been met is investigated.
4. *Reduction of toxicity, mobility, and volume through treatment.* The anticipated performance of the specific treatment technologies an alternative may employ is evaluated.
5. *Short-term effectiveness.* This is an examination of the effectiveness of alternatives in protecting human health and the environment during the construction and implementation of a remedy until response objectives have been met.
6. *Implementability.* This is an evaluation of the technical and administrative feasibility of alternatives and the availability of the required goods and services.
7. *Cost.* Capital and operation and maintenance costs of each alternative are evaluated.

The overall criteria include cost-effectiveness, utilization of permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable, and satisfaction of the preference for treatment to reduce toxicity, mobility, or volume as a principal element, or the provision of an explanation if this preference is not met.[12] This is needed in order to attain acceptance by the support agency and the community.

16.6.2.3 Factors Affecting Potentially Applicable Remedial Technologies

The following factors may affect the potentially applicable remedial technologies:

1. *Site characteristics*, which may limit or promote the use of certain remedial technologies
2. *Waste characteristics*, which may limit the effectiveness or feasibility of the remedial technologies: quantity/concentration, chemical composition, acute toxicity, persistence, biodegradability, radioactivity, ignitability, reactivity/corrosivity, infectiousness, solubility, volatility, density, partition coefficient, compatibility with chemicals, and treatability
3. *Technology limitations*, including level of technology development, performance record, inherent construction, operation, and maintenance problems

16.6.2.4 Procedure for Detailed Analysis of Alternatives

The procedure for a detailed analysis of alternatives can be generalized into the following steps[14]:

1. Data analyzing
2. Modeling, such as groundwater modeling
3. Defining the objectives of remedial actions
4. Identifying technologies
5. Posing alternatives—preliminary screening
6. Scrutinizing selected alternatives, including technical analysis, regulation compliance, public health and environmental analysis, and cost analysis
7. Recording the feasibility study
8. Selecting the remedial alternative

16.7 REMEDIAL TECHNOLOGIES

This section will cover site control for waste movement, site cleanup technologies, and point-of-entry protection. The main focus will be on site cleanup technologies including remediation for contaminated groundwater, soil, and sediments. The technologies involve *in situ* treatment, which converts contaminants to less hazardous materials, and *ex situ* methodologies, which use soil excavation or groundwater pumping to remove contaminants from the site, and then treat them.[14–102]

The techniques to remove the free product of nonaqueous phase liquids (NAPL) will not be included in this chapter, because NAPL is one of the main releases from leaking underground storage tanks and is covered in Chapter 18, "Remediation of Sites Contaminated by Underground Storage Tank Releases," which addresses remediation techniques for organic contaminants, especially volatile organic compounds (VOCs) in soil and groundwater.

16.7.1 SURFACE SITE CONTROL OF WASTE MOVEMENT

The purpose of site control is to achieve the following:

1. To prevent waste movement (in air, surface water, and groundwater)
2. To contain wastes in a limited area
3. To reduce and eliminate impact on the environment
4. To lower the overall remedial cost

Gas may be formed by microbiological degradation of organics, evaporation and volatilization of volatile materials, or chemical reactions. The high combustibility of methane—a major component of landfill-generated gas—is a potential hazard. The emission of gas can be accelerated by elevated temperatures and venting conditions. Air pollution, which may result from gaseous emissions and fugitive dusts, should be controlled at uncontrolled waste sites. The main tasks include control of air contamination associated with natural forces, control of air contamination associated with remedial actions, and monitoring air pollution.

16.7.1.1 Control of Hazardous Gas Emission

According to U.S. EPA, the techniques that are used to control air pollution include the following[15]:

1. Covering surface impoundments
2. Passive perimeter gas control systems
3. Active perimeter gas control systems
4. Active interior gas collection/recovery systems

Covering surface impoundments

Covering surface impoundments is important for the control of hazardous gases emission. A common covering method places a barrier at the water–air interface to reduce gaseous emissions. The technology available includes lagoon covers, floating immiscible liquids, and floating (polypropylene) spheres.

Covers provide temporary methods for reducing volatile emission from surface impoundment. Floating lagoon covers function as both a surface water control mechanism and a mechanism for controlling gaseous emissions. They are suitable in situations where more than a year will elapse before final closure of a lagoon. They are not suitable for lagoons with weak berms or for lagoons located in areas that cannot support heavy construction equipment.

Floating immiscible liquids are suitable for controlling emissions of water-soluble organics. However, the effectiveness is temporary, estimated to be between one and two weeks. Some chemicals in water may prevent the formation of a monolayer, and wave action can destroy the monolayer effectiveness.

Floating polyethylene spheres are capable of reducing volatile emissions by up to 90%. Polyethylene spheres are compatible with a broad range of compounds including inorganic acids and bases and most aromatic and aliphatic organic compounds.[16]

Passive perimeter gas control systems

Passive gas control systems control gas movement by altering the paths of flow without the use of mechanical components. There are generally two types, high-permeability and low-permeability.

High-permeability passive perimeter gas control systems entail the installation of highly permeable (relative to the surrounding soil) trenches or wells between the hazardous waste site and the area to be protected (Figure 16.6). The permeable material offers conditions more conductive to gas flow than the surrounding soil, and provides paths of flow to the points of release. High-permeability systems usually take the form of trenches or wells excavated outside the site, then backfilled with a highly permeable medium such as coarse crushed stone.

Low-permeability passive perimeter gas control systems (Figure 16.7) effectively block gas flow into the areas of concern by using barriers (such as synthetic membranes or natural clays) between the contaminated site and the area to be protected. In the low-permeability system, gases are not collected and therefore cannot be conveyed to a point of controlled release or treatment. The low-permeability system can also alter the paths of convective flow.

High-permeability and low-permeability passive perimeter gas control systems are often combined to provide controlled venting of gases and blockage of available paths for gas migration.[15]

The applications and limitations of passive gas control systems must also be understood. They can be used at virtually any site where there is the capability to trench or drill and excavate to at least the same depth as the landfill. Limiting factors could include the presence of a perched water table or rock strata. Passive vents should generally be expected to be less effective in areas of high rainfall or prolonged freezing temperatures.

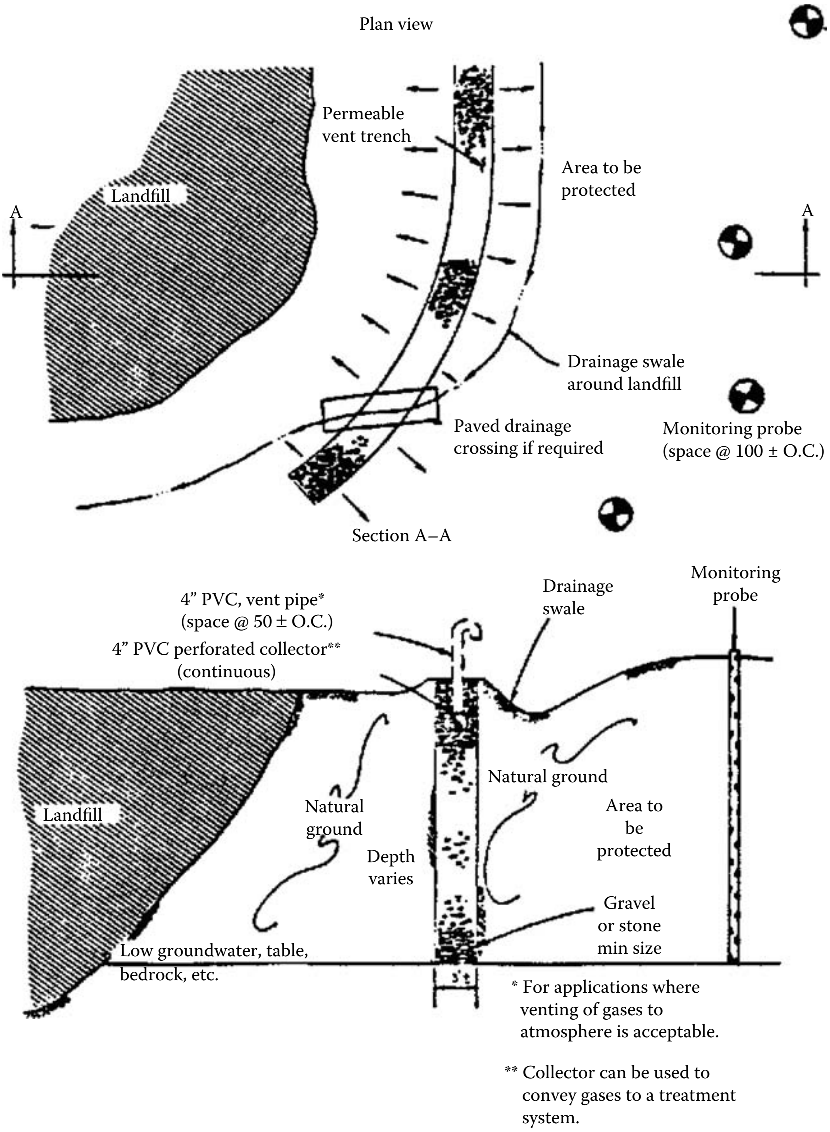


FIGURE 16.6 Passive gas control using a permeable trench.

The cost of passive gas control systems is low. The "passive" concept has virtually no operating or maintenance costs. However, it is recommended that periodic inspections be made and that the surface gas be periodically monitored in the area being protected to ensure that the systems are performing their intended functions.

Active perimeter gas control systems

Active perimeter gas control systems control off-site gas migration with the use of an active control system to alter pressure gradients and paths of gas movement by mechanical means. Three or four major components are required in active perimeter gas control systems:

1. Gas extraction wells
2. Gas collection headers

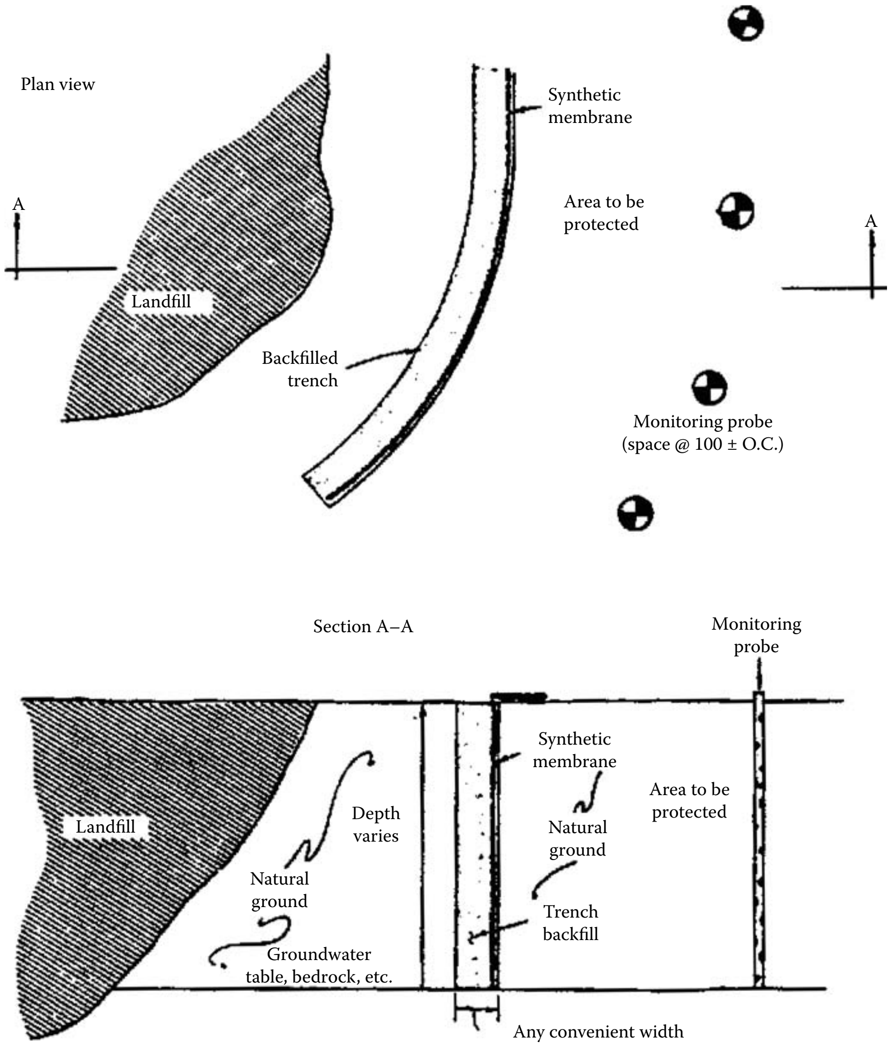


FIGURE 16.7 Passive gas control synthetic membrane.

3. Vacuum blowers or compressors
4. Gas treatment or utilization systems

Figure 16.8 shows an active perimeter gas extraction system. Active systems can be used at virtually any site where there is the capability to drill and excavate through the materials in the action area to the required depth. Limiting factors of active systems include the presence of free-standing leachate (i.e., saturation) or impenetrable materials. Active perimeter gas control systems are not sensitive to freezing or saturation of the surface or cover soils.

Centrifugal blowers create a vacuum through the collection headers and wells to the wastes and ground surrounding the wells. A pressure gradient is thereby established, inducing flow from the landfill (which is normally under positive pressure) to the blower (creating a negative, or vacuum, pressure). Subsurface gases flow in the direction of decreasing pressure gradient (through the wells, the header, and the blower) and are released directly to the atmosphere, treated and released to the atmosphere, or recovered for use as fuel.[15]

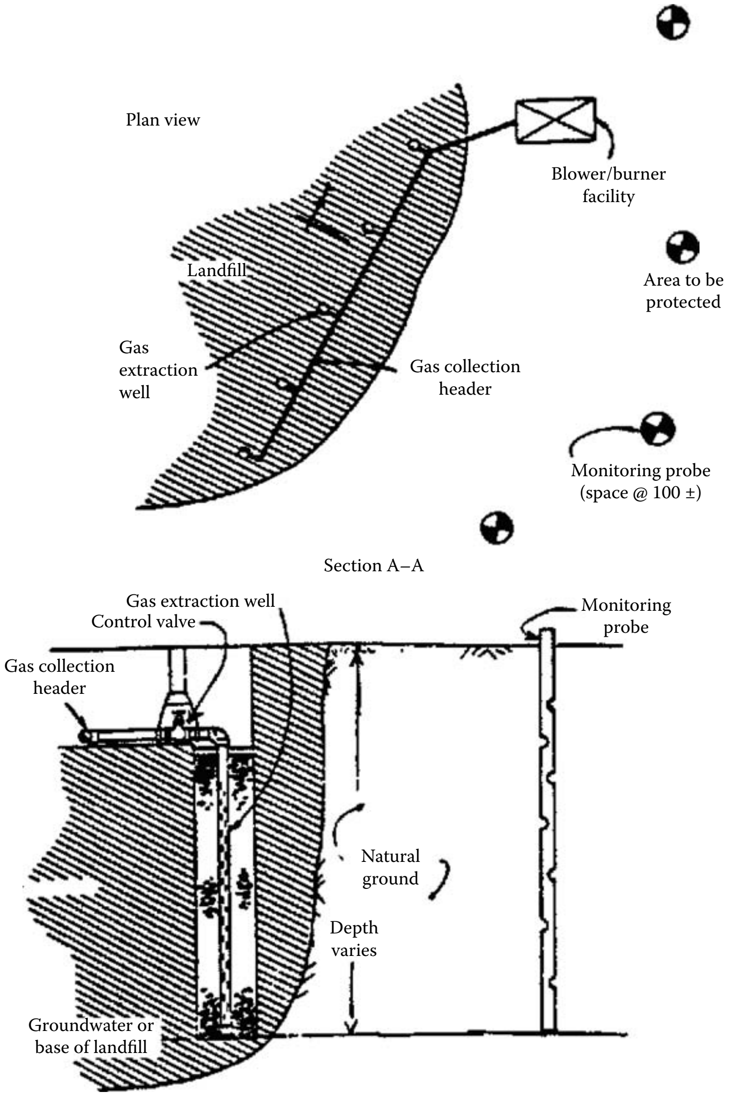


FIGURE 16.8 Active gas extraction.

Active interior gas collection/recovery system

Similar to the active perimeter gas control system, an active interior gas collection/recovery system consists of gas extraction wells, gas collection headers, vacuum blowers or compressors, and a treatment system. However, it is used to directly remove the hazardous gases from the site (beneath a landfill), instead of off-site removal. Figure 16.9 shows a schematic view of such a system.

Applications and limitations of the active interior gas collection/recovery system are similar to those of the active parameter gas control system. The active interior gas collection/recovery systems can be used at virtually any site where there is the capability to drill and excavate through landfilled material to the required depth. Limiting factors of the active interior gas collection/recovery systems include the presence of free-standing leachate or impenetrable materials within the landfill.

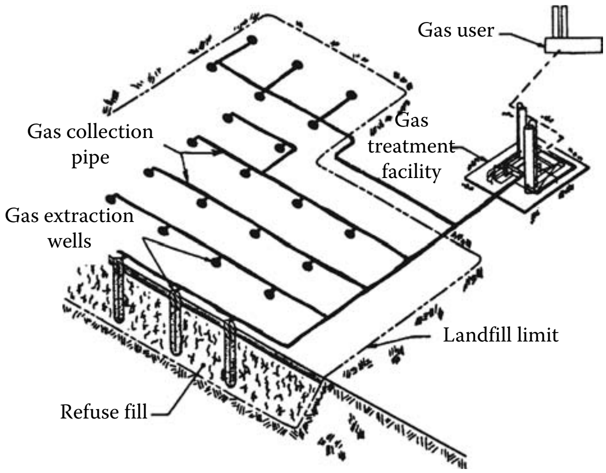


FIGURE 16.9 Gas collection and recovery system.

16.7.1.2 Control of Fugitive Dusts

Fugitive dusts are caused by wind erosion on waste sites, by vehicular traffic, and by excavation of waste during remedial action. The most commonly used control methods include the following:

1. Dust suppressants
2. Wind fences/screens
3. Water spraying

The dust suppressant method uses chemicals to (temporarily) strengthen bonds between soil particles and reduce fugitive dust emissions from inactive waste piles. Dust suppressant is expected to be 100% effective for a period of one to four weeks if the use of chemical is appropriate and undisturbed. Dust suppressants can also be used to control dust from work areas; however, it is less effective and requires frequent reapplications.

The wind fences/screens method uses screens, which take up or deflect a sufficient amount of wind so that the wind velocity is lowered below the threshold required for initiation of soil movement. The maximum reduction of wind velocity is expected for a distance of one to five fence heights downstream. Tests have shown that wind screens can achieve up to 60% efficiency in controlling inhalable particulates and 75% of total suspended particulates at wind speeds of about 10 to 13 mi/h.

The water spraying method is most commonly used to reduce fugitive dusts emission by spraying water onto the exposed surface area, for example, along active travel paths, excavation areas, and truck boxes loaded with soils.

16.7.1.3 Treatment of Emitted Gases

The gaseous phase of organic and inorganic contaminants that are collected from gaseous wastestreams can be treated. The most common methods are carbon adsorption and scrubbing with water or chemicals.

A mobile gaseous waste treatment unit developed by QUAD Environmental Technologies Corporation[17] utilizes atomizing nozzles within the scrubber chamber to disperse droplets of a controlled chemical solution, resulting in 85 to 100% removal (for benzene, toluene, phenol, and so on). Very small droplet sizes (less than 10 μm) and long retention times allow the use of a "once-through system" that generates low volumes of liquid residuals. This technology is best suited for

VOCs, although it is claimed to treat gaseous wastestreams containing a wide variety of organic or inorganic contaminants.

16.7.1.4 Surface Water Control through Control of Run-On and Runoff

Surface water control is necessary to minimize contamination of surface waters, to prevent surface water infiltration, and to prevent off-site transport of surface waters that have been contaminated. Control of run-on and runoff will accomplish the following:

1. It will prevent surface runoff, which carries contaminants to rivers and to places where the contaminants will infiltrate and percolate into soil and groundwater.
2. It will prevent surface water runoff from entering contaminated areas and in turn migrate into the contaminated plume. The methodology used involves dikes, terraces, diversion channels, floodwalls, grading, and revegetation, for example, using bench, terrace, or grading to divert or intercept surface water.

16.7.1.5 Surface Water Control through Prevention of Infiltration

Capping

Capping is a process used to cover buried waste materials to prevent them coming into contact with the land surface. Hence, capping on landfill can prevent infiltration of surface water to ensure minimum liquid migration through the waste. The materials used for capping usually have a permeability lower than or equal to the underlying liner system or natural soils, and high resistance to damage by settling or subsidence. Capping requires low cover maintenance and increases the efficiency of site drainage.

Capping is necessary whenever contaminated materials are to be buried or left in place at a site. Capping is often performed together with groundwater extraction or containment technologies to reduce further plume development, thus reducing the time needed to complete groundwater cleanup operations. In addition, groundwater monitoring wells are often used to detect any unexpected migration of capped wastes. A gas collection system should always be incorporated into a cap when wastes may generate gases. Capping is also associated with other surface water control technologies as discussed later. The main disadvantages of capping are the need for long-term maintenance and uncertain design life. A final cap should be inspected on a regular basis for signs of erosion, settlement, ponding liquid, invasion of deep-rooted vegetation, or subsidence, especially in the first six months when problems are most likely to appear. However, the long-term maintenance requirements are usually considerably more economical than excavation and removal of the wastes. Another disadvantage is the high cost of proper soil and drainage materials in certain areas of the country.

Caps can be single-layered or multilayered depending on the cap materials used. For construction and implementation considerations the reader can refer to U.S. EPA[15] and Matrecon, Inc.[18]

Grading

Grading is the technique used to reshape the surface in order to minimize infiltration by maximizing the amount of water thath will run off without causing significant erosion. Grading is often performed in conjunction with surface sealing practices and revegetation as part of an integrated landfill closure plan.

Grading is a relatively inexpensive remedial action component when suitable cover materials are available on site or close to the disposal site. Surface grading serves several functions:

1. It reduces ponding, which minimizes infiltration and reduces subsequent differential settling
2. It reduces runoff velocities and do reduces soil erosion
3. It roughens and loosens soils in preparation for revegetation
4. It is a factor in reducing or eliminating leaching of wastes

It is important upon completion of grading to establish vegetation cover as quickly as possible. This cover is essential to help prevent drying and erosion.

Revegetation

Revegetation is a cost-effective method to stabilize the surface of hazardous waste disposal sites, especially when preceded by capping and grading. Revegetation decreases erosion by wind and water and contributes to the development of a naturally fertile and stable surface environment. It may be part of a long-term site reclamation project, or it may be used on a temporary or seasonal basis to stabilize intermediate cover surfaces at waste disposal sites.

A systematic revegetation plan includes the following steps:

1. Selection of suitable plant species
2. Seedbed preparation
3. Seeding/planting
4. Mulching and/or chemical stabilization
5. Fertilization
6. Maintenance

Revegetation may not be feasible at disposal sites with high cover soil concentrations of phytotoxic chemicals, unless these sites are properly sealed and vented and then recovered with suitable topsoil. In some cases, clays or synthetic barriers below supporting topsoil in poorly drained areas may cause swamping of the cover soil and subsequent anaerobic conditions. A cover soil that is too thin may dry excessively in arid seasons and irrigation may be necessary. Improperly vented gases and soluble phytotoxic waste components may kill or damage vegetation. The roots of shrubs or trees may penetrate the waste cover and cause leaks of water infiltration and gas exfiltration. Also, periodic maintenance of revegetation areas (liming, fertilizing, mowing, replanting, or regarding eroded slopes) will add to the costs associated with this remedial technique.

Although vegetation cover requires frequent maintenance, it prevents the more costly maintenance that would result from erosion of surface soils.

16.7.1.6 Surface Water Control through Control of Erosion

Control of erosion is usually implemented through reducing slope length (using interception dikes, diversion channels, and terraces), slope steepness (using proper grading), or improving soil management, as well as controlling infiltration or erosion (using grading and revegetation). Most of these technologies have been addressed above (e.g., grading and revegetation) or will be addressed later (e.g., dikes and channels).

16.7.1.7 Surface Water Control through Collection and Transfer of Water

The purpose of the collection and transfer of water is to collect water that has been diverted away from the site or been prevented from infiltrating, and discharging or transferring the collected water to storage or treatment.[15] Surface water control can be carried out using dikes and berms, channels, chutes, and downpipes.

Dikes and berms are well-compacted earthen ridges or ledges located immediately upslope from or along the perimeter of a disturbed area (e.g., disposal sites). They can prevent excessive erosion of newly constructed slopes until more permanent drainage structures are installed or until the slope is stabilized with vegetation, and are widely used to provide temporary isolation of wastes until they can be removed or effectively contained, particularly during excavation and removal operations, to prevent runoff and mixing of incompatible wastes. For cost estimates of various technologies used to prevent infiltration one can refer to the U.S. EPA publication “Remedial Action at Waste Disposal Sites.”[15]

Dikes and berms usually provide short-term protection of critical areas by intercepting storm runoff and diverting the flow to natural or manmade drainage ways, to stabilized outlets, or to sediment traps. These can only handle relatively small amounts of runoff and are not recommended for drainage areas larger than five acres.[19] Channels are wide and shallow excavated ditches used to intercept or divert water as well as collect and transfer the diverted water elsewhere. Chutes (or flumes) and downpipes are used to carry surface runoff from one level to a lower level without erosive damage and to enable the transfer of water away from diversion structures. They provide temporary erosion control while slopes are being stabilized with vegetative growth. Chutes are limited to head-drops of about 5.5 m (18 ft) or less, and downpipes are limited to drainage areas five acres in size.

16.7.1.8 Surface Water Control through Protection from Flooding

Flood control dikes (or embankment), levees, and floodwalls are the most common flood protection structures. They are used in areas subject to inundation from tidal flow or riverine flooding, but not for areas directly within open floodways. Levees create a barrier to confine floodwaters to a floodway and to protect structures behind the barrier. Floodwalls perform much the same function as levees, but are constructed from concrete.

16.7.1.9 Surface Water Control through Storage and Discharge of Water

Sedimentation basins can be used to collect and store surface water flow and to settle suspended solid particles. Seepage basins and ditches can be used to discharge uncontaminated or treated water downgradient of the site. It is important to separate clean surface runoff from contaminated water and store and treat them separately. Table 16.4 summarizes the surface water control methods.

16.7.1.10 Control of Waste Movement at Roads and Residential Areas

Site control at roads and residential areas will include at least the following activities:

1. Clearing the road, or, alternatively, building a detour route
2. Establishing signs at dangerous areas

TABLE 16.4
Primary Functions of Various Surface Water Control

Technology	Prevent or Intercept Run-on/Runoff	Prevent or Minimize Infiltration	Reduce Erosion	Collect and Transfer Water	Protection from Flooding	Discharge Water
Capping		×				
Lagoon covers		×				
Grading	×		×			
Revegetation	×	×	×			
Dikes and berms	×		×		×	
Channels and waterways			×	×		
Terraces and benches	×		×			
Chutes and downpipes			×	×		
Seepage basins and ditches						×
Sedimentation basins and ponds	×					×
Levees and floodwalls	×				×	

Source: U.S. EPA, Remedial Action at Waste Disposal Sites, EPA/625/6-85/006, U.S. EPA, Washington, DC, 1985.

3. Preventing fire associated with low ignition point volatile organics
4. Evacuating residents and protecting the area, or providing a facility for treatment of drinking water and cleanup of the site
5. Providing subsurface control of migration of contaminants

16.7.2 SUBSURFACE SITE CONTROL OF WASTE MOVEMENT

16.7.2.1 Controls of Groundwater

The purpose of groundwater control includes the following aspects:

1. To contain a plume
2. To prevent migration of contaminated groundwater that may enlarge the size of the contaminated area and lead to the contamination of clean groundwater
3. To prevent clean groundwater from moving into the contaminated site, which may cause further migration and enlargement of the contaminated area
4. To prevent leachate formation by lowering the water table beneath a source of contamination or by preventing infiltration
5. To pump out the contaminated groundwater or perform *in situ* treatment to halt the source of contamination

Groundwater pumping

Groundwater pumping can remove the contaminated plume directly, or reconfigure the migration of groundwater through the cone of depression, which can either prevent further migration of contaminants or prevent movement into clean groundwater, or lower the water table. Extraction wells or a combination of extraction and injection wells can be used for this purpose. Figure 16.10a shows how an extraction well controls the movement of groundwater through the cone of depression, thus ensuring that clean water will be withdrawn from the domestic well. Figure 16.10b shows the use of a line of extraction wells to protect a domestic well.

The cone of depression can be evaluated based on an expression that relates to the measured saturated thickness of the aquifer, the height of water at the well from the bottom of the aquifer, pumping rate, hydraulic conductivity, and the radius of the observation wells (Jacob and Theis methods). Note that the formulae for calculation of the cone of depression are different for different confining conditions, for example, unconfined, artesian, and leaking confined aquifers. Various computer models have been established for groundwater flow, or associated with particle transfer or with chemical reactions (such as MODFLOW, MODPATH, and MOC, developed by the U.S. Geological Survey). Graphical or computer-aided calculations are usually used for composite drawdowns by multiwells (extraction or injection).

Subsurface drains

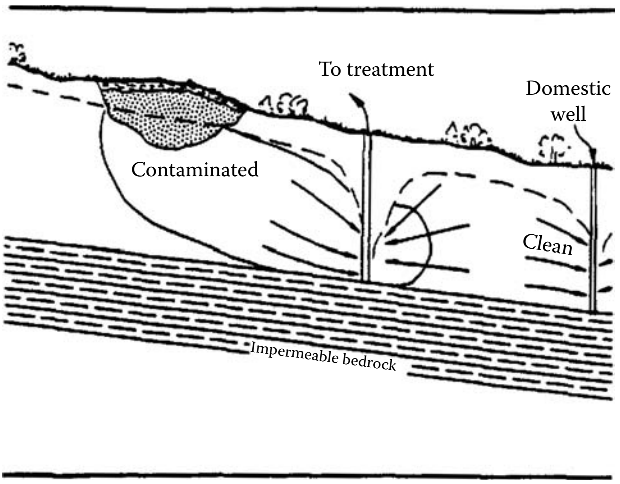
Subsurface drains include any type of buried conduits that convey and collect aqueous discharges by gravity flow (Figure 16.11). Water collected in a storage tank or a collection sump is then pumped for further treatment. Filters are usually needed in drain systems to prevent fine particles from causing clogging.

Subsurface drains function like an infinite line of extraction wells, and can be used to contain and remove a plume or to lower the groundwater table (Figure 16.12). They are more cost-effective than pumping for shallow contamination problems at depths of less than 12 m (40 ft). Depths may be increased if the site is stable, if the soil has a low permeability, and if no rock excavations are encountered.

Subsurface barriers

Subsurface barriers, low-permeability cutoff walls or diversions below ground are used to contain, capture, or redirect groundwater flow. The most common method uses bentonite slurry

(a) Cross-sectional view



(b) Plan view

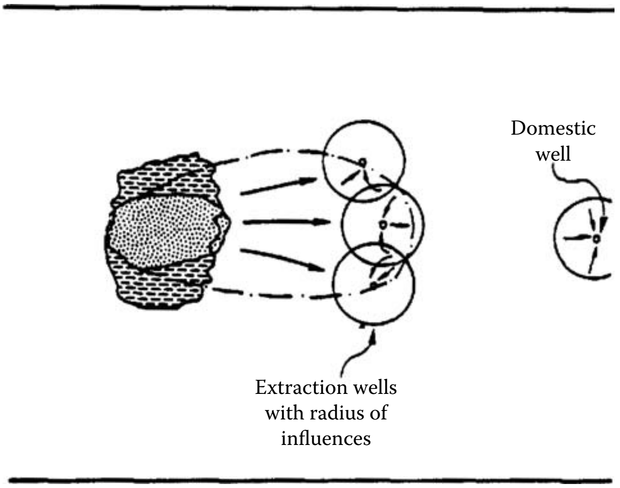


FIGURE 16.10 Containment using extraction wells: (a) cross-sectional view; (b) plan view.

walls. Less common are other types of slurry walls (such as concrete), grouted barriers, and sheet piling cutoffs. The limiting factor for slurry walls is site topography, which may cause increasing engineering effort and cost. Also, slurry walls may not maintain good performance over a long period of time.

Grouted barriers use a variety of fluids injected into a rock or soil mass, which is set in place to reduce water flow and strengthen the formation. Grouted barriers are seldom used for containing groundwater flow in unconsolidated materials around hazardous waste sites because they cost more and have lower permeability than bentonite slurry walls. Nevertheless, they are suited to sealing voids in rock for waste sites remediation.

Sheet piling uses wood, precast concrete, or steel to form barriers for groundwater. They are seldom used because of high costs and unpredictable wall integrity, except for temporary dewatering for other construction or as erosion protection for other barriers. Bottom sealing is the technique used to place a horizontal barrier beneath an existing site to act as a floor and prevent downward migration of contaminants.

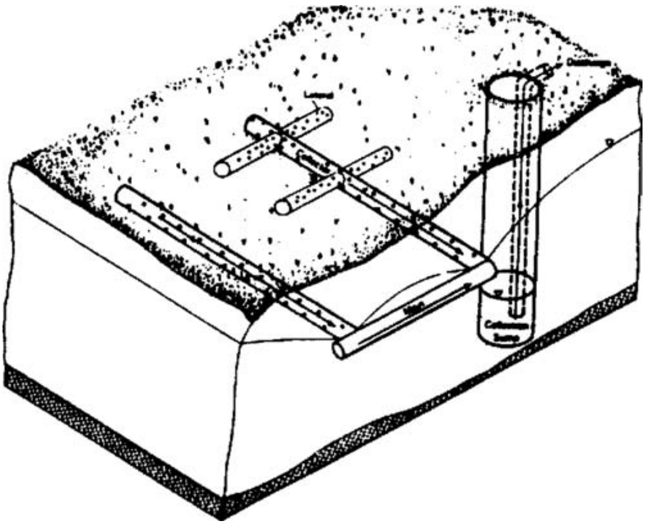


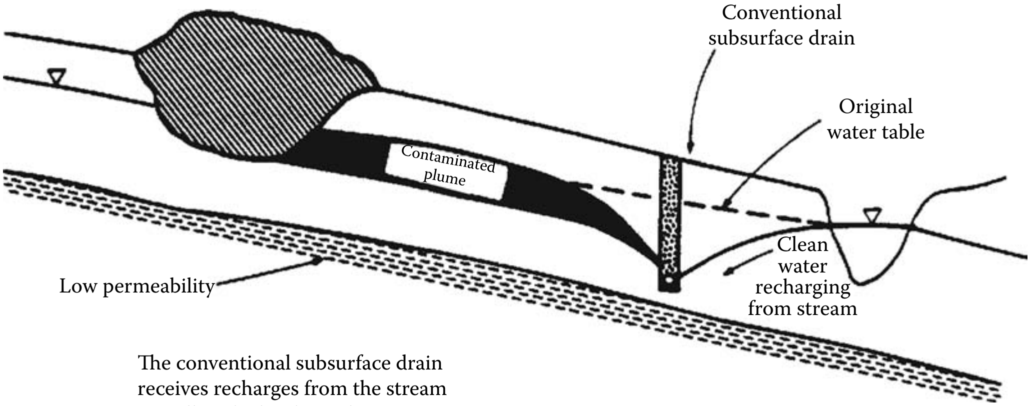
FIGURE 16.11 Subsurface drainage system components.

Control of sediments

Various technologies such as dikes, covers, and *in situ* grouting can be used for the control of migration of contaminants from contaminated sediments or for prevention of contamination of clean sediments.

16.7.3 *IN SITU* GROUNDWATER REMEDIATION

In situ groundwater treatment is an alternative to the conventional pump-and-treat methods. *In situ* treatment uses biological or chemical agents or physical manipulations that degrade, remove, or immobilize contaminants. *In situ* treatment technologies can usually treat both contaminated groundwater and soil. In many instances a combination of *in situ* and aboveground treatment will achieve the most cost-effective treatment at an uncontrolled waste site.



The conventional subsurface drain receives recharges from the stream as well as the leachate plume, resulting in larger collection and treatment.

FIGURE 16.12 Use of a one-sided subsurface drain for reducing flow from uncontaminated sources.

16.7.3.1 Biological Treatment

Bioremediation is a technique for treating zones of contamination by microbial degradation, which involves altering the environmental conditions to enhance microbial catabolism or cometabolism of organic contaminants, resulting in the breakdown and detoxification of those contaminants.[15] According to microbial metabolic activity, bioremediation can be classified into three categories[20,21]:

1. Aerobic respiration, in which oxygen is required as a terminal electron acceptor
2. Anaerobic respiration, in which sulfate or nitrate serves as the terminal electron acceptor
3. Fermentation, in which the microorganism rids itself of excess electrons by exuding reduced organic compounds

The *in situ* biological treatment technique for organic contaminants is fully discussed in the Chapter 17. An example of a cost estimate for bioremediation is shown in Table 16.5. The data is based on a U.S. EPA study[15] of a project performed by Biocraft Laboratories, Waldwick, New Jersey.

16.7.3.2 Chemical Treatment

Chemical treatment of groundwater uses chemicals to immobilize or detoxify the organic or inorganic contaminants. Appropriate chemicals should be selected and pH or Eh are generally controlled. For example, for *in situ* treatment of inorganics, the most commonly used chemicals are sulfide, carbonate/hydroxide, and phosphate, which lead to the oxidation or reduction of contaminants or cause the precipitation of target materials;[22–24] for *in situ* treatment of organics, the methods of chemical oxidation and hydrolysis are used for detoxification, and polymerization is used to reduce the mobility of the contaminants. Generally, it is easier to control chemical processes in pumped

TABLE 16.5

Example—Summary of Project Costs[a] (Biocraft Laboratories, Waldwick, NJ)

Task	Actual Expenditure	Unit Cost	Period of Performance
Hydrogeological study: problem definition	$73,948	—	1976–1978
In-house process development (R&D)	$446,280	—	1978–1981
Groundwater collection/injection system total	$184,243	—	
Design	($61,490)		
Installation	($122,753)		1980–1981
Biostimulation plant design and construction total	$193,187	—	1981
Engineering design	($58,400)	—	1981
Masonry construction	($73,975)	—	1981
Equipment and miscellaneous installation	($60,812)	—	1981
Capital and R&D total	$926,158	—	
Operation and maintenance (O&M)			
Utilities	$47.40/d		
Electricity: 26.4 kW (24 h/d)	($195.25/d)	$7.396/kW	1983 rates
Steam: 72 lb (33 kg)/d & 90 psi	($61.92/d)	$0.86/lb	1981
Maintenance (see text)	$159.93/d		
O&M total	$226.53/d		
Total water treated	13,680 gal/d (51,779 L/d)	$0.0165/gal ($0.0044/L)	

Source: U.S. EPA, Remedial Action at Waste Disposal Sites, EPA/625/6-85/006, U.S. EPA, Washington, DC, 1985.

[a] U.S. ACE (Cost Index for Utilities) may be used to convert costs into current USD.

TABLE 16.6
Chemical Costs[a]

Category	Chemical	Cost/Unit
Acids	Hydrochloric acid, 20° Baume tanks	\$55–105/t
	Nitric acid 36° to 42° Baume tanks	\$195/t
	Sulfuric acid	
	Virgin, 100%	\$61–95.9/t
	Smelter, 100%	\$48–65/t
Bases	Caustic soda, liquid 50%, low iron	\$255–285/t
Chelating agents	Ammonium chloride	\$18/100 lb
	Citric acid	\$0.81–\$1.19/lb
Fertilizers	Ammonia, anhydrous, fertilizer	\$140–\$215/t
(microbial nutrients)	Ammonium chloride	\$18/100 lb
	Ammonium sulfate	\$73–79/t
	Sodium monophosphate	\$55.75/100 lb
	Sodium diphosphate	\$54.50/100 lb
	Phosphoric acid	
	75%, commercial grade	\$27.5/100 lb
	52–54% a.p.a., agricultural grade	\$3.10/unit-ton[b]
	Potassium–muriate, 60 to 62%, minimum	\$0.82–0.92/unit-ton
	Potassium chloride	\$105/t
	Potassium-magnesium sulfate	\$59/t
Liming material	Agricultural limestone (dolomite)	\$3.50–34/t
	Lime	\$30.75–45/t
	Hydrated lime	\$32.5–34.5/t
Oxidizing agents	Hydrogen peroxide, 35%	\$0.24/1b
	Potassium permanganate	\$1.03–1.06/lb
Reducing agents	Caustic soda, liquid 50%, low iron	\$255–285/t
Precipitating agents	Ferrous sulfate	
	Heptahydrate	\$130/t
	Monohydrate	\$160/t
Surfactant		
Anionic	Witconate 605A	\$0.65–0.85/lb
	Witconate P–1020BV (calcium sulfonates)	\$0.70–0.88/lb
Nonionic	Adsee 799	\$0.75–0.87/lb

Source: U.S. EPA, Remedial Action at Waste Disposal Sites, EPA/625/6-85/006, U.S. EPA, Washington, DC, 1985.

[a] Use Appendix (USACE, Cost Index for Utilities) to convert costs into current USD.

[b] Unit-ton: 1% of 2000 lb of the basic constituent or other standard of the material. The percentage figure of the basic constituent multiplied by the unit-ton price gives the price of 2000 lb of the material.

groundwater than in *in situ* groundwater. Costs of chemicals are listed in Table 16.6. Oxidizing agents, such as hydrogen peroxide, are commonly used for *in situ* groundwater remediation.[23,24,72]

16.7.3.3 Permeable Reactive Barrier

A permeable reactive barrier (PRB) is defined as an *in situ* method for remediating contaminated groundwater that combines a passive chemical or biological treatment zone with subsurface fluid flow management. Treatment media may include zero-valent iron, chelators, sorbents, and microbes to address a wide variety of groundwater contaminants, such as chlorinated solvents, other organics, metals, inorganics, and radionuclides. The contaminants are concentrated and either degraded or retained in the barrier material, which may need to be replaced periodically. There are approximately 100 PRBs operating in the U.S. and at least 25 internationally.

PRBs can be installed as permanent or semipermanent units. The most commonly used PRB configuration is that of a continuous trench in which the treatment material is backfilled. The trench is perpendicular to and intersects the groundwater plume. Another frequently used configuration is the funnel and gate, in which low-permeability walls (the funnel) direct the groundwater plume toward a permeable treatment zone (the gate). Some gates are *in situ* reactors, which are readily accessible so as to facilitate the removal and replacement of reactive media. These PRBs use collection trenches, funnels, or complete containment to capture the plume and pass the groundwater, by gravity or hydraulic head, through a vessel containing either a single treatment medium or sequential media. In circumstances where *in situ* treatment is found to be impracticable, reactive vessels have been located above ground.

Zero-valent iron has performed so successfully in PRB technology that it is now being applied directly for source zone treatment. Alhough this measure is not considered a PRB, examples of the technology will be included under the heading PRB because the reactive media and treatment mechanism are related. Pneumatic fracturing and injection, hydraulic fracturing, and injection via direct push rigs have been used successfully to introduce the reactive media to the groundwater or soil source area.[74–76]

16.7.3.4 Circulating Wells and In-Well Air Stripping Technologies

Circulating wells (CWs) provide a technique for subsurface remediation by creating a three-dimensional circulation pattern of the groundwater. Groundwater is drawn into a well through one screened section and is pumped through the well to a second screened section where it is reintroduced to the aquifer. The flow direction through the well can be specified as either upward or downward to accommodate site-specific conditions. Because groundwater is not pumped above ground, pumping costs and permitting issues are reduced and eliminated, respectively. Also, the problems associated with storage and discharge are removed. In addition to groundwater treatment, CW systems can provide simultaneous vadose zone treatment in the form of bioventing or soil vapor extraction.

CW systems can provide treatment inside the well, in the aquifer, or a combination of both. For effective in-well treatment, the contaminants must be adequately soluble and mobile so they can be transported by the circulating groundwater. Because CW systems provide a wide range of treatment options, they provide some degree of flexibility to a remediation effort.

In-well vapor stripping technology involves the creation of a groundwater circulation pattern and simultaneous aeration within the stripping well to volatilize VOCs from the circulating groundwater. Air-lift pumping is used to lift groundwater and strip it of contaminants. Contaminated vapors may be drawn off for aboveground treatment or released to the vadose zone for biodegradation. Partially treated groundwater is forced out of the well into the vadose zone, where it reinfiltrates to the water table. Untreated groundwater enters the well at its base, replacing the water lifted through pumping. Eventually, the partially treated water is cycled back through this process until contaminant concentration goals are met.

16.7.3.5 Air Sparging in Aquifers

Air sparging involves the injection of air or oxygen through a contaminated aquifer. Injected air traverses horizontally and vertically in channels through the soil column, creating an underground stripper that removes volatile and semivolatile organic contaminants by volatilization. The injected air helps to flush the contaminants into the unsaturated zone. Soil vapor extraction (SVE) is usually implemented in conjunction with air sparging to remove the generated vapor-phase contamination from the vadose zone. Oxygen added to the contaminated groundwater and vadose-zone soils can also enhance biodegradation of contaminants below and above the water table.[77]

16.7.3.6 Multiphase Extraction

Multiphase extraction uses a vacuum system to remove various combinations of contaminated groundwater, separate-phase petroleum product, and vapors from the subsurface. The system lowers the water table around the well, exposing more of the formation. Contaminants in the newly exposed vadose zone are then accessible to vapor extraction. Once above ground, the extracted vapors or liquid-phase organics and groundwater are separated and treated.

16.7.4 PUMP-AND-TREAT GROUNDWATER REMEDIATION

The pump-and-treat methodology is effective for groundwater remediation. It is also an effective way to prevent the further extension of a contaminated area. The cleanup involves two steps:

1. Pumping the contaminated groundwater out from the site
2. Treating the pumped contaminated water on ground so that it can be returned to the system

In order to effectively pump all contaminated water out of an aquifer (or soil) pore space, water injection is usually needed, and sometimes a chemical flushing agent.

The pump-and-treat method is comparable to soil flushing. In fact, the pump-and-treat method can treat both groundwater and aquifer soil at the same time, and can also be directly applied to unsaturated soil zones. The soil flushing method is mainly considered as a treatment in unsaturated zones.

16.7.4.1 Pumping Systems

There are three common methods for groundwater collection using pumping systems: a well point system, a gravity drain system, and in combination with injection wells.

Well point system

A well point system consists of several individual well points spaced at 0.6 m to 1.8 m intervals along a specified alignment. A well point is a well screen (length 0.5 to 1.0 m) with a conical steel drive point at bottom. Individual well points are attached to a riser pipe (diameter 2.5 to 7.5 cm) and connected to a header pipe (diameter 15 to 20 cm). At the midpoint, the header pipe is connected to a centrifugal pump. As yield at different well points may vary, a valve at the top of each riser pipe is used to control the drawdown so that the screen bottom is exposed. The pump provides 6 to 7.5 m of suction, but friction losses reduce the effective suction to 4.5 to 5.4 m.

The well point system is the most economical method of groundwater collection where the water table is less than 3 m and the contaminant is less 9 m below the surface.

Gravity drain system

A trench is excavated perpendicular to the flow of groundwater to a depth below the water table. A perforated pipe is placed in the trench and the remainder of the trench is backfilled with gravel. Groundwater is collected in a main collector pipe and flows to a sump, from which it is pumped to the surface for treatment.

The gravity drain system is most effective when circumstances are suitable to gravity flow, the water table is less than 3 m and the contaminant is less than 9 m below the surface.

Combination with injection wells

The main purpose of recharging water into an aquifer is to elevate the hydraulic gradient to promote the movement of groundwater towards the collection system, thus enhance the efficiency of pumping.

There are two general recharge systems, recharge basins and injection wells. The recharge of treated groundwater into the system provides a method for the discharge of treated groundwater. The recharging of water can also have other purposes, such as creating a hydraulic barrier to restrict the migration of a contaminant plume, and providing a method for introducing flushing solutions into the groundwater to flush the pollutants out of soil.

16.7.4.2 Treatment of Pumped Water

Gravity liquid separation

Gravity liquid separation uses gravity force to separate the liquid-phase contaminant from water (immiscible with the contaminant) by the force of gravity.

Gravity separators can take many shapes and arrangement, depending in part on the characteristics of the waste. Typical design configurations include horizontal cylindrical decanters, vertical cylindrical decanters, and cone-bottomed settlers.

Sedimentation

Sedimentation is commonly applied to the treatment of pumped groundwater containing high concentrations of suspended solids.[25] It can also be used to remove the suspended solids from collected surface runoff, leachate or landfill toe seepage, and dredge slurries as a pretreatment step for biological treatment or many chemical processes, including precipitation, carbon adsorption, ion exchange, stripping, reverse osmosis, and filtration.[22–24]

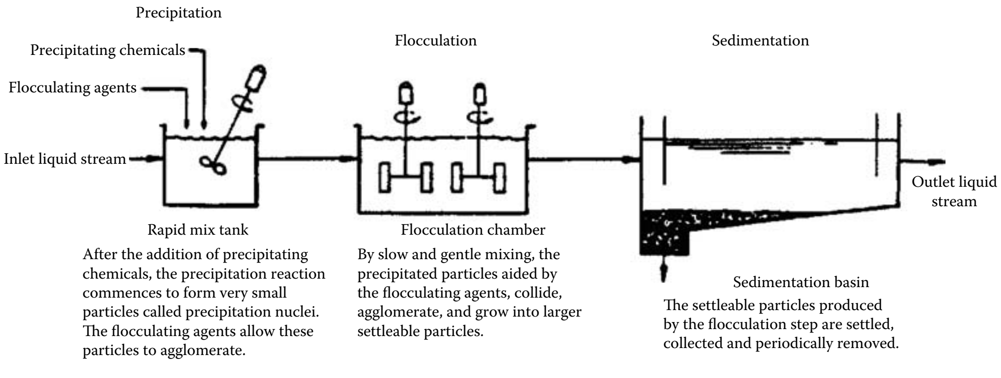
Chemical precipitation/coagulation, flocculation, and clarification

Chemical precipitation/coagulation methods transfer the target substances (mainly metals) in solution into a solid phase. Many heavy metal hydroxides and sulfides have very low solubility (within a certain pH range) and are therefore insoluble. The metal sulfides have significantly lower solubility than their hydroxide counterparts over a broad range of pH.[26] Precipitation/coagulation is also applicable for removing certain anionic species such as phosphate, sulfate, and fluoride.

Lime and sodium sulfide are the most common chemical agents added to contaminated water in a rapid mixing tank. Generally, flocculating agents (such as alum, lime, or iron salts) are added along with the precipitating agents.[27] Agglomerated particles are separated from the liquid phase by settling in a sedimentation clarifier, by floating in a dissolved air flotation (DAF) clarifier,[28,29,71–73] or by other physical processes such as filtration.[22] Figure 16.13 is a typical configuration for precipitation, flocculation, and sedimentation clarification,[15] in which the sedimentation clarifier may also be replaced by a DAF cell[28–30,71–73] for cost and space saving.

Certain physical or chemical characteristics of the wastestream may limit the application of precipitation. For example, some organic compounds (as well as cyanide or other ions) may form organometallic complexes with metals, decreasing the precipitation potential.

Wang and colleagues[71–73,100] have developed a physical–chemical sedimentation sequencing batch reactor (PCS-SBR) process and a physical–chemical flotation sequencing batch reactor (PCF-SBR) process for the treatment of contaminated groundwater, potable water, and wastewater. The reactor of a PCS-SBR process is similar to a conventional biological sequencing batch reactor (SBR), except that chemical flocs (instead of biological activated sludges) are used for water and wastewater treatment. A PCF-SBR is another physical–chemical SBR process in which flotation (instead of sedimentation) is used for the separation of chemical flocs from the flocculated water.



After the addition of precipitating chemicals, the precipitation reaction commences to form very small particles called precipitation nuclei. The flocculating agents allow these particles to agglomerate.

By slow and gentle mixing, the precipitated particles aided by the flocculating agents, collide, agglomerate, and grow into larger settleable particles.

The settleable particles produced by the flocculation step are settled, collected and periodically removed.

FIGURE 16.13 Representative configuration using precipitation, flocculation, and sedimentation.

Ion exchange

Ion exchange is a reversible interchange of ions between a liquid and a solid phase. The ions (contaminants) in a liquid wastestream and the ions on the surface of an ion-exchange resin are exchanged, purifying the wastestream while concentrating the waste constituent in the resin.[22–24] Mixed resins are sometimes effective in removing both cations and anions.

The ion-exchange process is applicable for removing a broad range of ionic species from water containing all metallic elements, inorganic anion such as halides, sulfates, nitrates, cyanides, organic acids such as carboxylics, sulfonics, some phenols at sufficiently alkaline pH conditions, and organic amines at sufficiently acidic conditions.

The upper concentration limit for ion exchange is about 2500 to 4000 mg/L. A high concentration of pollutants can result in the rapid exhaustion of the resin, resulting in high regeneration costs. The feed stream must be free of oxidants. Suspended soil material in the feed stream should be less than 50 mg/L to prevent plugging the resins. Recently, an ion-exchange sequencing batch reactor (IX-SBR) was developed by Wang and colleagues[71] for groundwater decontamination and industrial effluent treatment.[71,100]

Conventional filtration and automatic backwash filtration

Conventional filtration is widely used to remove suspended solids from solution by forcing the fluid through a porous medium. Filter media usually consist of a bed of granular particles, typically sand or sand with anthracite or coal. The filtrates are usually greater than 1 μm in diameter. The filtration is termed conventional, in order to distinguish it from other types of filtration such as membrane filtration (for particles less than 1 μm). As water passes through the filter bed, the particles become trapped on top of and within the filter bed, thus in time reducing the filtration rate. Therefore, backwash is periodically needed and filtration is often preceded by sedimentation[31] or flotation[28,32,33,71–73] to reduce the suspended solid load on the filter.

Membrane filtration processes

Membrane filtration processes have been successfully applied to the field of environmental engineering for air pollution control,[34] potable water purification,[22–24] groundwater decontamination,[35,36] industrial effluent treatment,[37] hazardous leachate treatment,[35,36] and site remediation,[36] mainly because membrane filtration can remove heavy metals and organics.

There are three major types of membrane processes, each with different physical means of operation: reverse osmosis (RO), ultrafiltration (UF), and microfiltration (MF). In addition, electrodialysis (ED) is also considered to be a membrane process.

In ED, cation-exchange membranes are alternated with anion-exchange membranes in a parallel manner to form compartments 0.5 to 1.0 mm thick. The entire membrane assembly is held between two electrodes. When an electrical potential is applied to the electrodes, all positive ions tend to travel towards the negative electrode, and all negative anions tend to move toward the positive electrode.

In the other three membrane processes, for example, in RO, a membrane is mounted in an apparatus so that a two-section compartment is formed. Contaminated water is pressurized and circulated through the high-pressure-solution compartment. Water permeates to the low-pressure side and is removed. The concentrated brine is removed separately.

The main difference between the UF, MF, and RO arrangements is membrane pore size, which allows different sizes of particles to pass through the membrane. All three processes allow certain solvent molecules to pass through, and impede certain sizes of particles. MF impedes the passage of large colloids and small particles, UF membranes impede the passage of molecules with a molecular weight of 100 or higher, and the membranes used in RO allow the passage of water, but impede the passage of salts and small molecules. of the three membrane filtration processes, RO requires the highest pressure.

The main advantages of membrane processes are their ability to separate impurities from water for recovery, low operation cost, and a requirement for only a small amount of space for installation. Their limitation lies in the possibility of deterioration of the membranes by certain kinds of water streams, for example, water containing certain strong oxidizing compounds or at high temperatures.

Recently, Wang[100] introduced a membrane sequencing batch reactor (membrane-SBR) process for groundwater decontamination, water purification, and industrial effluent treatment. A membrane-SBR is similar to conventional SBR except that membrane filtration is used (instead of sedimentation) for the separation of mixed liquor suspended solids (MLSS) from the mixed liquor.

Activated carbon adsorption

Activated carbon has high specific surface area with respect to its volume, and thus has high adsorption capacity. Activated carbon adsorption is considered to be one of the most versatile treatment technologies and can remove classical pollutants such as COD, TOC, BOD, and nitrogen, as well as toxic pollutants such as phenol, refractory organic compounds, VOCs, and soluble heavy metals.[38] Activated alumina and peat have also demonstrated similar abilities.

Once the micropore surfaces of activated carbon are saturated with target material, the spent carbon must be replaced or regenerated. Granular activated carbon (GAC) is favored over powder activated carbon (PAC) in most cases, because the former is considered to be capable of regeneration and sustainable to flow, although the costs of both carbons and the cost of regeneration are high.

Activated carbon adsorption is used to remove soluble organics, suspended solids, and refractory organics that cannot be biodegraded in groundwater. Because of its high cost and its ability to result in low pollutant concentration in effluents, activated carbon is usually used following biological treatment or granular media filtration in order to reduce the load on the carbon columns. PAC can be dosed into an SBR for facilitating physical–chemical or biological reactions for groundwater decontamination.[71–73]

Biological sorption

The biological sorption technique uses biogenetic materials for the adsorption of contaminants. The AlgaSorb sorption process developed by Bio-Recovery Systems, Inc., is designed to remove heavy metal ions from aqueous solution based on the mutual affinity of the cell walls of algae and heavy metal ions. The sorption medium comprises algal cells immobilized in a silica gel polymer. The system functions as a biological ion-exchange resin to bind both metallic cations (positively charged ions) and large metallic anions. Like ion-exchange resins, the algae–silica medium can be recycled. This technology is useful for removing metal ions from groundwater and surface leachate that contain high levels of dissolved solids.[23,24]

Solvent extraction

Solvent extraction is the separation of constituents from a liquid solution by contact with another immiscible liquid. It is mainly used for the recovery of organics from liquid solutions.[39] Specifically, solvent extraction uses an organic solvent as an extractant to separate organic and metal contaminants from soil. The organic solvent is mixed with contaminated soil in an extraction unit. The extracted solution is then passed through a separator, where the contaminants and extractant are separated from the soil. Organically bound metals may be extracted along with the target organic contaminants.[78]

From a process viewpoint, three steps are involved:

1. Actual extraction of the solvent by forced mixing or countercurrent flow
2. Solute removal from the extracting solvent
3. Solvent and extracted solute recovery

Significant energy consumption and other operating costs are expected. This method of treatment becomes cost-effective when material recovery is significant.

Chemical oxidation

Chemical oxidation typically involves reduction/oxidation (redox) reactions that chemically convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, or inert. Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents most commonly used for the treatment of hazardous contaminants in soil are ozone, hydrogen peroxide, hypochlorites, chlorine, chlorine dioxide, potassium permanganate, and Fentons reagent (hydrogen peroxide and iron). Cyanide oxidation and dechlorination are examples of a chemical treatment. This method may be applied *in situ* or *ex situ*, to soils, sludges, sediments, and other solids, and may also be applied to the *in situ* treatment of groundwater.[22–24,79,80]

Chemical oxidation technology is primarily used for the detoxification of cyanide and other oxidizable organics such as aldehydes, mercaptans, phenols, unsaturated acids, and certain pesticides.[40]

For example, cyanide detoxification involved the following process[106]:

$$NaCN + KMnO_4 + H^+ \longrightarrow MnO_2 + NaCNO + KOH$$

Oxidation can be an effective way of pretreating waste prior to biological treatment either by detoxification or by rendering refractory compounds to be more amenable to biological treatment.

Chemical Waste Management, Inc., has developed a technique that is a combination of evaporation and catalytic oxidation processes. Contaminated water is concentrated in an evaporator by boiling off most of the water and its volatile contaminants, both organic and inorganic. Air or oxygen is added to the vapor and the mixture is forced through a catalyst bed, where the organic and inorganic compounds are oxidized. This stream, composed mainly of steam, passes through a scrubber, if necessary, to remove any acid gases formed during oxidation. The stream is then condensed or vented to the atmosphere. This technique can be used to treat complex contaminated waters that contain volatile and nonVOCs, salts, soluble heavy metals, and volatile inorganic compounds.

The limitation for chemical oxidation is that oxidation is frequently not completed to the final products CO_2 and H_2O. This can be due to a number of factors, including oxidant concentration, pH, redox potential, or the formation of stable intermediate toxic oxidation products.

Chemical reduction

Chemical reduction is used to transform a toxic substance with a higher valence to a nontoxic or less-toxic substance with lower valence. The most promising application is the reduction of hexavalent chromium to trivalent chromium. This method is also applicable to other multivalent metals such as lead and mercury. Commonly used chemical agents for this purpose are sulfite salts, sulfur dioxide, and base metals (e.g., iron and aluminum).[22–24]

Biological treatment

Biological treatment technology, also known as bioremediation technology, is mainly used to treat organic contaminants (as terminal electron acceptor to bacteria). Bioremediation techniques include the use of two primary respiratory pathways: aerobic and anaerobic.[20,21] Each approach has advantages and limitations. To date, aerobic systems using naturally occurring microorganisms are most widely implemented. Aerobic systems tend to be more efficient when degrading petroleum-based organic contaminants such as benzene, toluene, ethylbenzene, xylenes (BTEX), and naphthalene. Research suggests that aerobic systems are not as effective for the treatment of highly chlorinated compounds such as PCBs (polychlorinated biphenyls). However, genetically engineered microbial system (GEMS) are increasingly used in research applications for recalcitrant compounds. Research scientists[41] have developed techniques to modify microbial DNA to enable organisms to degrade contaminants that are currently very recalcitrant (i.e., PCBs) or extremely toxic (i.e., dioxin). Some bacteria can use certain inorganics as the terminal electron acceptor, so biological decontamination of inorganic materials is feasible. The following presents an example on biological decontamination of inorganic materials.

Ehrlich[42] used biotechnology coupled with physicochemical extraction to remove chromium from contaminated soil including recovery and reuse. Ehrlich's biological treatment is based on an oxygen-insensitive bacterial respiration, with chromate as the terminal electron acceptor using intact cells and cell extracts. The bacterial strain used to reduce chromate is *Pseudomonas fluorescens* LB300, which has chromate resistance to more than 2000 mg/L of potassium chromate, although very slight resistance to potassium dichromate. In the Ehrlich process, the highly Cr-concentrated solution was recovered through ion exchange, and the low-concentration solution was then treated by reducing Cr(VI) to Cr(III) in a rotating biological contactor (RBC). The Cr(III) slurry was recovered through sedimentation and purification for reuse.

Wang and colleagues[43,71,100] have developed a biological flotation process for the treatment of contaminated groundwater. The process has a built-in air emission control device for the removal of toxic organics and inorganics from water without causing air pollution problems. One of the biological processes is a conventional biological SBR equipped with an enclosure on top for air emission control. Another new biological high rate process is the dissolved air flotation sequencing batch reactor (DAF-SBR), which is also equipped with an air pollution control enclosure on top, which is suitable for temporary groundwater decontamination in the field. The DAF-SBR process is similar to a conventional biological SBR process, except that DAF (instead of sedimentation) is used in the reactor for the separation of mixed liquor suspended solids (MLSS) from the mixed liquor.

Air and steam strippings

Stripping methods, including steam stripping and air stripping, are mainly used for the removal of volatile organics from contaminated water. The difference between steam stripping and air stripping is the stripping agent, the former obviously using steam and the latter air. Moreover, steam stripping is more like a distillation process, in which steam is used as both the heating medium and the driving force for removal of the volatile materials. After condensing the steam, the waste compounds are concentrated and separated from the water. Air stripping, on the other hand, is based on the distribution coefficients of volatile organics between the contaminated water and the stripping stream at a certain temperature.

Stripping can be integrated with vapor extraction for a better contamination removal. The stripping technology can also be combined with activated carbon adsorption to result in a higher removal efficiency. The conventional air stripping process can only remove VOCs from contaminated water while its gaseous effluent may pollute the air environment. A new stripping process developed by Wang and colleagues[32] and Hrycyk and colleagues[44] can remove VOCs, VICs (volatile inorganic compounds), and radioactive radon from water, without the creation of an air pollution problem.

16.7.5 *In Situ* Soil Treatment

16.7.5.1 *In Situ* Heating

In situ soil remediation with physical methods includes the *in situ* heating (*in situ* thermal treatment), ground-freezing, hydraulic fracturing, immobilization/stabilization, flushing, chemical detoxification, vapor extraction, steam extraction, biodegradation/bioremediation, electroosmosis/electrokinetic processes, etc.

In situ heating (*in situ* thermal treatment) uses thermal decomposition, vaporization, and distillation techniques to destroy or remove organic contaminants. The most common *in situ* heating methodologies include electrical resistance heating, radio frequency heating, hot air/water/steam injection, and thermal vitrification. These different methods or their combinations can be used to apply heat to polluted soil or groundwater *in situ*. The heat can destroy or volatilize organic chemicals. As the chemicals change into gases, their mobility increases, and the gases can be extracted via collection wells for capture and cleanup in an *ex situ* treatment unit. Thermal methods can be particularly useful for dense or light nonaqueous phase liquids (DNAPLs or LNAPLs). Heat can be introduced to the subsurface by electrical resistance heating, radio frequency heating, dynamic underground stripping, thermal conduction, or injection of hot water, hot air, or steam.

The main advantage of *in situ* thermal methods is that they allow soil to be treated without being excavated and transported, resulting in significant cost savings; however, *in situ* treatment generally requires longer time periods than *ex situ* treatment, and there is less certainty about the uniformity of treatment because of the variability in soil and aquifer characteristics and because the efficacy of the process is more difficult to verify.

Electrical resistance heating

Electrical resistance heating uses an electrical current to heat less permeable soils such as clays and fine-grained sediments so that water and contaminants trapped in these relatively conductive regions are vaporized and ready for vacuum extraction. Electrodes are placed directly into the less permeable soil matrix and activated so that electrical current passes through the soil, creating a resistance, which then heats the soil. The heat dries out the soil, causing it to fracture. These fractures make the soil more permeable, allowing the use of SVE to remove the contaminants. The heat created by electrical resistance heating also forces trapped liquids to vaporize and move to the steam zone for removal by SVE. Six-phase soil heating (SPSH) is a typical electrical resistance heating, and uses low-frequency electricity delivered to six electrodes in a circular array to heat the soil. With SPSH, the temperature of the soil and contaminant is increased, thereby increasing the contaminant's vapor pressure and its removal rate. SPSH also creates an *in situ* source of steam to strip contaminants from the soil. SPSH has been demonstrated, and all large-scale *in situ* projects utilize three-phase soil heating.

Radio frequency/electromagnetic heating

Radio frequency heating (RFH) is an *in situ* process that uses electromagnetic energy to heat soil and enhance SVE. The RFH technique heats a discrete volume of soil using rows of vertical electrodes embedded in the soil (or other media). Heated soil volumes are bounded by two rows of ground electrodes with energy applied to a third row midway between the ground rows. The three rows act as a buried triplet capacitor. When energy is applied to the electrode array, heating begins at the top center and proceeds vertically downward and laterally outward through the soil volume. The technique can heat soils to over 300°C.[45] RFH enhances SVE in four ways:

1. Contaminant vapor pressure and diffusivity are increased by heating
2. Soil permeability is increased by drying
3. There is an increase in the volatility of the contaminant from *in situ* steam stripping by the water vapor
4. There is a decrease in viscosity, which improves mobility

The technology is self-limiting; as the soil heats and dries, current will stop flowing. Extracted vapor can then be treated by a variety of existing technologies, such as GAC or incineration.

Hot air injection

Hot air, hot water, or hot steam are injected below the contaminated zone to heat the contaminated soil. The heating enhances the release of contaminants form the soil matrix. Some VOCs and semivolatile organic compounds (SVOCs) are stripped from the contaminated zone and brought to the surface through soil vapor extraction. Hot air is introduced at high pressure through wells or soil fractures. In surface soils, hot air is usually applied in combination with soil mixing or tilling, either *in situ* or *ex situ*.

Hot water injection

Hot water injection via injection wells heats the soil and groundwater and enhances contaminant release. Hot water injection also displaces fluids (including LNAPL and DNAPL free product) and decreases contaminant viscosity in the subsurface to accelerate remediation through enhanced recovery.

Hot steam injection

Hot steam injection heats the soil and groundwater and enhances the release of contaminants from the soil matrix by decreasing viscosity and accelerating volatilization. Steam injection may also destroy some contaminants. As steam is injected through a series of wells within and around a source area, the steam zone grows radially around each injection well. The steam front drives the contamination to a system of groundwater pumping wells in the saturated zone and SVE wells in the vadose zone.[82,83] Figure 16.14 show the operation of a typical hot steam injection process.

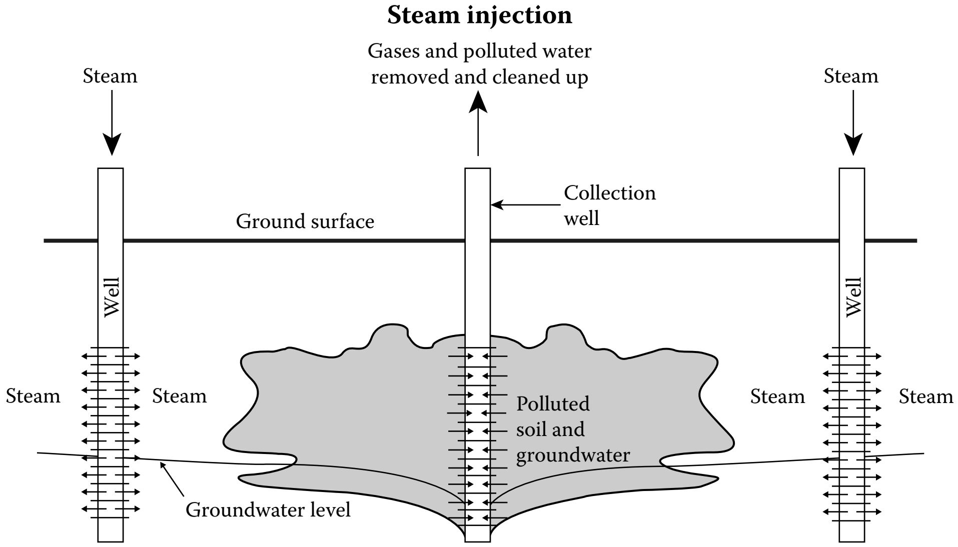


FIGURE 16.14 *In situ* thermal treatment by steam injection. (Taken from U.S. EPA, A Citizen's Guide to *In situ* Thermal Treatment Methods, Technical Report EPA-542-F-01-012, U.S. EPA, Washington, DC, 2001.)

In situ *thermal vitrification*

In situ thermal vitrification is based on electric melter technology. Contaminated soil is converted into durable glass and the waste is pyrolyzed or crystallized. Off-gases released during the melting process are trapped in an off-gas hood. The depth of the waste is a significant limiting factor for this application.[17,82] In essence, vitrification is a process that permanently traps harmful chemicals in a solid block of glass-like material. This keeps the chemicals from leaving the site. Vitrification can be done either in place (*in situ*) or above ground (*ex situ*). Specifically, vitrification uses electric power to create the heat needed to melt contaminated soil at elevated temperatures (1600 to 2000°C or 2900 to 3650°F). The high-temperature component of the process destroys or removes organic materials. Radionuclides and heavy metals are retained within the vitrified product.

Figure 16.15 shows that four rods (electrodes) are drilled in the polluted area. An electric current is passed between the electrodes, melting the soil between them. Melting starts near the ground surface and moves downward. As the soil melts, the electrodes sink further into the ground, causing deeper soil to melt. When the power is turned off, the melted soil cools and vitrifies, which means it

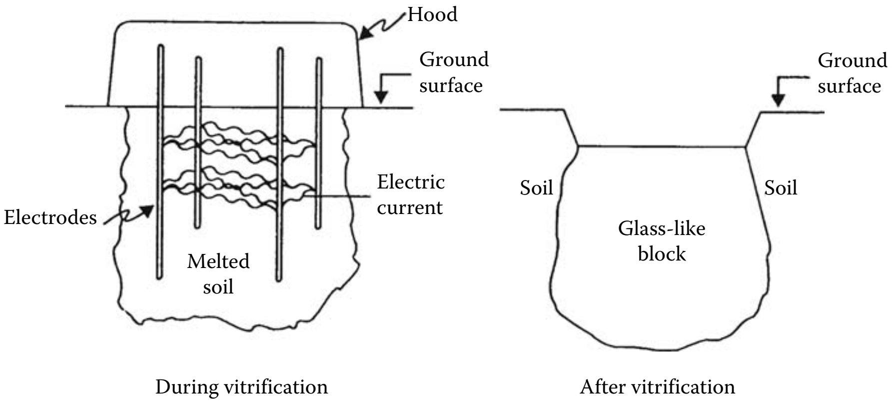


FIGURE 16.15 During the vitrification process and after vitrification. (Taken from U.S. EPA, A Citizen's Guide to Vitrification, Technical Report EPA-542-F-01-017, U.S. EPA, Washington, DC, 2001.)

turns into a solid block of glass-like material. The electrodes become part of the block. When vitrified, the original volume of soil shrinks. This causes the ground surface in the area to sink slightly. To level it, the sunken area is filled with clean soil. When used properly, vitrification can be quite safe. The gas hood must be large enough to cover the polluted area so it can capture all the chemicals released from the soil. Any wet soil must be dried first to prevent steam from forming. The release of steam can splash hot, melted soil above ground. The hood further prevents site workers from being splashed.[82] The vitrified block that is left in place is permanent and not harmful to people.

Thermal conduction

Thermal conduction (also referred to as electrical conductive heating or *in situ* thermal desorption) supplies heat to the soil through steel wells or with a blanket that covers the ground surface. As the polluted area is heated, the contaminants are destroyed or evaporated. Steel wells are used when the polluted soil is deep. The blanket is used where the polluted soil is shallow. Typically, a carrier gas or vacuum system transports the volatilized water and organics to a treatment system.

16.7.5.2 Artificial Ground Freezing

Artificial ground freezing involves the installation of freezing loops in the ground and a self-confined refrigeration system that pumps coolant around the freezing loop. This method is useful only as a temporary treatment approach because of the high thermal maintenance expense.

16.7.5.3 Fracturing

Fracturing is a way to crack rock or very dense soil, like clay, below ground. It is not necessarily a cleanup method in itself. Rather, fracturing is used to break up the ground to help other cleanup methods work better. The cracks, which are called fractures, create paths through which harmful chemicals can be removed or destroyed.[17,46,84]

Hydraulic fracturing

Hydraulic fracturing uses a liquid, usually water. The water is pumped under pressure into holes drilled in the ground. The force of the water causes the soil (or sometimes rock) to crack. It also causes existing fractures to grow larger. To fracture soil at greater depths, sand is pumped underground with the water. The sand helps prop the fractures open and keep them from closing under the weight of the soil.

Pneumatic fracturing

Pneumatic fracturing uses air to fracture the soil. It can also help to remove chemicals that evaporate or change to gases quickly when exposed to air. When air is forced into the soil, the chemicals evaporate and the gases are captured and treated above ground.

Air can be forced into the ground at different depths within a hole. When air is forced near the ground surface, the surface around the holes may rise by as much as an inch, but will settle back close to its original level. In both pneumatic and hydraulic fracturing, equipment placed underground directs the pressure to the particular zone of soil that needs to be fractured.

Blast-enhanced fracturing

Blast-enhanced fracturing uses explosives, such as dynamite, to fracture rock. The explosives are placed in holes and detonated. The main purpose is to create more pathways for polluted groundwater to reach wells drilled for pump-and-treat cleanup.

16.7.5.4 Immobilization and Stabilization

Immobilization and stabilization render contaminants insoluble and prevent leaching of the contaminants from the soil and their movement from the contamination area. The techniques used for immobilization are precipitation, chelation, redox reaction, and polymerization.

Precipitation is the most promising method for immobilizing dissolvable metals such as lead, cadmium, zinc, and iron.[15] Some forms of arsenic, chromium, mercury, and some fatty acids can also be treated by precipitation.[47] The common precipitating chemicals for metal cations are sulfide, phosphate, hydroxide, or carbonate. Among them, sulfide is the most promising, because sulfides have low solubility over a broad pH range. Precipitation is most applicable to sites with sand or coarse silt strata.

The use of chelating agents may also be a very effective means of immobilizing metals.

Redox reactions may cause mobile toxic ions to become either immobile or less toxic. Hexavalent chromium is mobile and highly toxic. It can be reduced to be rendered less toxic in the form of trivalent chromium sulfide by the addition of ferrous sulfate. Similarly, pentavalent (V) or trivalent (III) arsenic, arsenate or arsenite are more toxic and soluble forms. Arsenite (III) can be oxidized to As(IV). Arsenate (V) can be transformed to highly insoluble $FeAsO_4$ by the addition of ferrous sulfate.

Polymerization involves the injection of a catalyst into the groundwater plume to cause polymerization of organic monomers (e.g., vinyl chloride, isoprene, and methyl methacrylate), transforming the once fluid substance into a gel-like, nonmobile mass. It has been reported that 90% of an acrylate monomer leakage was polymerized by the injection of a catalyst, activator, and wetting agents.[48] *In situ* polymerization is suitable for groundwater cleanup following land spills or underground leaks of pure monomers. Applications for uncontrolled hazardous waste sites are very limited.

Various immobilization and stabilization methods can be applied to soils contaminated with heavy metals, petroleum products, PCB, peroxyacetyl nitrate (PAN), and so on.[17] The disadvantages of immobilization and stabilization methods include the following:

1. There is a requirement for numerous, closely spaced injection wells, even in coarse-grained deposits
2. Contaminants are not removed, and some of the chemical reactions could be reversed, producing monomers, which will again migrate with the groundwater
3. There is a possibility of the injection of a potential groundwater pollutant that in association with chemicals forms toxic byproducts
4. There is a potential for the clogging of soil pore spaces

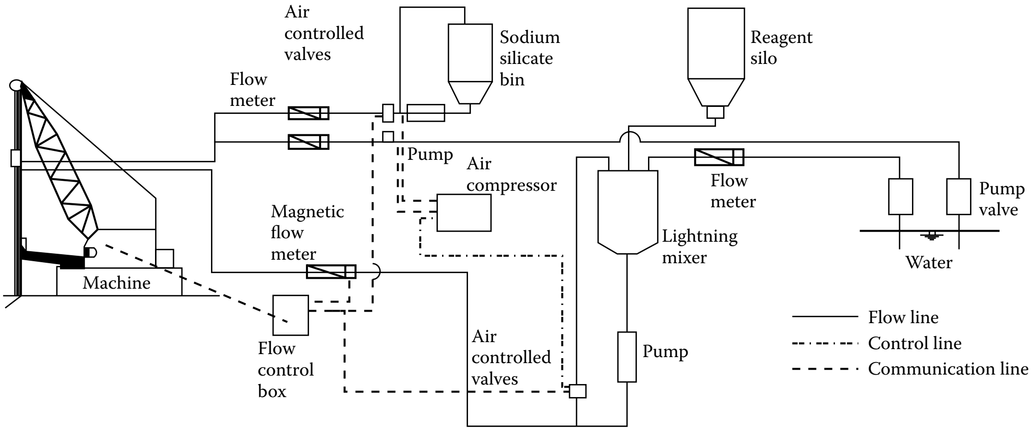


FIGURE 16.16 *In situ* solidification batch mixing plant process.

International Waste Technologies/Geo-Con, Inc., has used a deep soil mixing system to deliver and mix the chemicals with the soil *in situ*. The system involves mechanical mixing and injection, as shown in Figure 16.16.

ChemFix Technologies, Inc., has used silicates and silicate setting agents to stable polyvalent metal ions. Usually, there is a need to separate coarse and fine pollutants so as to crush coarse materials and reduce the material size required for the stabilization technology.

The soil–cement mixing wall technology developed by S. M. W. Seiko, Inc., involves the *in situ* fixation, solidification, and stabilization of contaminated soils by mixing soil, cement, and chemical grout, by including cutoff walls and soil stabilization, and by using hollow-stem augers to inject solidification and stabilization agents and blend them with contaminated soil *in situ*.

Table 16.7 and Table 16.8 summarize some promising *in situ* chemical treatment methods for organics and inorganics that can be applied to soil. Some of them can also be applied to groundwater.

TABLE 16.7
Summary of *In Situ* Chemical Treatment Methods for Organics

Method	Amenable to Treatment	Treatment Reagents	Process
Soil flushing Water flushing	Hydrophilic compounds (high solubility, low R_{ow})	Water	Contaminated soils are flooded with water or a water chemical mixture and the elutriated solution is collected
Water with surfactants	Hydrophobic compounds (low solubility, high K_{ow})	Aqueous solutions of surfactants	Contaminants are mobilized into solution by reason of solubility, formation of emulsion or reaction
Oxidation	Benzene and substituted benzenes Phenols Halogenated phenols	Ozone, hypochlorite, or hydrogen peroxide	Oxidation state of compounds is increased by loss of electrons
	Nitro aromatics		Contaminants are detoxified, mobility is increased or compounds are made more amenable to biological degradation
	PAHs Heterocyclic nitrogen and oxygen compounds Aldehydes and ketones Sulfides, disulfides		
Hydrolysis (base-catalyzed)	Esters Amides Carbamates Organophosphorus compounds Certain pesticides (i.e., parathion, malathion, 2-4D esters, DDT)	Water with lime or NaOH	Attack of nucleophile (e.g., water or hydroxyl ion) on an electrophile (e.g., carbon or phosphorus), resulting in bond cleavage and displacement of the leaving group
Polymerization	Aliphatic, aromatic and oxygenated monomers Vinyl chloride Isoprene	Catalyst activation	Conversion of a compound to a larger chemical multiple of itself
	Acrylonitrile		Reduces mobility of compound in soil

Source: U.S. EPA, Field Standard Operating Procedures for Decontamination of Response Personnel, FSOP7, U.S. EPA, Washington, DC, 1985.

TABLE 16.8
Summary of *In Situ* Chemical Treatment Methods for Inorganics

Method	Amenable to Treatment	Treatment Reagents	Process
Precipitation Sulfide	Heavy metals	Sodium or calcium sulfide	Formation of insoluble metal precipitate, thereby reducing the mobility of the metal
Carbonate/hydroxide	Heavy metals	Lime, calcium carbonate	
Phosphate	Heavy metals	Superphosphate fertilizer	
Soil flushing			
Acids/bases	Heavy metals	Dilute solutions of acids or bases	Involves solubilizing the metals followed by extraction of the metal ions
Chelates	Heavy metals	Chelating agents such as citric acid or EDTA	Formation of stable metal chelates; depending on chelating agent, metal chelate is either strongly sorbed to soil or is highly mobile and can be flumbed using water or dilute acid solutions.
Oxidation	Trivalent arsenic	Potassium permanganate	Oxidizes trivalent arsenic to pentavalent arsenic, and results in precipitation of arsenic-iron-manganese compounds.
Reduction	Hexavalent chromium	Ferrous sulfate	Reduces Cr(VI) to Cr(III)
	Hexavalent selenium	Ferrous sulfate	Reduces Se(VI) to Se(IV)

Source: U.S. EPA, Field Standard Operating Procedures for Decontamination of Response Personnel, FSOP7, U.S. EPA, Washington, DC, 1985.

16.7.5.5 Soil Flushing

For *in situ* soil flushing, large volumes of water, at times supplemented with surfactants, cosolvents, or treatment compounds, are applied to the soil or injected into the groundwater to raise the water table into the contaminated soil zone. Injected water and treatment agents are isolated within the underlying aquifer and recovered together with flushed contaminants.[50–52,85]

Water can be used to flush water-soluble or water-mobile organics and inorganics. The inorganics to which this can be applied include soluble salts such as the carbonates of nickel, zinc, and copper. The organics that it is feasible to remove from soil should have a certain degree of water affinity, in other words, they should have low soil–water partitioning coefficients ($P < 1000$; i.e., $k = \log P \leq 3$). Among them, the high-solubility organics ($k \leq 1$) include low-molecular-weight alcohols, phenols, and carboxylic acids, and the medium-solubility organics ($1 \leq k \leq 3$) include low- to medium-molecular-weight ketones, aldehydes, and aromatics, and lower-molecular-weight halogenated hydrocarbons such as TCE (tetrachloroethylene) and PCE (pentachloroethylene). It has been reported that an 18-month period of water flushing on soil for a PCE spill site in Germany removed 50% of the material.[49]

Adjusting pH to the optimum solubility of salt by adding dilute acid or base solution can enhance inorganic solubilization and removal. Week acids are recommended to avoid the high toxicity resulting from acidity. Sodium dihydrogen phosphate and acetic acid have low toxicity and are relatively stable. A stronger dilute acid such as sulfuric acid may be used for neutralizing soils containing sufficient alkalinity. Acidic solutions may also be used to flush some basic organics such amines, ethers, and anilines. Complexing and chelating agents (such as EDTA, DTPA, and acetic and citric acids) are also used to removal heavy metals.[50–52]

Some contaminants are adsorbed by iron and manganese oxides (which may exist as coatings on soil particles) in soil. By using acids or chelating agents (such as sodium dithionite/citrate), the iron and manganese coating can be dissolved, thus mobilizing the adsorbed contaminants.

Surfactant washing is among the most promising *in situ* chemical treatment methods. Surfactants can improve the solvent property of the flushing water, emulsify nonsoluble organics, and enhance the removal of hydrophobic organics sorbed onto soil particles.

In situ soil flushing should involve the design of a series of injection wells (for washing agents) and extraction wells. An economically feasible soil flushing method may involve the recycling of the elutrate through the contaminated material, with make-up solvent being added to the system while a fraction of the elutrate stream is routed to the portable wastewater treatment system. Soil flushing operations require soils with moderate to high permeability, and tend to work best for sandy soil conditions.[53]

16.7.5.6 Chemical Detoxification

Chemical detoxification uses oxidation, reduction, neutralization, and hydrolysis to reduce the toxicity of the contaminants. The basic theory is similar to that of treating pumped groundwater.

16.7.5.7 Soil Vapor Extraction

Soil vapor extraction (SVE) can be used to remove volatile contaminants and, when combined with another technology, to treat nonvolatile contaminants. If contamination has reached the aquifer, it is necessary to use SVE in combination with groundwater pumping and air stripping.

Soils with low air permeability are more difficult to treat. Heterogeneity can cause variable flow and desorption, making remediation more difficult. High organic carbon content causes a high sorption capacity for VOCs and is more difficult to remedy. Contaminants with low vapor pressure or high water solubilities become difficult to remove. The lower limit on vapor pressure is 1 mmHg absolute. The moisture in the soil hinders the removal of soluble compounds because water moisture acts as a sink for the compounds. Figure 16.17 shows how SVE works.[86]

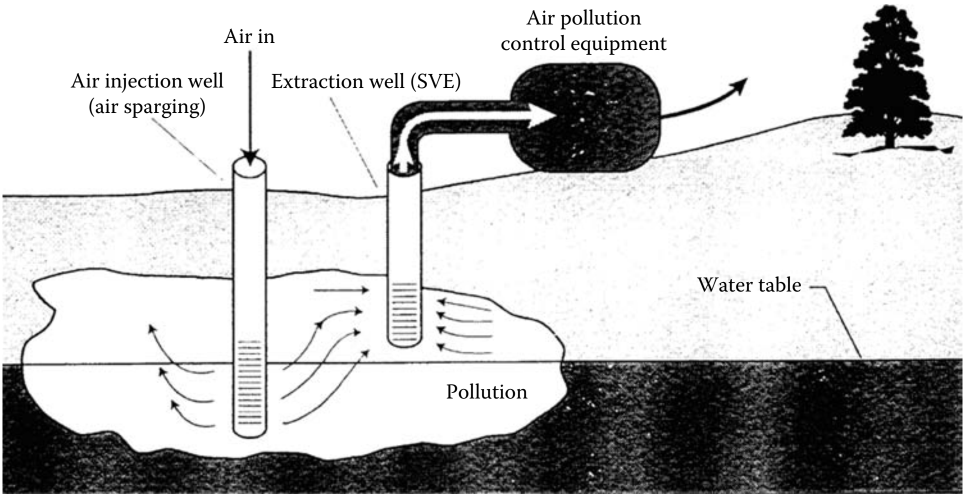


FIGURE 16.17 Soil vapor extraction and air sparging. (Taken from Rohayo, A.J., Cameron, R.J., Teters, B.B., Rossabi, J., Riha, R., and Downs, W., Passive Soil Vapor Extraction, Technical Report DE98051208, 20 p., U.S. Department of Commerce, National Technical Information Service, Springfield, VA, 1997. With permission.)

16.7.5.8 *In Situ* Steam Extraction

In situ steam extraction treatment is provided to effectively remove volatile and semivolatile soil contaminants, including volatile organic compounds, petroleum wastes, soluble inorganics (acids, bases, salts, and heavy metals). Steam is injected into the soil or groundwater and acts as a stripping agent, heating the soil/water and releasing the volatile contaminants. This produces both air and water streams that must be further treated.

Raising the temperature of the soil increases the vapor pressure of the contaminants, improving their ability to volatilize. Many semivolatile compounds will eventually be released as the temperature rises, although these compounds tend to need longer residence times.

Two types of *in situ* steam extraction systems, mobile and stationary, are available. The mobile system may have rotating cutter blades that release steam as they tunnel through the soil. This system treats small areas sequentially. The stationary system injects the steam into drilled wells, without disturbing the soil.

The mobile *in situ* steam extraction system has certain restrictions on its use. High silt and clay content may cause stability problems with respect to the support of the system (causing equipment to sink or tip), and may also require longer treatment times due to its lower permeability. The mobile *in situ* steam extraction system is also limited to a depth of 9 m (30 ft), and a height requirement of 9 m (30 ft) is needed for clearance. A slope of less than 1° is also required. Temperatures of –7 to 38°C (20 to 100°F) are desirable. Figure 16.18 shows a schematic illustration of the mobile unit system developed by Novaterra, Inc.[54] The boring unit contains two counter-rotating blades with nozzles that release steam and compressed air. The steam (at 400°F; 204°C) and air (at 275°F; 135°C) volatilize the organics, which are caught and collected. A blower provides suction to draw up the vapor and protect against leakage. The vapor is then separated into gas and water and treated. The mobile system can treat areas of 2.2 m × 1.2 m × 9 m (7 ft 4 in. × 4 ft × 30 ft).

The stationary *in situ* steam extraction system uses injection wells to introduce the steam, and recovery wells for removing it. Soil permeability is a major factor. Low-permeability soils require a far greater number of wells compared to high-permeable soil, driving up costs. To be effective

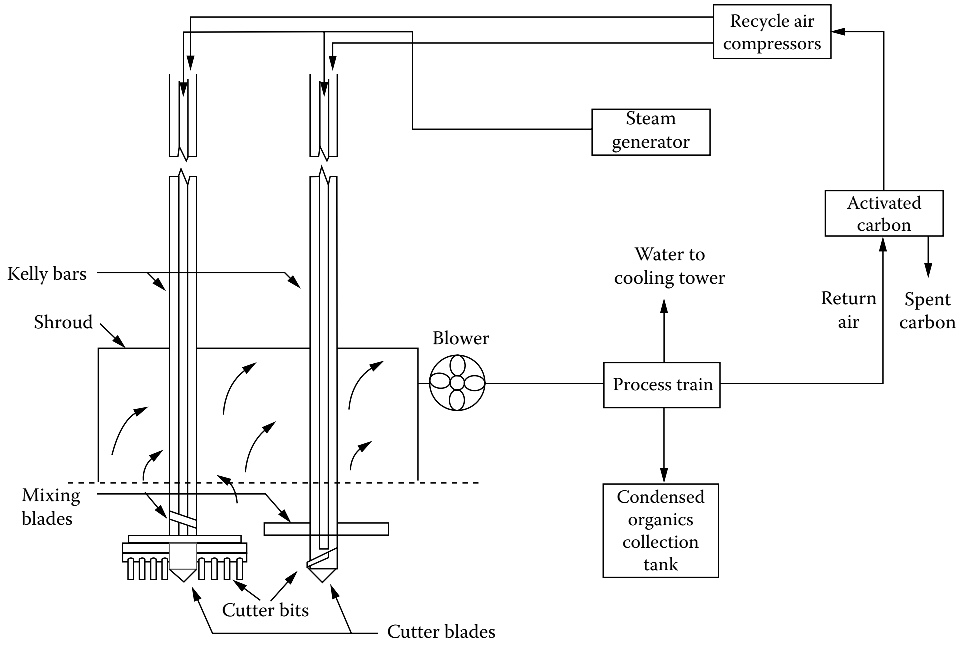


FIGURE 16.18 A mobile steam extraction system.

(85% contaminants removal), the stationary *in situ* steam extraction system requires homogeneous soils with high to medium permeability. Accordingly, further treatment may be necessary.

Steam extraction has been used for gasoline and diesel fuel. High-molecular-weight components of the diesel fuel cannot be removed easily, although a total removal of up to 91% is possible. When used to remove low-volatility compounds in a soil with a high percentage of clay, performance is expected to be ca. 85%. The mobile *in situ* steam extraction system can reduce VOCs in soils by more than 50% of their initial level. Based on pilot studies, the stationary steam extraction system is expected to have a 90% removal efficiency.[54]

16.7.5.9 *In Situ* Biodegradation/Bioremediation and Bioventing

Biodegradation or bioremediation has so far been developed for aerobic degradation of organic contaminants in soil.[41,87] Anaerobic bioremediation approaches have several limitations. For a strict anaerobic system to be effective, no oxygen should be present in the environment, because oxygen itself is toxic to strictly anaerobic microorganisms. This anaerobic condition is difficult to implement under field conditions, especially when a mechanical pumping system is used to extract groundwater. Also, anaerobic degradation of some contaminants can produce intermediate end products that may be less desirable than the target substance. For example, tetrachloroethylene (TCE) can be anaerobically degraded to vinyl chloride. This partial-breakdown end product does not undergo further anaerobic degradation. Vinyl chloride, a potent carcinogen, can accumulate in the environment. Furthermore, anaerobic degradation can produce unpleasant and potentially dangerous off-gases such as H_2S and CH_4. For these reasons, full-scale anaerobic bioremediation technologies have lagged behind aerobic approaches.

The bioventing system developed by the U.S. EPA Risk Reduction Engineering Laboratory[54] comprises mainly the injection of atmospheric air to treat contaminated soil *in situ* (Figure 16.19). This air provides a continuous oxygen source, which enhances the growth of microorganisms naturally present in the soil. The provided low-pressure air allows for an inflow of oxygen without volatilization of contaminants. Additional additives such as ozone or nutrients may also be required to stimulate microbial growth.[17]

16.7.5.10 Electroosmosis Remedial Technology

Electroosmotic soil processing is an *in situ* separation/removal technique for extracting heavy metals and organic contaminants from soils.[17,55,89] The fluid between the soil particles moves because a constant, low DC current is applied through electrodes inserted into the soil mass. The electroosmosis (EO) remedial method provides an advantage over conventional pumping techniques for *in situ* treatment of contaminated fine-grained soils and is more efficient in saturated conditions.

Electroosmosis is an electrokinetic effect, so a direct electric potential causes a movement of liquid through stationary particles. From primary electrode reactions,

$$2H_2O - 4e^- = O_2 + 4H^+ \quad \text{(anode)}$$

$$4H_2O + 4e^- = 2H_2 + 4OH^- \quad \text{(cathode)}$$

Electrokinetics relies upon the application of a low-intensity direct current through the soil between ceramic electrodes, which are divided into a cathode array and an anode array. This mobilizes charged species, causing ions and water to move toward the electrodes. Metal ions, ammonium ions, and positively charged organic compounds move toward the cathode. Anions such as chloride, cyanide, fluoride, nitrate, and negatively charged organic compounds move toward the anode. Removal of contaminants at the electrode may be accomplished by several means, among which are electroplating at the electrode, precipitation or coprecipitation at the electrode, pumping of water near the electrode, or complexing with ion-exchange resins.[89]

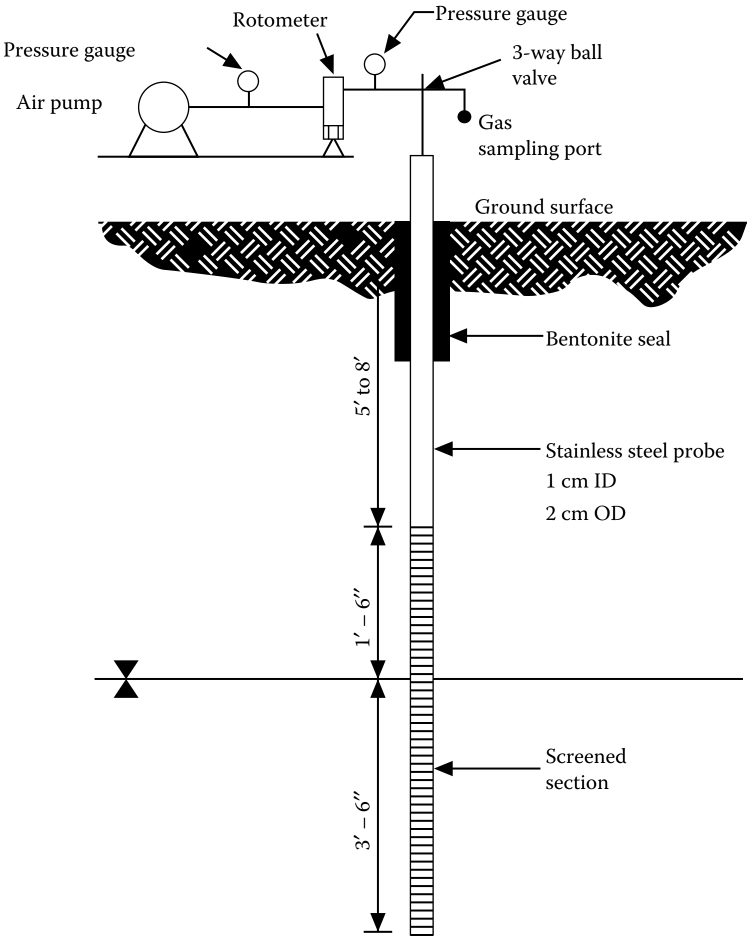


FIGURE 16.19 An air injection system.

For the same quantity of electricity, twice as many water molecules are electrolyzed at the cathode than at the anode, producing a chemical gradient of molecular water. As a consequence of the reactions, two supplemental ionic species, H^+ and OH^- (in addition to the migration of existing anions and cations in the pore fluid under the electrical field), are generated, and can have a significant influence on local conductance.

The electrical potential difference is initially distributed linearly across the specimen. The changing chemistry across the cell may result in variations in electrical potential difference in time and space. Specifically, an acid front is generated at the anode by the electrolysis reactions. A corresponding base front appears at the cathodes. This acid front generated at the anode advances toward the cathode in time under the influence of the imposed electrical, chemical, and hydraulic potential gradients. It is suggested that the movement of the acid front by migration (electrical potential), diffusion (chemical potential), and advection (hydraulic potential) will cause desorption of cations and other species from clay surfaces and facilitate their release into the pore fluid. With an open electrode configuration this front flushes through the specimen and reaches the cathode.[55] This phenomenon, together with the concurrent electroosmotic flow, would then constitute the mechanism for removing contaminants from soils.

Several factors influence the efficiency of removing contaminants from soils by EO. The first factor is the chemistry generated at the electrodes. Low-pH conditions generated at the anode cause desorption and ionization of most heavy metals and inorganic chemicals. However, a flux of high H^+ ion concentration results in an increase in conductivity and a decrease in electroosmotic flow. The pH conditions at the anode and the cathode should be strictly controlled and adjusted for continued flow. This adjustment depends on the cation-exchange capacity of the soil, the type and concentration of the chemicals in the soil, and the initial pH of the medium.

The second factor is the type and concentration of chemicals in soil. Soils with low initial ionic strengths favor high EO efficiencies. A lower initial ionic strength is responsible for a higher conductivity of the specimen, which in turn results in a decrease in the resistance offered to current flow, and hence the ion flow is governed more by diffusion and migration.

The third factor is the behavior of primary chemicals in the soil at different pH conditions. The chemistry in the system is governed by the pH gradients across the soil mass. Knowledge of the behavior of the primary chemicals in different pH environments is necessary for a better understanding of the efficiency and to enable a decision to be made on the required processing conditions and time.

The fourth factor is the current density. At an inert anode and for 100% Faradaic efficiency for water oxidation, the density of the current controls the flux of H^+ ions. The cathodic current density and the species available in its vicinity establish the efficiency of the reduction processes ($Pb^{2+} \rightarrow Pb$). These vary to a greater extent than the anode process, because the pH and the species reaching the cathode vary with processing time. Thus, control of the current density is critical to ensure optimal EO efficiency and contaminant removal.

The fifth factor is the water content of the soil. Electroosmotic flow is promoted at higher water contents. Therefore, high moisture content, and in particular saturated conditions are favored. However, the technique can be used in partially saturated deposits by supplying a pore fluid at the anode.

The sixth factor is conditioning. Similar to the changes in current density, the pore fluid at the anode and cathode compartments can be conditioned to a specific pH or chemistry to increase the efficiency of the process.

Preliminary laboratory data demonstrate the feasibility of removing Pb, Cr, Cd, Ni, Cu, Zn, As, TCE, BTEX compounds, and phenol from soils (clays and sandy clayey deposits, and dredged sediments) using EO technology. It has been demonstrated that 75 to 95% of Pb can be removed across the cell, in which a significant amount of the removed Pb can be electroplated at the cathode.

Metallic electrodes may dissolve as a result of electrolysis and may introduce corrosion products into the solid mass. However, if the electrodes are made of carbon or graphite, no residue will be introduced in the treated soil mass as a result of the process. The energy expenditure for Pb removal has been estimated to in the range 30 to 60 kWh/m^3 of soil. The EO method also provides an advantage over conventional pumping techniques for *in situ* treatment of contaminated fine-grained soils.

16.7.6 SOIL EXCAVATION AND *EX SITU* TREATMENT

If an *in situ* treatment method is not feasible, a soil excavation and treatment method should be conducted. The soil excavation and treatment method is usually more cost-effective for small sites and shallow contamination. Before excavation, planning is needed regarding the following steps of the treatment, among others:

1. Protecting fugitive gas accompanying the excavation
2. Pumping to remove liquids from the pounds and surface impoundments
3. Avoiding the mixing of clean soil with the excavated contaminated soil, and uncontrolled mixing of incompatible wastes
4. Covering excavated contaminated soils to prevent water leaching and fugitive dust production

16.7.6.1 Soil Washing Technology

For soil washing, contaminants sorbed onto fine soil particles are separated from bulk soil in a water-based system on the basis of particle size. The wash water may be augmented with a basic leaching agent, surfactant, or chelating agent, or by adjustment of pH to help remove organics and heavy metals. Soils and wash water are mixed *ex situ* in a tank or other treatment unit. The wash water and various soil fractions are usually separated using gravity settling.[90]

There are various agents that can be used to wash soil and drive its contaminants out, as discussed in the section on *in situ* soil flushing technology.

Washing with water may be used for the dissolution of soluble metallic ions and desorption of adsorbed metals and organics (such petroleum products), as long as the soil has high water affinity.

Surfactants or organic solvents are generally required for hydrophobic contaminants. When dealing with certain pesticides and metals that are insoluble in water, it may be necessary to add acids or chelating agents for their proper removal. However, these agents may create difficulties in wastewater treatment processes. If the soil contains a wide variety of contaminants, sequential washing steps may be needed along with adjustments in wash formulation or soil/wash-fluid ratios. A high percentage of silt and clay-sized particles in soil creates removal difficulties due to the contaminants being strongly adsorbed to these particles. Some sophisticated soil washing systems, such as the one developed by BioTrol, Inc., is claimed to be effective in washing contaminants (metals, PCB, pesticides, and petroleum products) concentrated in the fine-sized fraction of soil.[17]

16.7.6.2 Solvent Extraction

Solvent extraction has a similar procedure to the soil washing treatment. The difference is that solvent extraction uses organic chemicals as a solvent, whereas soil washing uses mainly water. Figure 16.20 illustrates the flow diagram of solvent extraction developed by CF System Corporation.[17,56] The waste and solvent are mixed, resulting in the organic contaminant dissolving into the solvent. The extracted organics are removed from the extractor with the solvent, which is transferred to a separator, where the pressure or temperature is changed, causing the organic contaminants to separate from the solvent. The solvent is recycled to the extractor and the concentrated contaminants are removed from the separator, disposed of, or reclaimed.

Solvent extraction shows effectiveness in the removal of organic wastes such as PCBs, VOCs, halogenated solvents, and petroleum wastes, but is less effective in removing inorganic compounds.[39] The removal of organic contaminants depends on the nature of the extracting solvent. Organic bound metals can become a constituent of the concentrated waste, which is undesirable because it can restrict both disposal and recycle options.

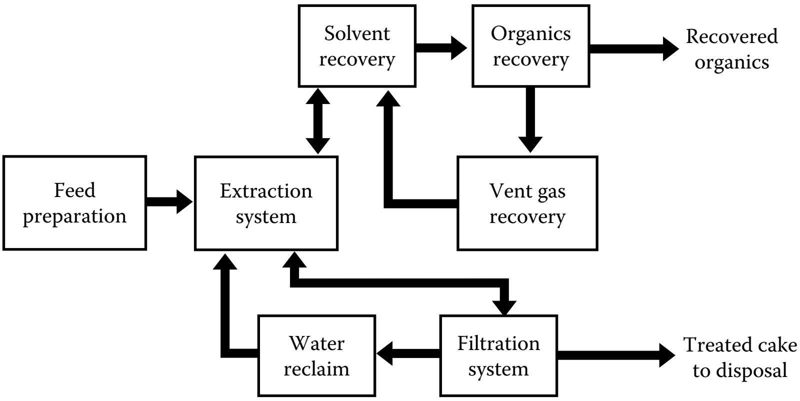


FIGURE 16.20 Solvent extraction remediation system.

Treated solids leave the extraction subsystem with trace amounts of extraction solvent, which usually volatilizes quickly. Ambient air should be monitored to determine if the volatilization of the solvent presents a problem.

16.7.6.3 Treatment of Washed Wastewater

The washed wastewater treatment techniques are basically the same as those used for pumped groundwater. Several integrated treatment technologies have been developed that can wash soil and treat washing water, such as that by BioTrol, Inc., in which the excavated soil is first screened, then washed, and finally the contaminated water is treated. As contaminants are difficult to wash from silt and clay, the clay and silt slurry contaminated with organics is treated in a bioslurry reactor.

In a technology developed by Excalibut Enterprises, Inc., a soil/liquid separator, such as a centrifuge or a cyclone, is used to separate the decontaminated soil from contaminated water.[17] Water is then treated with ozone and ultraviolet light, with ultrasound catalyzing the oxidation. This method is claimed to be able to treat soils contaminated with inorganics including cyanides, and organics such as PCBs, PCP, pesticides, herbicides, and dioxins.

Dissolved air flotation (DAF) technology, requiring a short detention time (less than 15 min) and a small space, combined with its mobility, is technologically and economically feasible for treatment of washed wastewater or contaminated groundwater.[57,58]

WasTech, Inc., has applied proprietary bonding reagents to a waste (soil or wastewater) containing organic and inorganic contaminants. The waste and reagent mixture is mixed with cementing materials that form a stabilizing matrix. The resultant material is a nonleaching, high-strength monolithic material that can be used to refill the excavated site.[17]

16.7.6.4 *Ex Situ* Thermal Desorption

In the thermal desorption technique excavated soil is heated to around 200 to 1000°F (93 to 538°C). Volatile and some semivolatile contaminants are vaporized and carried off by air, combustion gas, or inert gas. Off-gas is typically processed to remove particulates. Volatiles in the off-gas may be burned in an afterburner, collected on activated carbon, or recovered in condensation equipment. Thermal desorption systems are physical separation processes that are not designed to provide high levels of organic destruction, although some systems will result in localized oxidation or pyrolysis.

The thermal desorption process could be an excellent first step in soil treatment if used in conjunction with another *ex situ* treatment. Thermal desorption can remove TCE, most diesel fuel, and perhaps organically bound lead. Chemical Waste Management, Inc., has claimed that thermal desorption can reduce volatile organics to less than 1 mg/L and inorganics to less than 10 mg/L (sometimes even to less than 1 mg/L), and has shown a removal of 96 to 99+% of PCBs from soils containing 120 to 6000 mg/L of initial PCBs.[17,91]

16.7.6.5 Plasma Arc Verification

A plasma centrifugal furnace uses thermal heat transferred from arc plasma to create a molten bath that detoxifies the feed material. Organic contaminants are vaporized at temperatures of 2000 to 2500°F (1093 to 1371°C) to form innocuous products. Solids melt and are vitrified in the molten bath at 2800 to 3000°F (1540 to 1650°C). Metals are retained in this phase, which is a nonleachable, glassy residue. This method is applicable to soils contaminated with organic compounds and metals.

16.7.6.6 Direct Incineration

Direct incineration is mainly used for organically contaminated soil with sufficient concentration that no or little additional fuel is needed. Incineration of contaminated soil in a rotary kiln would result in virtually complete destruction of TCE and diesel fuel. The organic portion of lead dithiocarbonate would be destroyed, leaving lead and lead oxides in the soil. If lead cannot be removed from the soil subsequently, then it has to be disposed of as a hazardous waste.

Note that U.S. EPA regulations (under the RCRA) for hazardous waste incineration require that particulate emissions be no more than 180 mg/m^3 and that hydrogen chloride removal efficiency from the exhaust gas can be no less than 99%. Therefore, trial burns to determine the maximum ash and chlorine content that a waste can handle are needed prior to issuance of a permit.

16.7.6.7 Bioreactor Landfill

The Solid Waste Association of North America (SWANA) has defined a bioreactor landfill as "any permitted Subtitle D landfill or landfill cell where liquid or air is injected in a controlled fashion into the waste mass in order to accelerate or enhance biostabilization of the waste."

A bioreactor landfill operates to rapidly transform and degrade organic waste. The increase in waste degradation and stabilization is accomplished through the addition of liquid and air to enhance microbial processes. This bioreactor concept differs from the traditional "dry tomb" municipal landfill approach.[92,93] A bioreactor landfill is not just a single design and will vary to correspond to the operational process invoked. There are three different general types of bioreactor landfill configurations:

1. *Aerobic*. Leachate is removed from the bottom layer, piped to liquids storage tanks, and recirculated into the landfill in a controlled manner. Air is injected into the waste mass, using vertical or horizontal wells, to promote aerobic activity and accelerate waste stabilization.
2. *Anaerobic*. Moisture is added to the waste mass in the form of recirculated leachate and from other sources to obtain optimal moisture levels. Biodegradation occurs in the absence of oxygen (anaerobically) and produces landfill gas. Landfill gas, primarily methane, can be captured to minimize greenhouse gas emissions and for energy projects.
3. *Hybrid (aerobic–anaerobic)*. The hybrid bioreactor landfill accelerates waste degradation by employing a sequential aerobic–anaerobic treatment to rapidly degrade organics in the upper sections of the landfill and collect gas from lower sections. Operation as a hybrid results in an earlier onset of methanogenesis compared to aerobic landfills.

The bioreactor landfill is a remedial alternative that can be applied either on site or off site. However, landfilling is regarded as the least attractive alternative at a site cleanup action. Landfilling of hazardous materials is becoming increasingly difficult and more expensive due to steadily growing regulatory control.[92,93]

Bioreactor landfill operations should comply with RCRA landfill facility standards under 40 CFR Part 264. It should be noted that SARA strongly recommends on-site treatment that permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, and utilizes cost-effective permanent solutions. The legislation prohibits land disposal of hazardous wastes unless U.S. EPA determines otherwise. U.S. EPA guidance for CERCLA responses requires most on-site disposal actions to attain or exceed applicable and relevant standards of all Federal public health and environmental laws unless specific circumstances dictate otherwise.

The site conditions for an on-site landfill, such as location, geology, hydrogeology, physiography, climate, and so on, should also be suitable. Landfill should meet the minimum technology requirements and regulations for hazardous waste landfills such as double liners and leachate collection and removal systems, leak detection systems, closure procedures and final cover, and construction quality assurance.[59]

Off-site landfill is not desirable, because it faces more problems associated with off-site transportation. Other off-site treatment and disposal, such as incineration or other waste treatment methods performed off site, are also not attractive, because they are not the on-site permanent treatments as recommended by U.S. EPA. Off-site waste treatment should be used only if on-site applications are not possible.

The RCRA manifest requirements (40 CFR Parts 262 and 263) must be complied with for all wastes that are shipped off site. The regulations for transportation of hazardous wastes by the U.S. Department of Transportation, U.S. EPA, and states and local regulation agencies, should be complied with. A knowledge of RCRA regulations (40 CFR Parts 261–265) and other regulations developed by State Governments is required to determine the feasibility of off-site disposal.

16.7.7 SEDIMENTS REMEDIATION

Similar to soil remediation, *in situ* control and excavation-and-treat methods can be applied to sediment remediation.

16.7.7.1 *In Situ* Control and Containment

The aim of *in situ* control and containment is to reduce dispersion and leaching of a hazardous substance to other areas in the water body, in particular if removal of the substance is determined to be an unacceptable singular remedial response. The following briefly presents some common methods:

1. *Retaining dikes and berms*. Retaining dikes and berms include earthen embankments, earth-filled cellular and double-sheet pile walls, water inflated dams, and so on, which aim to minimize the transport of contaminated sediments.
2. *Cover methods*. Cover methods are used to cover contaminated sediments in order to minimize leaching of contaminants and prevent erosive transport of contaminated sediments.
3. *Surface sealing*. Surface sealing applies cement, quicklime, or other grouting materials to the surface or mixed with bottom sediments to create a seal.
4. *In situ grouting*. The *in situ* grouting method involves injecting grouting materials into sediments to stabilize the contaminated sediments. *In situ* containments can be either temporary or permanent. However, permanent containment of contaminated sediments has not been well demonstrated or widely used.

In situ methods have potential use as an interim or emergency measure until dredging can be undertaken or as a primary remedial action where it is determined to be more cost-effective than removal. The biggest advantages are that they are much less costly than dredging, eliminate the need for dredged material management, and minimize the resuspension of contained sediments.[15]

16.7.7.2 Sediment Removal

There are several methods used in the removal of contaminated sediments[60]:

1. *Mechanical dredging*. Mechanical dredging methods use mechanical excavation equipments such as backhoes, draglines, clamshells, and bucket ladder dredges.
2. *Hydraulic dredging*. Hydraulic dredging removes and transports sediment in a liquid slurry form.
3. *Pneumatic dredging*. The pneumatic dredging method utilizes pumping, operated using compressed air and hydrostatic pressure, to draw sediments to the collection head through transport piping. The dredged sediments are subsequently treated and disposed of. Other than the use of different instrumentation, the approaches used for soil remediation can be applied to sediments remediation.

16.7.8 POINTS-OF-ENTRY CONTROL AND ALTERNATIVE METHODS

The protection of human health from the threat of contaminated sites is mainly relevant during site cleanup and site control. However, if residential well water is contaminated, then point-of-entry control has to be applied. Point-of-entry control is used to avoid contaminated well water from entering houses for drinking and other in-contact uses. It has been pointed out by U.S. EPA[61] that taking showers in contaminated groundwater (especially in the case of VOC contamination) probably leads to far greater exposure to the chemicals than drinking the same water. The following sections present some common methods used as point-of-entry control.

16.7.8.1 Aeration

Aeration can be applied to well water contaminated by VOCs. It has been reported that 95–99% reduction in high-level (>100 μg/L) VOCs can be obtained by aeration. However, it should be noted that aeration is less effective for VOCs removal at lower concentrations (<10 μg/L). Boiling can further enhance the reduction of VOCs.[60,101,102]

Aeration is also an efficient process for removing radioactive radon from contaminated well water.

16.7.8.2 Distillation

Distillation can cause the evaporation of compounds that have boiling temperatures lower than 100°C. Thus, distilled water will contain more of those compounds, but will have lower concentrations of heavy metals and other components that have high boiling temperatures. Although VOCs are also evaporated with the water, they mostly evaporate in the early phase and can be removed; the recondensation of water at high temperatures (less than 100°C but higher than the boiling temperatures of VOCs) allows the separation of water from its contaminants that have lower boiling points. The VOCs will, however, continue to pose a health hazard in the atmosphere.[22,23]

16.7.8.3 Chemical Precipitation

Chemical precipitation is commonly used to remove heavy metal cations through pH adjustment. However, it is not appropriate to adjust the pH far from neutral for household drinking water applications. Alum (which has only a mild pH effect) is commonly used for the removal of colloids and ions from water.[22,23]

16.7.8.4 Flotation

Both dissolved air flotation (DAF) and electroflotation have been successfully applied to the removal of contaminants from surface water as well as groundwater.[62–64]

The contaminants that can be removed by flotation include conventional pollutants such as BOD, COD, total suspended solids (TSS), phosphorus, phenols, oil and grease, as well as toxic pollutants including heavy metals, toxic organics, pathogenic microorganisms, and radioactive radon.[22,28,33,54,64,100–102]

16.7.8.5 Ion Exchange

Ion exchange is effective for the removal of cationic or anionic heavy metal contaminants. It can also be used for water softening. Ion-exchange resins are usually regenerable with salt.[65]

16.7.8.6 Activated Carbon Adsorption

Granular activated carbon (GAC) is commonly used to remove contaminants from drinking water. It has the ability to remove contaminants to very low concentrations. Brunotts and colleagues[66] have studied 11 chemical spills and 18 groundwater contamination cases, which have shown that most contaminants were removed to less than 1 μg/L. GAC can be used effectively to remove both inorganic and organic contaminants.[22–24,38]

Water pH, temperature, hardness, and type and concentration of other solutes can influence GAC adsorption capacity. Certain types of pathogenic bacteria that are frequently colonized in carbon treatment units can also be released to the treated water. As in most conventional water treatment applications the pH, hardness, and pathogens are controlled, carbon adsorption can work effectively in conjunction with conventional water treatment technologies. Research conducted by Wang and colleagues[67] indicates that activated carbon adsorption is extremely effective for removing radioactive radon from contaminated groundwater. Although GAC is regenerable, the completely exhausted GAC should be replaced.

16.7.8.7 Membrane Methods

Membrane methods such as RO, MF, UF, and so on, are effective for removing certain sizes of molecules from contaminated water. However, energy is required for this removal technique.

16.7.8.8 Alternative Water Supply

Providing an alternative water supply, instead of treatment of contaminated well water, can be an alternative method of point-of-entry control. The cost of alternative water supply varies widely depending on site locations.[100–102]

16.7.9 NATURAL ATTENUATION

Natural attenuation relies on natural processes to clean up or attenuate pollution in soil and groundwater. Natural attenuation occurs at most polluted sites. However, the right conditions must exist underground to clean sites properly. If not, cleanup will not be quick enough or complete enough. Scientists monitor or test these conditions to make sure natural attenuation is working. This is called monitored natural attenuation (MNA).[94–96]

When the environment is polluted with chemicals, nature can work in four ways to clean it up:

1. Tiny bugs or microbes that live in the soil and groundwater use some chemicals for food. When they completely digest the chemicals, they can change them into water and harmless gases.
2. Chemicals can stick or sorb to soil, which holds them in place. This does not clean up the chemicals, but it can keep them from polluting groundwater and leaving the site.
3. As pollution moves through soil and groundwater, it can mix with clean water. This reduces or dilutes the pollution.
4. Some chemicals, such as oil and solvents, can evaporate, which means they change from liquids to gases within the soil. If these gases escape to the air at the surface, sunlight may destroy them.

MNA works best where the source of pollution has been removed. For instance, buried waste must be dug up and disposed of properly. Or it can be removed using other available cleanup methods. After the source is removed, the natural processes get rid of the small amount of pollution that remains in the soil and groundwater. The soil and groundwater are monitored regularly to make sure they are cleaned up.

The U.S. EPA publishes natural attenuation reports[94–96] that provide a general description on approaches to clean up contaminated waste sites. One U.S. EPA report lists five questions about each cleanup approach:

1. What is it?
2. How does it work?

3. Is it safe?
4. How long will it take?
5. Why use it?

Other U.S. EPA reports explain what MNA means when the term is used to describe a potential strategy to remediate a contaminated site. They also describe the various physical, chemical, and biological processes of natural attenuation that may occur at a site. Other informational materials are in preparation and will provide more specific details and scientific depth for the evaluation of MNA as a remedy at specific sites.

Surampalli, Ong, Seagren, and Nuno compiled and edited a book by the American Society of Civil Engineers (ASCE) called *Natural Attenuation of Hazardous Wastes*.[97] In addition to a discussion of the regulatory framework, this book covers major pollutants and basic scientific principles on physical, chemical, and biological processes involved in natural attenuation. It also contains an extensive review of literature, examples of applications of natural attenuation, and site characterization and monitoring requirements and procedures.

16.7.10 PHYTOREMEDIATION

Phytoremediation is a process that uses plants to remove, transfer, stabilize, or destroy contaminants in soil, sediment, and groundwater. The phytoremediation process may be applied *in situ* or *ex situ*, to soils, sludges, sediments, other solids, or groundwater.[98]

The mechanisms of phytoremediation include enhanced rhizosphere biodegradation (takes place in soil or groundwater immediately surrounding plant roots), phytoextraction (also known as phytoaccumulation, the uptake of contaminants by plant roots and the translocation/accumulation of contaminants into plant shoots and leaves), phytodegradation (metabolism of contaminants within plant tissues), and phytostabilization (production of chemical compounds by plants to immobilize contaminants at the interface of the roots and soil). Phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants (including the rhizosphere) and that aid in the cleanup of the contaminated substances. Plants can be used in site remediation, both through the mineralization of toxic organic compounds and through the accumulation and concentration of heavy metals and other inorganic compounds from soil into aboveground shoots.

16.7.11 REMEDIATION OPTIMIZATION

Remediation optimization uses defined approaches to improve the effectiveness and efficiency with which an environmental remedy reaches its stated goals. Optimization approaches might include third-party site-wide optimization evaluations conducted by expert teams, the use of mathematical tools to determine optimal operating parameters or monitoring networks, or the consideration of emerging technologies. Since 1999, U.S. EPA has promoted remediation optimization in the following manner:

1. It has commissioned over 40 third-party optimization evaluations known as Remediation System Evaluations (RSEs) at Superfund, RCRA, and Leaking Underground Storage Tank sites.
2. It has applied or demonstrated new mathematical tools for optimizing pumping strategies and monitoring networks.
3. It has developed fact sheets and training seminars to educate the remediation community about optimization and to convey lessons learned from U.S. EPA optimization projects.
4. It has worked on outreach efforts with many State and Federal partners to disseminate information on new optimization approaches for streamlining long-term remedial action.

Optimization efforts conducted by other organizations can be found at the Federal Remediation Technologies Roundtable (FRTR) optimization website.

16.8 CASE STUDY

This case example illustrates how the results of individual and comparative analyses of remedial alternatives may be presented in a feasibility study report. The study uses a U.S. EPA example[12] that focuses on a detailed analysis of the alternatives that had been selected after screening.

16.8.1 SITE BACKGROUND

The site is an old battery and cleaning solution storage facility located in a rural area. Improper handling and storage activities at the site during a ten-year period, from 1968 to 1978, resulted in soil and groundwater contamination.

Figure 16.21 presents a site map, showing the extent and types of contamination. Area 1 contains 19,110 m^3 (25,000 yd^3) of contaminated soil with concentrations of lead exceeding 200 mg/kg (reaching 500 mg/kg at several locations). Area 2 outlines a discrete area of approximately 15,290 m^3 (20,000 yd^3) of TCE-contaminated soil. A plume having TCE concentrations over 5 μg/L, the maximum contaminant level (MCL) (at certain points measured as high as 50 mg/L) is estimated to be moving in the direction of residential wells at an interstitial velocity of 19.82 m/yr (65 ft/yr). The large ruled area indicates the approximate location of groundwater contaminated with concentrations above the MCL. Analysis of soil samples from this area shows TCE concentrations up to 6% and slightly elevated levels of metals compared to background concentrations. Although the risk assessment did not identify a human health or environmental risk from these metals, there is a

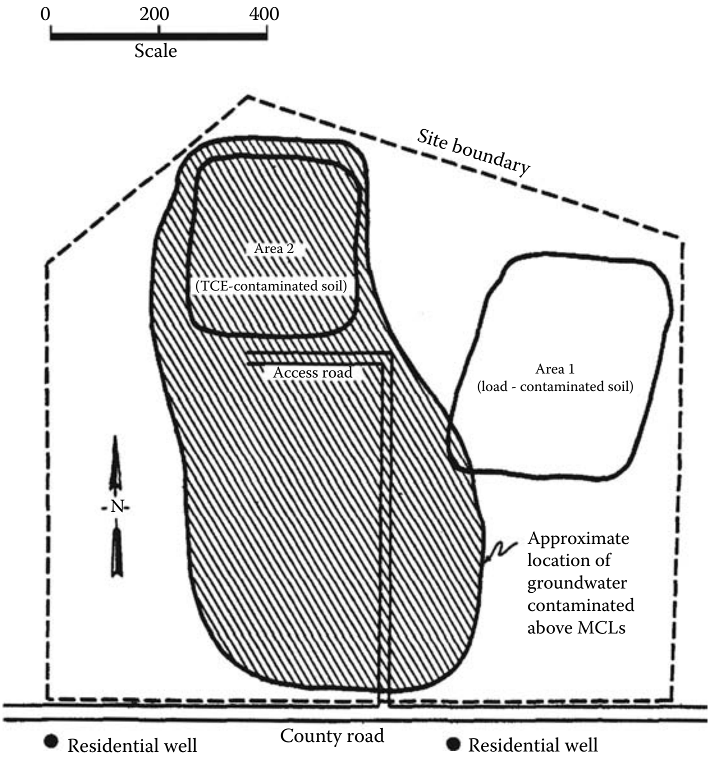


FIGURE 16.21 Site map: case example.

possibility that hot spots of metal contamination may have been missed. The soils of both Areas 1 and 2 are fairly permeable.

The affected aquifer that is used for drinking water is shallow. The water table lies approximately 3.66 m (12 ft) under the site. The aquifer consists of fractured bedrock, making groundwater containment difficult to implement. Groundwater extraction may also be difficult due to the fractured bedrock. The nearest residential well is 183 m (600 ft) from the site boundary, and the plume of contaminated groundwater is likely to reach the well in an estimated 1 to 3 yr at concentrations exceeding federal drinking water standards. Sampling conducted during the RI shows that no existing residential wells are currently contaminated.

The exposure pathways of concern identified during the baseline risk assessment include direct contact, with the possible ingestion of contaminated soil (1×10^{-3} associated excess cancer risk), and potential ingestion of contaminated groundwater in the future through existing or newly installed offsite wells (2×10^{-2} associated excess cancer risk).

The MCL for TCE (5 μg/L) has been determined to be a relevant and appropriate remediation level for the contaminated groundwater at this site because the groundwater is used as a source for drinking water. Based on the site-specific risk assessment, the MCL has been determined to be sufficiently protective as the aquifer remediation goal.

The risk assessment has also concluded that a level of 200 mg/kg for lead in the soil will be a protective level for expected site exposures along with an excess cancer risk level for TCE-contaminated soil (56 μg/L). Based on investigations of activities at the site, the TCE-contaminated soil has not been determined to be a listed RCRA hazardous waste, as the cleaning solution records indicate the solution contained less than 10% TCE. However, the lead-contaminated soil is an RCRA hazardous waste by characteristic in this instance due to extraction procedure (EP) toxicity. None of the waste is believed to have been disposed at the site after November 19, 1980 (the effective date for most of the RCRA treatment, storage, and disposal requirements).

16.8.2 THE LISTING OF ALTERNATIVES

Table 16.9 lists five remedial alternatives and their primary components. The nonaction alternative (Alternative 1) provides a baseline for comparison of other alternatives. Because no remedial activities will be implemented with the nonaction alternative, long-term human health and environmental risks for the site essentially will be the same as those identified in the baseline risk assessment. All other action alternatives with action have four common components:

1. *Fencing.* Fencing can be installed around the perimeter of a contaminated site to restrict public access. Signs warning of the presence and potential danger of hazardous materials can be posted on the fence to further discourage unauthorized access to the site.
2. *Institutional controls.* Many states are allowed by the current owner to place a deed restriction on the site that prohibits soil excavation and construction of buildings on any part of the site still containing hazardous materials upon completion of the remedy. In addition, a local groundwater well regulation requiring state review of all installation plans for groundwater wells can be used to prohibit the installation of drinking water supply wells in contaminated parts of the aquifer.
3. *Road reconstruction.* Some roads on the site can be restabilized and improved to allow construction activities and the movement of materials.
4. *Groundwater monitoring.* A selected number of new monitoring wells can be installed off site. Analytical results from new wells, some existing wells, and residential wells can be used to monitor future conditions and to assess the effectiveness of the final action. If the mean value of any compound at any facility boundary well is greater than the background concentration at the 0.05 significance level in two successive sampling rounds, appropriate investigative and remedial action(s) may be initiated as necessary.

TABLE 16.9
Alternative Component Case Example

	Alternative				
	1[a]	2[b]	3[c]	4[d]	5[e]
Groundwater					
Monitoring		●	●	●	●
Natural attenuation	NO ACTION	●			
Extraction wells			●	●	●
Onsite air stripping			●	●	●
Soil					
Soil/clay cap (Area 1)		●	●	●	●
Soil/clay cap (Area 2)		●			
Fixation (Area 1)				●	●
Soil vapor extraction (Area 2)			●	●	
Onsite incineration (Area 2)					●
Others					
Institutional controls		●	●	●	●
Road reconstruction		●	●	●	●
Fence		●	●	●	●

[a] Alternative 1—No action.

[b] Alternative 2—Cap and natural attenuation.

[c] Alternative 3—*In situ* soil vapor extraction, cap, and groundwater pump-and-treat.

[d] Alternative 4—*In situ* soil vapor extraction/soil fixation, cap, and groundwater pump-and-treat.

[e] Alternative 5—Incineration, *in situ* soil fixation, and groundwater pump-and-treat.

In fact, the nonaction alternative also requires groundwater monitoring and fencing. The following paragraphs describe the actions posed by the nonaction alternative and the four alternatives with actions, considering the site remediation case shown in Figure 16.21 and Table 16.9.

16.8.2.1 Alternative 1: No Action

The nonaction alternative (1) provides no control of exposure to the contaminated soil and no reduction in the risk to human health posed through the groundwater. It also allows for possible continued migration of the contaminated plume and further degradation of the groundwater.

16.8.2.2 Alternative 2: Cap and Natural Attenuation

The primary action in this alte rnative is capping of one or more contaminated areas (such as Areas 1 and 2 of Figure 16.21) and then natural attenuation of the contaminated groundwater. The cap would be consistent with the state RCRA (which is more stringent than the Federal requirement) landfill closure requirements.

A Geonet drainage layer can be chosen if the HELP model shows it to be more effective than sand in controlling leachate production and is comparable in cost. It is assumed that the HELP model predicts a 75 to 80% reduction in leachate production. A Geotextile layer would be laid on either side of the Geonet drain to prevent clogging. A minimum slope of 3% would be provided to meet state requirements.

Two assumptions about the surface have been made to determine the effect of natural attenuation on the contaminated groundwater. First, despite the fractured nature of the bedrock, it has been assumed that the subsurface is homogeneous so as to facilitate the evaluation. Second, the potential for reduction in TCE concentrations has been assessed using a hydrogeologic model in which the fact that the cap would reduce existing leachate production by 75% is taken into account. This model is assumed to predict that the concentration of TCE in the groundwater would be reduced to an excess cancer risk level of 28 μg/L in 60 yr and an excess cancer risk level of 5 μg/L, approximately equal to the MCL, in approximately 100 yr.

An alternative water supply would be included to provide a safe and reliable source of drinking water until the concentrations in the aquifer reach acceptable levels.

16.8.2.3 Alternative 3: *In Situ* SVE, Cap, and Groundwater Pump-and-Treat

This alternative consists of capping Area 1 (lead-contaminated soil), using *in situ* vapor extraction to treat the TCE-contaminated soil in Area 2, extracting the groundwater, and treating it on site through an air stripping system, and discharging it to the tributary of nearby receiving water.

It is demonstrated in the pilot tests that TCE can be removed by 99% for the direct contact exposure route within 3 to 5 yr using the vapor extraction system. The potential for fugitive losses of air contaminants would be minimal under good control conditions. A countercurrent packed tower air stripper (13.72 m tall and 1.22 m in diameter) would be used to treat the extracted groundwater to meet the performance goal of 5 μg/L TCE concentration. The exhaust air would be discharged through carbon beds for adsorption.

16.8.2.4 Alternative 4: *In Situ* SVE/Soil Fixation, Cap, and Groundwater Pump-and-Treat

For the site remediation case shown in Figure 16.21, this alternative consists of *in situ* SVE of TCE-contaminated soil (Area 2), *in situ* soil fixation of lead-contaminated soil (Area 1), cap (Area 1), and the groundwater pump-and-treat components of Alternative 3.

It is assumed that the moisture content of the soil has been determined to be approximately 50% under worst-case conditions. Using this information and the results from vendor tests, it has been determined that a minimum dose of one part solidification reagent to two parts soil is required for the migration control of lead. Testing has shown that the optimum solidification reagent mixture would comprise ca. 50% fly ash and ca. 50% kiln dust. Thus, ca. 7000 t (6364 T) each of fly ash and cement kiln dust would be required. The reagents would be added *in situ* with a backhoe. As one area of the soil is fixed, the equipment could be moved onto the fixed soil to blend the next section. It may be anticipated that the soil volume would expand by ca. 20% as a result of the fixation process. This additional volume would be used to achieve the required slope for the cap. An RCRA soil/clay cap placed over the solidified material is necessary to prevent infiltration and additional hydraulic stress on the fixed soil. It is estimated that the fixation would reduce lead migration by 40% and that the fixed soil may pass the U.S. EPA levels for lead.

16.8.2.5 Alternative 5: Incineration, *In Situ* Soil Fixation, and Groundwater Pump-and-Treat

This alternative includes components of Alternatives 3 and 4 and introduces a thermal destruction component to address the TCE-contaminated soil. For the site remediation case shown in Figure 16.21, the lead-contaminated soil in Area 1 would be fixed and covered with a soil/clay cap, as described in Alternative 4. The groundwater would be addressed through pumping and treating, via an air stripper, as described in Alternatives 3 and 4. The TCE-contaminated soil in Area 2 would be excavated and treated on site by a thermal destruction unit comprisng a mobilized rotary kiln.

It is estimated that approximately 15,290 m^3 (20,000 yd^3) of contaminated soil would need to be excavated and treated. The incinerator would be operated continuously (24 h/d, 365 d/yr), although some downtime would be required (20%) for regular maintenance. It is assumed that the incinerator would be operated to achieve 99.8% TCE removal from the soil and destruction efficiency as required by RCRA. Specific operating practices would be enforced to meet performance objectives, including 99.99% destruction of stack emissions as dictated by subtitle O of RCRA.

The facility would use a dry scrubber system for emission control, which would eliminate the need for wastewater treatment. Any water from emission control and from decontamination procedures would be treated in the on-site groundwater treatment system. The residual soil and collected ash is assumed to be nonhazardous and can be disposed of in a solid waste disposal facility in compliance with subtitle D of RCRA. In the event that they cannot be delisted due to the presence of metals, the residuals will be managed as part of the closure of Area 2 shown in Figure 16.21 (lead-contaminated soil).

The groundwater model simulation indicates that the shallow aquifer could be restored to 5 μg/L (MCL) in 25 to 40 yr with soil remediation. Without soil remediation, between 60 and 100 yr would be required.

16.8.3 COMPARATIVE ANALYSIS OF ALTERNATIVES

The alternatives are evaluated in relation to one another for each of seven evaluation criteria. The purpose of this analysis is to identify the relative advantages and disadvantages of each alternative. Table 16.10 shows how these five alternatives comply with the seven major criteria:

1. Overall protection of human health and the environment
2. Compliance with ARARs
3. Long-term effectiveness and permanence
4. Reduction of toxicity, mobility, or volume through treatment
5. Short-term effectiveness
6. Implementability
7. Cost

16.8.3.1 Overall Protection of Human Health and the Environment

All of the alternatives, except Alternative 1, provide adequate protection of human health and the environment. Risk through direct contact and groundwater ingestion is reduced to cancer risk levels less that 1×10^{-6} through each pathway. Alternatives 3, 4, and 5 prevent further migration of the contaminated groundwater by extracting and treating the plume to health-based ARAR levels.

Alternative 2 achieves protection by preventing exposure through capping and natural attenuation of the contaminated groundwater. Alternative 3 combines treatment to reduce the risk from the TCE-contaminated soil and groundwater and capping of the lead area. Alternatives 4 and 5 reduce risks posed by all portions of the site through treatment.

There is some uncertainty about the potential presence of metal in the TCE-contaminated soil of Area 2. If metal concentrations of concern are present, only Alternatives 2 and 5 would protect against direct contact and further groundwater contamination through a cap and incineration, respectively. Incineration of metal-contaminated soil may result in a hazardous waste residue, which would have to be disposed of in a hazardous waste landfill. Alternatives 3 and 4 rely on vapor extraction and would not lower risks from metal to human health or the environment.

16.8.3.2 Compliance with Applicable, Relevant and Appropriate Requirements (ARARs)

The evaluation of the ability of the alternatives to comply with ARARs includes a review of chemical-specific and action-specific ARARs as listed in Table 16.10. All alternatives will meet all of their respective ARARs except the nonaction alternative.

TABLE 16.10
Individual Evaluation of Final Alternatives: Case Study

Evaluation	Alternative 1 (No Action)	Alternative 2 (Cap, Natural Attenuation)	Alternative 3 (*In Situ* Soil Vapor Extraction, Cap, Groundwater Pump-and-Treat)	Alternative 4 (*In Situ* Soil Vapor Extraction, *In Situ* Soil Fixation, Cap, Groundwater Pump-and-Treat	Alternative 5 (*In Situ* Soil Fixation, Cap, Incineration, Groundwater Pump-and-Treat)
Overall protectiveness					
Human health protection					
Direct contact/soil ingestion	No significant reduction in risk; some reduction in access to risk through fence	Cap reduces direct contact risk and soil ingestion risk to less than 1×10^{-6}	Cap and vapor extraction reduce direct contact/soil ingestion risk to less than 1×10^{-6}	Cap, fixation, vapor extraction reduce direct contact/soil ingestion	Cap, fixation, incineration reduce direct contact/soil ingestion risk to less than 1×10^{-6}
Groundwater ingestion for existing users	No reduction in risk	Protect against existing risk by providing an alternative water supply	Reduces risk to less than 1×10^{-6} by pump-and-treat	See Alternative 3	See Alternative 3
Groundwater ingestion for future users	No reduction in risk	Institutional controls provide protection against risk from groundwater ingestion	Reduces risk to less than 1×10^{-6}	See Alternative 3	See Alternative 3
Environmental protection	Allows continued contamination of the groundwater	Continued contamination is curtailed by use of cap. Continued migration of contaminated groundwater is allowed	Continued contamination is curtailed by SVE and by cap; migration of contaminated groundwater is curtailed by pump-and-treat	Continued contamination is curtailed by SVE, soil fixation, and cap; migration of contaminated groundwater is curtailed by pump-and-treat	Continued contamination is curtailed by soil fixation and Incineration; migration of contaminated groundwater is curtailed by pump-and-treat
Compliance with ARARs					
Chemical-specific ARARS	Does not meet groundwater standards past the site boundary	Would meet MCLs at the waste boundary in over 50 years	Would meet MCLs at the waste boundary in 25–40 yr	See Alternative 3.	See Alternative 3
Location-specific ARARs	Not relevant; there are no location-specific ARARs	See Alternative 1	See Alternative 1	See Alternative 1	See Alternative 1
Action-specific ARARs	Would not meet any ARARs as there will be no action	Will meet RCRA landfill closure requirements	Would meet RCRA landfill closure requirements; would also meet air release standards from the vapor extraction system; would meet NPDES requirements	Would meet air release standards from air strippers and vapor extraction system; would meet NPDES requirements; would meet RCRA landfill closure requirements	Would meet regulations concerning incineration and air stripping; would meet NPDES requirements; would meet RCRA landfill closure requirements

Other criteria and guidance	Would allow ingestion of groundwater exceeding 1×10^{-4}; would not protect against Pb levels above 200 mg/kg in soil	Protects against soil ingestion 1×10^{-6} level and groundwater ingestion at 1×10^{-6} level; covers soil with Pb above 200 mg/kg	See Alternative 2	See Alternative 2	See Alternative 2
Long-term effectiveness and permanence					
Magnitude of residual risk					
Direct contact/soil ingestion	Source has not been removed; existing risk will remain	Risk is eliminated as long as cap is maintained; because source is only contained, inherent hazard of waste remains	Risk eliminated through vapor extraction and cap; some inherent hazard remains in the Pb material under the cap; risk from Pb would only occur if the cap were destroyed	Slight chance of future risk from fixed Pb-contaminated soil	See Alternative 4
Groundwater ingestion for existing users	Future risk greater as plume migrates to residents; eventually natural attenuation and dilution may decrease risk; risk significant for about 100 yr	Risk eliminated by providing alternative water supply; some risk would remain for over 100 yr if the groundwater is used	Risk eliminated by extracting groundwater exceeding 1×10^{-6} cancer risk levels; safe drinking water achieved in 25–40 yr with source control	See Alternative 3	See Alternative 3
Groundwater ingestion for future users	Risk greater as area of contamination increases; eventually natural attenuation and dilution may decrease risk; risk significant for about 100 yr	Institutional controls used to control use of contaminated groundwater; unauthorized use of groundwater would result in increased risk	Risk eliminated by extracting groundwater exceeding 1×10^{-6} cancer risk levels; safe drinking water achieved in 25–40 yr with source control	See Alternative 3	See Alternative 3
Adequacy and reliability of controls	No controls over remaining contamination; no reliability	Risk to groundwater controlled by alternative water supply and institutional controls; soil/clay cap controls contaminated soil; cap effective for Area 2 even if metals are present;	Soil/clay cap controls remaining contaminated soil in Area 1; would need additional controls for Area 2 if metals are present as SVE would not remove metals; groundwater extraction controls	See Alternative 3. Reliability of fixation with cap high, as are vapor extraction and groundwater pump-and-treat	Similar to Alternative 3; incinerator ash disposed in municipal landfill. If metals are present in Area 2, incinerator ash would be disposed in RCRA landfill. Incineration very reliable because material is

Continued

TABLE 16.10 (continued)

Evaluation	Alternative 1 (No Action)	Alternative 2 (Cap, Natural Attenuation)	Alternative 3 (*In Situ* Soil Vapor Extraction, Cap, Groundwater Pump-and-Treat)	Alternative 4 (*In Situ* Soil Vapor Extraction, *In Situ* Soil Fixation, Cap, Groundwater Pump-and-Treat	Alternative 5 (*In Situ* Soil Fixation, Cap, Incineration, Groundwater Pump-and-Treat)
		institutional controls are limited in effectiveness; reliability of cap can be high if maintained; institutional controls to control use of groundwater not very reliable	contaminated groundwater; both are adequate; reliability of vapor extraction high because no long-term O&M is required; cap reliable if maintained; groundwater pump-and-treat is reliable		destroyed; fixation with cap and groundwater pump-and-treat are reliable
Need for 5 yr review	Review could be required to ensure that adequate protection of human health and the environment is maintained	See Alternative 1; TCE and Pb soil would remain on site	See Alternative 1; Pb-contaminated soil would remain on site	See Alternative 1; fixed Pb residuals would remain on site	See Alternative 1; fixed lead residuals would remain on site
Reduction of toxicity, mobility, or volume through treatment					
Treatment process used	None	None	Vapor extraction of soil and groundwater air stripping	Vapor extraction, soil fixation, and groundwater air stripping	Incineration, soil fixation, and groundwater air stripping
Amount destroyed or treated	None	None	9.99% of volatiles in soil and 96% volatiles in groundwater removed and destroyed by carbon regeneration	Same as Alternative 3 and 25,000 cy of contaminated soil is fixed	99.8% of volatiles in 20,000 cy of soil destroyed and 25,000 cy of contaminated soil is fixed
Reduction of toxicity, Mobility or volume	None	None	Reduced volume and toxicity of contaminated groundwater; toxicity of soil contamination reduced	Reduced volume and toxicity of contaminated groundwater; toxicity of soil contamination in Area 2 reduced by 97% mobility of contaminants in Area 1 reduced by 10% while volume increased by 20%	Incineration reduces volume of contaminated soil by 20,000 cy and reduces toxicity; mobility of contaminants in Area 1 is reduced; volume and toxicity of contaminated groundwater is reduced

Irreversible treatment	None	None	Vapor extraction and air stripping with irreversible regeneration of carbon used for air stream treatment	See Alternative 3	Incineration is irreversible; air stripping with subsequent gaseous carbon treatment and regeneration is irreversible
Type and quanity of residuals remaining after treatment	No residuals remain	None	No detectable residuals in Area 2 remain; carbon from gaseous treatment requires regeneration	No detectable residuals in Area 2 remain; 30 000 cy of fixed soils remain in Area 1	Incinerated soil (18,000 cy) and fixed soil (30,000 cy) remain; incinerated soil expected to nonhazardous; carbon from gaseous treatment remains requiring regeneration
Statutory preference for treatment	Does not satisfy	Does not satisfy	Satisfies	Satisfies	Satisfies
Community protection	Risk to community not increased by remedy implementation, but, contaminated water may reach the residents within 1–3 yr	Temporary increase in dust production through cap installation; contaminated soils remain undisturbed	Soil would remain uncovered during vapor extraction for 3–5 yr Temporary increase in dust production during cap installation	Similar to Alternative 3 Fixation may result in dust and odor increase	Soil would remain uncovered during incineration (about 1 yr); excavation and fixation would release dust and odors to the atmosphere
Worker protection	No significant risk to workers	Protection required against dermal contact and inhalation of contaminated dust during cap construction	Protection required against dermal contact, vapor, or dust inhalation during construction and operation of vapor extraction system and air stripper	Protection required against dermal contact, vapor, or dust inhalation during construction and operation of vapor extraction system, fixation, and air stripper	Protection required against dermal contact and inhalation of volatiles and particulates as a result of exacavation, fixing, and incinerating TCE soil
Environmental impacts	Continued impact from existing conditions	Would be some migration of contaminant pluma as part of attenuation process	Vapor extraction may affect air quality and odors although it will meet emission standards; would be aquifer drawdown during groundwater extraction	See Alternative 3; fixation may also affect air quality and produce odors	Incineration may affect air quality by producing odors, although if will meet emission standards
Time until action is not applicable	Complete	Cap installed in 6 months; risk from groundwater reduced within 3 months due to	SVE complete in 3–5 yr; capping complete in 6 months; groundwater	Fixation and capping completed in 9 months; SVE complete in 3–5 yr;	Incineration complete in 2 yr from design completion; fixation and capping

Continued

TABLE 16.10 (continued)

Evaluation	Alternative 1 (No Action)	Alternative 2 (Cap, Natural Attenuation)	Alternative 3 (*In Situ* Soil Vapor Extraction, Cap, Groundwater Pump-and-Treat)	Alternative 4 (*In Situ* Soil Vapor Extraction, *In Situ* Soil Fixation, Cap, Groundwater Pump-and-Treat	Alternative 5 (*In Situ* Soil Fixation, Cap, Incineration, Groundwater Pump-and-Treat)
		alternative water supply and institutional controls	remedial action complete in 25–40 yr	groundwater action complete in 25–40 yr	complete in 9 months; groundwater action complete in 25–40 yr
Implementability					
Ability to construct and operate	No construction or operation	Simple to operate and construct; would require materials handling of about 50,000 cy of soil and clay	Vapor extraction requires some operation; fairly straightforward to construct; cap construction would require materials handling of 25,000 cy of soil and clay; on-site groundwater treatment requires operation	Fixation with cap somewhat difficult to construct; otherwise similar to Alternative 3	Incineration is difficult to operate; fixation with cap is somewhat difficult to construct; similar to Alternative 3 with respect to groundwater
Ease of more action if needed	If monitoring indicates more action is necessary, may need to go through the FS/ROD process again	Simple to extend extraction system and cap; cap would be sufficient if metals were significant in Area 2; could implement groundwater treatment if necessary	Simple to extend groundwater extraction system, vapor extraction system, and cap; however, if significant metal concentration are present in Area 2, may need additional soil treatment or would need to extend cap	Fairly complete alternative; can increase volume of or modify all technologies; if significant metal concentrations are present in Area 2, could use fixation	Complete alternative; can handle varying volumes or concentrations

Ability to monitor effectiveness	No monitoring; failure to detect contamination means ingestion of contaminated groundwater	Proposed monitoring will give notice of failure before significant exposure occurs	See Alternative 2	See Alternative 2	See Alternative 2
Ability to obtain appropriate and coordinate with other agencies permit	No approval necessary	See Alternative 1	Need a NPDES permit. Should be easy to obtain	See Alternative 3	Need to demonstrate technical intent of incenerator permit. Need an NPDES permit
Availability of services and capacities	No services or capacities required	See Alternative 1	See Alternative 1	Need fixation services	Need fixation and incineration services
Availability of equipment, specialists, and materials	No services capacities required	No special equipment, material, or specialists required; cap materials available within 20 miles	Needs readily available specialists to install and monitor vapor extraction system; need treatment plant operators; cap materials available within 20 miles		Need a mobile incinerator and trained operators; need treatment plant operators; closest source of incinerator is 50 miles from site
Availability of technologies	None required	Cap technology readily available	Vapor extraction will need to be developed; require pilot testing	Vapor extraction and fixation well developed; will require pilot testing	Incineration and fixation well developed; will require pilot testing
Cost					
Capital cost ($)	0	$4,200,000	$3,300,000	$6,200,000	$13,000,000
First year annual O&M cost	0	$60,000	$440,000	$480,000	$1,200,000
Present worth cost	0	$4,800,000	$7,300,000	$10,200,000	$16,000,000

Source: U.S. EPA, Guidance for Conduction Remedial Investigations and Feasibility Studies under CERCLA, EPA/540/G-89/004, U.S. EPA, Washington, DC, October 1988.

cy, cubic yard.

16.8.3.3 Long-Term Effectiveness and Performance

Alternatives 4 and 5 afford the highest degrees of long-term effectiveness and permanence because both alternatives use treatment or fixation technologies to reduce the hazards posed by all known wastes at the site. Although some contaminated soil would remain after implementation of both alternatives, it would be fixed to reduce mobility. These two alternatives differ only in the technology used to treat the TCE-laden soil. Although incineration would destroy more TCE than SVE, both alternatives reduce risks posed by the waste to a 1×10^{-6} cancer risk level through both the groundwater and soil pathways.

Alternatives 4 and 5 would rely on a soil/clay cap to control infiltration for Area 1 (lead-contaminated) as well as treatment or fixation. Upon completion, some long-term maintenance of the cap and groundwater monitoring would be required until each alternative has met the health-based cleanup goals for groundwater. These alternatives would have almost no long-term reliance on institutional controls.

Alternative 3 eliminates the risk of exposure at the site to the same levels as Alternatives 4 and 5 in the short term; however, it relies solely on a cap for controlling the waste remaining in Area 1. Although capping is an effective and accepted approach for reducing risk from direct contact with wastes, it is less reliable in the long term than treatment, because the inherent hazard of the lead would remain.

Alternative 2 leaves all of the contaminated waste at the site and relies solely upon a cap and institutional controls to prevent exposure. Although the alternative water supply lowers the risk of ingesting contaminated groundwater from existing wells, the institutional controls would not be effective for more than 5 to 10 years in preventing the installation of new wells and the injection of contaminated groundwater.

Long-term groundwater monitoring and cap maintenance requirements are more critical for Alternative 2, because all of the waste remains at the site.

16.8.3.4 Reduction of Toxicity, Mobility, or Volume through Treatment

Alternatives 4 and 5 use treatment or fixation technologies to reduce the inherent hazards posed by all known waste at the site, posing more than a 1×10^{-6} excess cancer risk level by ingestion. However, neither alternative completely treats all of the soil at the site. Both alternatives produce 22,937 m^3 (30,000 yd^3) of fixed soil, and 13,762 to 15,291 m^3 (18,000 to 20,000 yd^3) of treated soil. Under Alternative 5, there would remain 13,762 m^3 (18,000 yd^3) of soil (with 99.8% TCE removal). Under Alternative 4, there would remain 15,291 m^3 (20,000 yd^3) of soil (with 99.9% TCE removal). These two alternatives would satisfy the statutory preference for treatment as a principal element.

Alternative 3 also treats soil and groundwater for TEC. However, ca. 19,114 m^3 (25,000 yd^3) of lead-contaminated soil would remain untreated on site, although the lead mobility would be very low.

Alternative 2 uses no treatment technologies. All contaminated soil and groundwater would remain; however, contaminates will in time attenuate naturally.

16.8.3.5 Short-Term Effectiveness

Alternative 2 is anticipated to have the greatest short-term effectiveness, and presents the least amount of risk to workers, the community, and the environment. The other alternatives could release volatiles during excavation activities or SVE.

The time required to achieve short-term protection would be shorter than for any other alternative. It is anticipated that only 6 months would be required to install a new cap and to provide an alternative water supply. Alternatives 3 and 4, involving vapor extraction, require 3 to 5 yr before the risk from direct soil contact and ingestion is controlled.

Alternative 4 would take longer to implement than Alternative 2 and has a greater potential of releasing volatiles to the atmosphere during excavation than Alternatives 3 and 4. However, implementation of Alternative 5 would take less time than Alternatives 3 and 4 because incineration would require less time than SVE to remediate the soil to safe levels. Alternative 5 has the disadvantage of requiring incineration equipment, which could increase the risk to workers in the event of a failure.

16.8.3.6 Implementability

Alternative 2 is the simplest system to construct and operate. Alternative 3 is fairly simple with regard to construction requirements but has more operational requirements than Alternatives 1 and 2 because of the adoption of the SVE system and the air stripper. Alternative 4 is more complex than Alternative 3 because of the inclusion of *in situ* soil fixation components.

Alternative 5 is the most complex alternative to construct and, during implementation, to operate. During operation of the incinerator, this alternative would require the most attention because incinerators require periodic sampling of the residue and modification of operating parameters. It is expected that the incinerator would operate for slightly more than a year, whereas the SVE system of Alternative 4 would operate for 3 to 5 yr.

16.8.3.7 Cost Analysis

Alternative 2 has a lower present worth and O&M cost than Alternative 3, but because of the additional cap required it has a higher capital cost (USD 11,200,000 versus USD 8,000,000). The cap is one of the most expensive components to construct. Alternative 4 has a higher capital, O&M, and present worth cost than Alternatives 2 and 3. Alternative 5 has the highest capital (USD 34,600,000), first-year O&M (USD 3,200,000), and present worth cost (USD 42,600,000) of all of the alternatives because of the incinerator component. All costs have been updated in terms of 2007 USD.[68]

16.9 REMEDIATION, DECONTAMINATION, AND SAFETY MANAGEMENT

16.9.1 Site Preparation and Work Zones

Several site control procedures can be implemented to reduce worker and public exposure to chemical, physical, biological, and safety hazards[69,70,102–105]:

1. Compiling a site map, showing topographic features, prevailing wind direction, drainage, and the location of buildings, containers, impoundments, pits, ponds, and tanks
2. Preparing the site for subsequent activities (see Table 16.11)
3. Establishing work zones
4. Using the buddy system when necessary
5. Establishing and strictly enforcing decontamination
6. Establishing site security measures
7. Setting up communication networks
8. Enforcing safe work practices

Time and effort must be spent in preparing a site for the cleanup activity to ensure that response operations go smoothly and that worker safety is protected. Site preparation can be as hazardous as site cleanup. Therefore, safety measures should be afforded the same level of care at this stage as during actual cleanup. Table 16.11 presents the major steps in site preparation prior to any cleanup activities.

To reduce the accidental spread of hazardous substances by workers from a contaminated area to a clean area, zones should be delineated on the site where different types of operations will occur, and the flow of personnel among the zones should be controlled. The establishment of work zones will help ensure that personnel are properly protected against the hazards present where they are working, that work activities and contamination are confined to the appropriate areas, and that personnel can be located and evacuated in an emergency.

TABLE 16.11
Site Preparation

- Construct roadways to provide ease of access and a sound roadbed for heavy equipment and vehicles
- Arrange traffic flow patterns to ensure safe and efficient operations
- Eliminate physical hazards from the work area as much as possible, including:
  - Ignition sources in flammable hazard areas
  - Exposed or unground electrical wiring, and low overhead wiring that may entangle equipment
  - Sharp or protruding edges, such as glass, nails, and torn metal, which can puncture protective clothing and equipment and inflict puncture wounds
  - Debris, holes, loose steps or flooring, protruding objects, slippery surfaces, or unsecured railings, which can cause falls, slips, and trips
  - Unsecured objects, such as bricks and gas cylinders, near the edges of elevated surfaces, such as catwalks, roof tops, and scaffolding, which may dislodge and fall on workers
  - Debris and weeds that obstruct visibility
- Install skid-resistant strips and other antiskid devices on slippery surfaces
- Construct operation pads for mobile facilities and temporary structures
- Construct loading docks, processing and staging areas, and decontamination pads
- Provide adequate illumination for work activities. Equip temporary lights with guards to prevent accidental contact
- Install all wiring and electrical equipment in accordance with the National Electric Code

Source: U.S. GPO, Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, DHHS-NIOSH-85-115, U.S. Government Printing Office, Washington, DC, October, 1985. With permission.

Hazardous waste sites should be divided into as many different zones as needed to meet operational and safety objectives. For illustration, the following are three frequently used zones:

1. *Exclusion zone.* This is the contaminated area.
2. *Contamination reduction zone (CRZ).* This is the area where decontamination takes place.
3. *Support zone.* This is the uncontaminated area where workers should not be exposed to hazardous conditions (Table 16.12).

Delineation of these three zones should be based on sampling and monitoring results and on an evaluation of the potential routes and amount of contaminant dispersion in the event of a release. Movement of personnel and equipment among these zones should be minimized and restricted to specific access control points to prevent cross-contamination from contaminated areas to clean areas. A decision for evaluating health and safety aspects of decontamination methods is presented in Figure 16.22.[105]

To establish the hot lines, an environmental engineer will do the following:

1. Visually survey the immediate site
2. Determine the locations of (a) hazardous substances, (b) drainage, leachate, and spilled material, and (c) visible discolorations
3. Evaluate data from the initial site survey indicating the presence of (a) combustible gases, (b) organic and inorganic gases, particulates, or vapors, and (c) ionizing radiation
4. Evaluate the results of soil and water sampling
5. Consider the distances needed to prevent an explosion or fire from affecting personnel outside the exclusion zone
6. Consider the distances the personnel must travel to and from the exclusion zone
7. Consider the physical area necessary for site operation

8. Consider meteorological conditions and the potential for contaminants to be blown from the area
9. Secure or mark the hotline
10. Modify its location, if necessary, as more information becomes available

The support zone activities are briefly presented in Table 16.12.

TABLE 16.12
Support Zone Activities

Facility	Function
Command post	Supervision of all field operations and field teams
	Maintenance of communications, including emergency lines of communication
	Recordkeeping, including: – Accident reports – Chain-of-custody records – Daily logbooks – Manifest directories and orders – Personnel training records – Site inventories – Site safety map – Up-to-date site safety plans
	Providing access to up-to-date safety and health manuals and other reference materials
	Interfacing with the public: government agencies, local politicians, medical personnel, the media, and other interested parties
	Monitoring work schedules and weather changes
	Maintaining site security
	Sanitary facilities
Medical station	First-aid administration
	Medical emergency response
	Medical monitoring activities
	Sanitary facilities
Equipment and supply centers	Supply, maintenance, and repair of communications, respiratory, and sampling equipment
	Maintenance and repair of vehicles
	Replacement of expendable supplies
	Storage of monitoring equipment and supplies—storage may be here or in an on-site field laboratory
Administration	Sample shipment
	Interface with home office
	Maintenance of emergency telephone numbers, evacuation route maps, and vehicle keys
	Coordination with transporters, disposal sites, and appropriate federal, state, and local regulatory agencies
Field laboratory	Coordination and processing of environmental and hazardous waste samples; copies of the sampling plans and procedures should be available for quick reference in the laboratory
	Packaging of materials for analysis following the decontamination of the outsides of the sample containers, which should be done in the CRZ
	This packaging can also be done in a designated location in the CRZ
	Shipping papers and chain-of-custody files should be kept in the command post
	Maintenance and storage of laboratory notebooks in designated locations in the laboratory while in use, and in the command post when not in use

Source: U.S. EPA, Remedial Action at Waste Disposal Sites, EPA/625/6-85/006, U.S. EPA, Washington, DC, 1985.

16.9.2 HEALTH AND SAFETY HAZARDS

Although decontamination is performed to protect health and safety, it can pose hazards under certain circumstances. Decontamination methods may have the following characteristics:

1. They may be incompatible with the hazardous substances being removed (i.e., a decontamination method may react with contaminants to produce an explosion, heat, or toxic products)
2. They may be incompatible with the clothing or equipment being decontaminated (e.g., some organic solvents can permeate or degrade protective clothing)
3. They may pose a direct health hazard to workers (e.g., vapors from chemical decontamination solutions may be hazardous if inhaled or they may be flammable)

The chemical and physical compatibility of decontamination solutions or other decontamination materials must be determined before use. Any decontamination method that permeates, degrades, damages, or otherwise impairs the functioning of the personal protective equipment (PPE) is incompatible with such PPE and should not be used. If a decontamination method does pose a direct health hazard, measures must be taken to protect both decontamination personnel and the workers being decontaminated. Figure 16.22 presents a decision aid for the evaluation of health and safety aspects of decontamination methods.

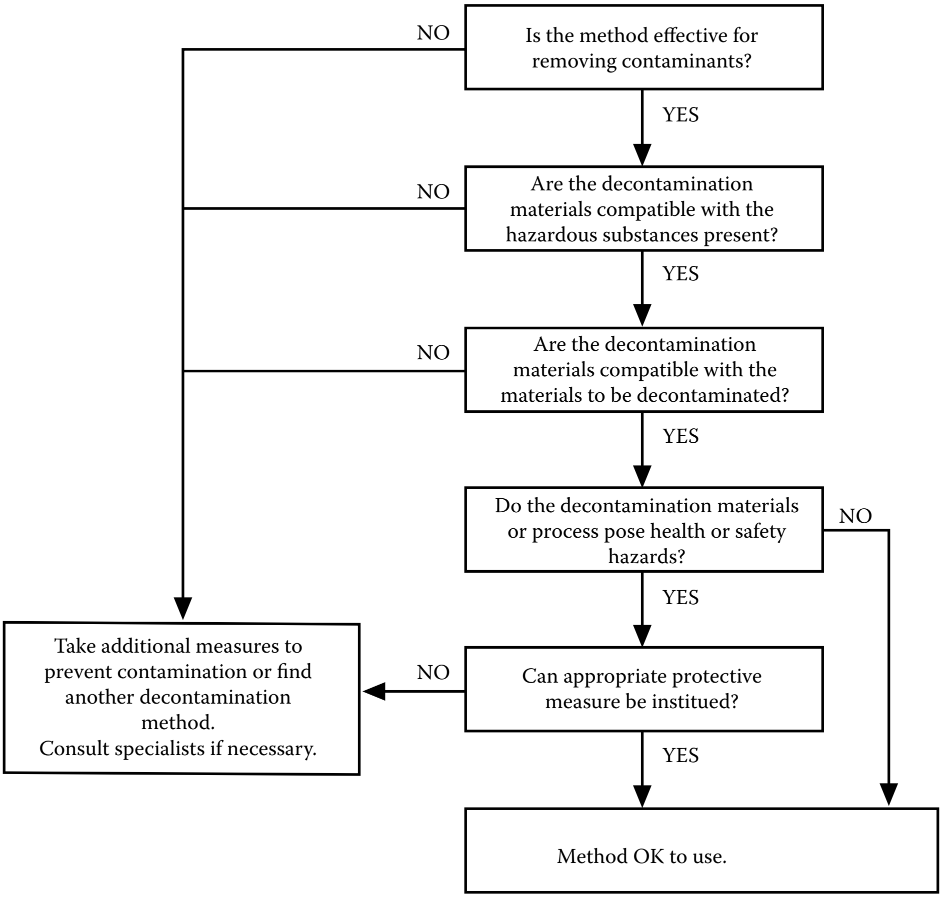


FIGURE 16.22 Decision aid for evaluating health and safety aspects of decontamination.

16.9.3 REMEDIATION/DECONTAMINATION FACILITY DESIGN

At a hazardous waste site, remediation and decontamination facilities should be located in the CRZ, that is, the area between the exclusion zone (the contaminated area) and the support zone (the clean area). The level and types of remediation and decontamination procedures required depend on several site-specific factors:

1. The chemical, physical, and toxicological properties of the wastes
2. The pathogenicity of infectious wastes
3. The amount, location, and containment of contaminants
4. The potential for, and location of, exposure based on assigned worker duties, activities, and functions
5. The potential for wastes to permeate, degrade, or penetrate materials used for personal protective clothing and equipment, vehicles, tools, buildings, and structures
6. The proximity of incompatible wastes
7. The movement of personnel or equipment among different zones
8. Emergencies
9. The methods available for protecting workers during decontamination
10. The impact of the decontamination process and compounds on worker safety and health

Decontamination procedures must provide an organized process by which levels of contamination are reduced. The decontamination process should consist of a series of procedures performed in a specific sequence. Each procedure should be performed at a separate station in order to prevent cross-contamination. The sequence of stations is called the decontamination line.

Stations should be separated physically to prevent cross-contamination and should be arranged in order of decreasing contamination, preferably in a straight line. Separate flow patterns and stations should be provided to isolate workers from different contamination zones containing incompatible wastes. Entry and exit points should be conspicuously marked, and the entry to the CRZ from the exclusion zone should be separate from the entry to the exclusion zone from the CRZ. Dressing stations for entry to the CRZ should be separate from redressing areas for exit from the CRZ. Personnel who wish to enter clean areas of the decontamination facility, such as locker rooms, should be completely decontaminated.

NOMENCLATURE

ARARs	Applicable, relevant, and appropriate requirements
ATSDR	Agency for Toxic Substances and Disease Registry
BOD	Biochemical oxygen demand
BTEX	Benzene, toluene, ethylbenzene, and xylenes (collectively)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COD	Chemical oxygen demand
CRP	Community relations plan
CRZ	Contamination reduction zone
CW	Circulating well
DAF	Dissolved air flotation
DAF-SBR	Dissolved air flotation sequencing batch reactor
ED	Electrodialysis
EO	Electroosmosis
FS	Feasibility study
FSP	Field sampling plan
GAC	Granular activated carbon

GEMS	Genetically engineered microbial system
HSP	Health and safety plan
HSWA	Hazardous and Solid Waste Amendments
MF	Microfiltration
NAPL	Nonaqueous phase liquids
NCP	National Contingency Plan
NPL	National Priorities List
PAC	Powder activated carbon
PCB	Polychlorinated biphenyls
PCE	Pentachloroethylene
PCF-SBR	Physical-chemical flotation sequencing batch reactor
PCS-SBR	Physical-chemical sedimentation sequencing batch reactor
PPE	Personal protective equipment
PRB	Permeable reactive barrier
PRP	Potential responsible party
QA	Quality assurance
QAPP	Quality assurance project plan
RBC	Rotating biological contactor
RCRA	Resource Conservation and Recovery Act
Redox	Reduction/oxidation
RF	Radio frequency
RFH	Radio frequency heating
RI	Remedial investigation
RO	Reverse osmosis
SAP	Sampling and analysis plan
SARA	Superfund Amendments and Reauthorization Act
SBR	Sequencing batch reactor
SPSH	Six-phase soil heating
SVE	Soil vapor extraction
SVOC	Semi-volatile organic compounds
SWANA	Solid Waste Association of North America
TBC	To be considered
TCE	Tetrachloroethylene
TOC	Total organic carbon
UF	Ultrafiltration
USACE	United States Army Corps of Engineers
U.S. EPA	United States Environmental Protection Agency
U.S. GPO	United States Government Printing Office
USGS	United States Geological Services
VICs	Volatile inorganic compounds
VOCs	Volatile organic compounds

APPENDIX

U.S. Army Corps of Engineers Civil Works Construction Yearly Average Cost Index for Utilities

Year	Index	Year	Index
1967	100	1988	369.45
1968	104.83	1989	383.14
1969	112.17	1990	386.75
1970	119.75	1991	392.35
1971	131.73	1992	399.07
1972	141.94	1993	410.63
1973	149.36	1994	424.91
1974	170.45	1995	439.72
1975	190.49	1996	445.58
1976	202.61	1997	454.99
1977	215.84	1998	459.40
1978	235.78	1999	460.16
1979	257.20	2000	468.05
1980	277.60	2001	472.18
1981	302.25	2002	484.41
1982	320.13	2003	495.72
1983	330.82	2004	506.13
1984	341.06	2005	516.75
1985	346.12	2006	528.12
1986	347.33	2007	539.74
1987	353.35		

Source: U.S. ACE, Civil Works Construction Cost Index System Manual—Index for Utilities, 110-2-1304, U.S. Army Corps of Engineers, Washington, 2007, p. 44. With permission.

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17 Enzymatic Removal of Aqueous Pentachlorophenol

Khim Hoong Chu, Eui Yong Kim, and Yung-Tse Hung

CONTENTS

17.1 INTRODUCTION

Pentachlorophenol (PCP) has been used extensively as a pesticide, herbicide, and wood-preserving agent at many wood treating sites. The chemical structure of PCP is shown in Figure 17.1. It is a probable human carcinogen and has been placed on the U.S. EPA priority pollutant list. Its presence in the environment is therefore of particular concern. In recent years many countries have banned the use of PCP. Unfortunately, past legal disposal practices coupled with the environmental stability of PCP have led to widespread contamination of soil, surface water, and groundwater aquifers. Many of the more than 700 wood preserving sites identified in the U.S. are currently being dealt with under federal, state, or voluntary cleanup programs.[1]

Various treatment methods can be used to remove PCP from contaminated environmental compartments, and the treatment of PCP-contaminated soil usually involves a combination of physical, chemical, and biological methods. An integrated system combining soil washing with a solvent, recovery of the spent solvent for reuse, and biodegradation of the desorbed PCP in aqueous solution has been proposed.[2–4] The biodegradation of aqueous PCP by microorganisms has several advantages over chemical and physical methods, including mild operating conditions and better environmental compatibility. Several species of bacteria and fungi can biodegrade PCP.[5–15] These organisms secrete

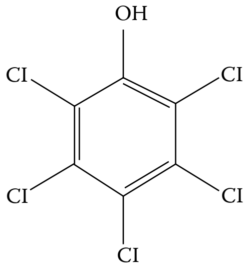


FIGURE 17.1 Chemical structure of pentachlorophenol (PCP).

a series of oxidative enzymes that are capable of catalyzing the oxidation of PCP. However, high concentrations of PCP can be inhibitory to the activity of the degrading organisms. Cho and colleagues[9] have shown that PCP concentrations higher than 50 mg/L inhibit the growth of some PCP-degrading white rot fungi such as *Gloeophyllum odoratum* and *Trametes versicolor* completely. As a result, the direct application of isolated enzymes has been proposed as an alternative method of removing PCP from aqueous solution. A number of reviews on the *in vitro* use of oxidative enzymes to catalyze the oxidation of phenolic substances including PCP are available in the literature.[16–18] For PCP oxidation, the enzymes that have been tested include horseradish peroxidase (HRP),[19–25] laccase,[26–28] ligninase,[29] and other extracellular peroxidases.[30]

Because HRP has been used extensively to transform a wide range of phenolic contaminants, this chapter focuses on the salient aspects of the HRP-catalyzed oxidation of PCP in the presence of hydrogen peroxide (H_2O_2). The oxidation process generates free aromatic radicals, which combine to form polymers of low solubility that eventually precipitate from solution. Thus, the enzyme-mediated removal process is also known as polymerization precipitation. The major product of the HRP-catalyzed oxidation of PCP over the pH range 4 to 7 is 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone (PPCHD).[31] PPCHD is formed by the coupling of two pentachlorophenoxyl radicals, the expected products of one-electron oxidation reactions catalyzed by HRP and other peroxidases. The chemical structure of PPCHD is shown in Figure 17.2. Although the HRP-mediated oxidative coupling process has enormous potential for remediation of aqueous solutions contaminated by PCP, its application is hampered by the low operational stability of HRP as a result of inactivation by the enzyme's own substrate, H_2O_2.[32] The key area of interest reported in this chapter is the elucidation of the inhibitory effect of H_2O_2 on HRP activity. To this end, a theoretical model incorporating saturation kinetics and formation of a catalytically inactive form of HRP in the presence of excess H_2O_2 was developed to facilitate the quantitative evaluation of the oxidative inactivation of HRP.[20] It should be noted that HRP inactivation can occur via two other mechanisms: radical attack and sorption by precipitated products. The analysis of such mechanisms is beyond the scope of this chapter.

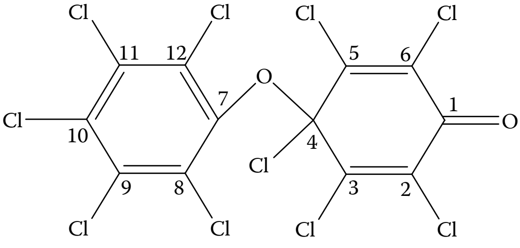


FIGURE 17.2 Chemical structure of 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone (PPCHD).

17.2 DESCRIPTION OF HORSERADISH PEROXIDASE

As its name implies, HRP (EC 1.11.1.7) is isolated from the roots of horseradish (*Armoracia rusticana*). A comprehensive description of the structure, function, mechanism of action, and practical applications of HRP has recently been given by Veitch.[33] HRP exists in the form of several distinctive isoenzymes, with the C isoenzyme (HRP C) being the predominant form. It consists of 308 amino acid residues, a ferric heme prosthetic group, and 2 mol of calcium per mol of protein, adding up to a molecular weight of 34,520. It is glycosylated and contains four highly conserved disulfide bridges. Recently, there have been key advances in our understanding of HRP and some of these include X-ray crystallographic studies of the crystal structure[34] of HRP C as well as the intermediate species in the catalytic cycle of the enzyme.[35] HRP can accommodate a broad range of substrates in a variety of reactions. Although it is widely used in analytical diagnostics such as in enzyme immunoassays and biosensors, its low operational stability hampers its commercial applications in organic synthesis for the biotransformations of various drugs and chemicals and in the detoxification of aromatic contaminants.

17.3 MODEL DEVELOPMENT

17.3.1 Catalytic Cycle and Inactivation of HRP

HRP catalyzes the oxidation of a variety of organic and inorganic substances, with H_2O_2 as electron acceptor. The global reaction catalyzed by HRP is described by Equation 17.1, in which an oxidant (H_2O_2) reacts with a reducing substrate (AH_2) to produce a radical product ($\bullet AH$) and H_2O:

$$H_2O_2 + 2\,AH_2 \xrightarrow{\text{HRP}} 2\,\bullet AH + 2\,H_2O \tag{17.1}$$

The above reaction proceeds in three distinct steps. First, the native ferric enzyme reacts with the oxidizing substrate (H_2O_2). Following binding of H_2O_2 to the heme in the Fe(III) state, the heterolytic cleavage of the oxygen–oxygen bond of H_2O_2 results in the two-electron oxidation of the heme to form an intermediate (compound I) comprising a ferryl species (Fe(IV) = O) and a prophyrin radical cation, with the concomitant release of a water molecule. Compound I is a reactive intermediate with a higher formal oxidation state (+5 compared with +3 for the resting enzyme). Compound I is then converted back to the resting enzyme via successive single-electron transfers from two reducing substrate molecules (AH_2). The first reduction, of the prophyrin radical cation, yields a second enzyme intermediate, compound II, which retains the heme in the ferryl (Fe(IV) = O) state and the free radical $\bullet AH$. The second reduction regenerates the ferric heme resting state of the enzyme and delivers another free radical $\bullet AH$ and a water molecule. The catalytic cycle of HRP involving the oxidation and reduction of the heme group can be described by the following reaction scheme:

$$E + H_2O_2 \longrightarrow E_{\text{i}} + H_2O \tag{17.2}$$

$$E_{\text{i}} + AH_2 \longrightarrow E_{\text{ii}} + \bullet AH \tag{17.3}$$

$$E_{\text{ii}} + AH_2 \longrightarrow E + \bullet AH + H_2O \tag{17.4}$$

In these equations, E, E_{i}, and E_{ii} represent the resting enzyme, compound I, and compound II, respectively.

Numerous studies have shown that oxidation of a wide range of AH_2 by HRP in the presence of H_2O_2 is characterized by a loss of enzyme activity. It is now well established that HRP is inactivated by H_2O_2.[32] Because the final step (Equation 17.4), during which the oxidized ferryl intermediate is reduced, is very slow, inactivation of HRP is thought to occur by reaction of compound II with an additional molecule of H_2O_2:

$$E_{ii} + H_2O_2 \longrightarrow E_{iii} + H_2O \tag{17.5}$$

where E_{iii} is known as compound III, which is an inactive form of the enzyme. The degree of inactivation appears to depend on several factors, including the chosen electron donor AH_2, the amount of H_2O_2, and the concentration ratio of H_2O_2 and the electron donor. The above reaction scheme describes and summarizes the major catalytic and inactivation pathways that have been identified. Because the enzyme is a significant contributor to the cost of contaminant degradation, judicious control of H_2O_2 concentration to avoid enzyme inactivation will help to enhance the commercial viability of this approach. We describe here a mathematical model that can be used to predict the inhibitory effect of H_2O_2 on the catalytic behavior of HRP.

17.3.2 Proposed Reaction Mechanism

A kinetic model describing the HRP-catalyzed oxidation of PCP by H_2O_2 should account for the effects of the concentrations of HRP, PCP, and H_2O_2 on the reaction rate. To derive such an equation, a reaction mechanism involving saturation kinetics is proposed. Based on the reaction scheme described in Section 17.3.1, which implies that the catalytic cycle is irreversible, the three distinct reactions steps (Equations 17.2 to 17.4) are modified to include the formation of Michaelis–Menten complexes:

$$E + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E^* \xrightarrow{k_2} E_i + H_2O \tag{17.6}$$

$$E_i + PCP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} E_i^* \xrightarrow{k_4} E_{ii} + \bullet P \tag{17.7}$$

$$E_{ii} + PCP \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} E_{ii}^* \xrightarrow{k_6} E + \bullet P + H_2O \tag{17.8}$$

In these equations, E^*, E_i^*, and E_{ii}^* represent Michaelis–Menten complexes, $\bullet P$ is the PCP-derived radical, k_{-1}, k_{-3}, k_{-5} and k_1 to k_6 are the rate constants of the respective reactions. The existence of the Michaelis–Menten complexes between HRP and H_2O_2 (E^*) and between compound I or compound II and certain reducing substrates (E_i^* or E_{ii}^*) has been demonstrated by van Haandel and colleagues,[36] Baek and van Wart,[37] and Rodríguez-López and colleagues,[38] respectively. It should be noted that the radical generation steps in Equation 17.7 and Equation 17.8 have also been proven to be reversible.[39] The overall reaction is given by

$$H_2O_2 + 2PCP \xrightarrow{HRP} 2\bullet P + 2H_2O \tag{17.9}$$

The radical intermediates $\bullet P$ can couple with each other, leading to the formation of polymeric precipitates that can be readily removed from water (see Figure 17.2). The polymerization of the free radicals is known to be extremely fast, and it is therefore not included in the above reaction scheme.

17.3.3 Derivation of the Reaction Rate Equation

To derive a rate equation based on Equations 17.6, 17.7, and 17.8, the following assumptions are made. First, at the start of the reaction the concentrations of the products are assumed to be zero in comparison with those of the reactants. Thus, these equations can be considered to be essentially irreversible during the early stages of reaction. Second, Equation 17.8 is assumed to be the rate-limiting step, because under most steady-state conditions the reaction of HRP with H_2O_2 is very fast, and the reaction of compound II with the reducing substrate is at least 10 to 20 times slower than that of compound I.[40] The overall reaction rate V is thus given by

$$V = k_6[E_{\mathrm{ii}}^*] \tag{17.10}$$

Applying steady-state assumptions, the rate equation for the reaction mechanism described by Equations 17.6, 17.7, and 17.8 can be obtained:

$$V = \frac{\dfrac{1}{\dfrac{1}{k_2}+\dfrac{1}{k_4}+\dfrac{1}{k_6}}[E_0][\mathrm{H_2O_2}][\mathrm{PCP}]}{\dfrac{\dfrac{k_{-1}+k_2}{k_1k_2}}{\dfrac{1}{k_2}+\dfrac{1}{k_4}+\dfrac{1}{k_6}}[\mathrm{PCP}] + \dfrac{\dfrac{k_{-3}+k_4}{k_3k_4}+\dfrac{k_{-5}+k_6}{k_5k_6}}{\dfrac{1}{k_2}+\dfrac{1}{k_4}+\dfrac{1}{k_6}}[\mathrm{H_2O_2}] + [\mathrm{H_2O_2}][\mathrm{PCP}]} \tag{17.11}$$

where $[E_0]$ denotes the initial concentration of enzyme. Further details concerning the derivation of Equation 17.11 by the schematic method of King and Altman[41] are given in the Appendix. Equation 17.11 indicates that the reaction mechanism follows the well-known Ping–Pong Bi–Bi mechanism. This mechanism is characterized by the product of the enzyme's reaction with the first substrate (i.e., H_2O_2), being released before the reaction of the enzyme with the second substrate (i.e., PCP). The general form of the rate equation based on the Ping–Pong Bi–Bi mechanism is given by

$$V = \frac{K_{\mathrm{cat}}[E_0][A][B]}{K_{\mathrm{m}}^{\mathrm{A}}[B] + K_{\mathrm{m}}^{\mathrm{B}}[A] + [A][B]} \tag{17.12}$$

where $[A]$ and $[B]$ denote the concentrations of two different substrates, and K_{cat}, $K_{\mathrm{m}}^{\mathrm{B}}$, and $K_{\mathrm{m}}^{\mathrm{A}}$ are constants.

Recasting Equation 17.11 in the form of Equation 17.12 gives

$$V = \frac{K_{\mathrm{cat}}[E_0][\mathrm{H_2O_2}][\mathrm{PCP}]}{K_{\mathrm{m}}^{\mathrm{H_2O_2}}[\mathrm{PCP}] + K_{\mathrm{m}}^{\mathrm{PCP}}[\mathrm{H_2O_2}] + [\mathrm{H_2O_2}][\mathrm{PCP}]} \tag{17.13}$$

where

$$K_{\mathrm{cat}} = \frac{1}{\dfrac{1}{k_2}+\dfrac{1}{k_4}+\dfrac{1}{k_6}};\quad K_{\mathrm{m}}^{\mathrm{H_2O_2}} = \frac{\dfrac{k_{-1}+k_2}{k_1k_2}}{\dfrac{1}{k_2}+\dfrac{1}{k_4}+\dfrac{1}{k_6}};\quad K_{\mathrm{m}}^{\mathrm{PCP}} = \frac{\dfrac{k_{-3}+k_4}{k_3k_4}+\dfrac{k_{-5}+k_6}{k_5k_6}}{\dfrac{1}{k_2}+\dfrac{1}{k_4}+\dfrac{1}{k_6}}$$

Equation 17.13 has been derived without taking account of HRP inactivation by H_2O_2, which is described in Equation 17.5. One simple way to remedy this situation is to introduce an inactivation constant into Equation 17.13:

$$V = \frac{K_{\text{cat}}[E_0][\text{H}_2\text{O}_2][\text{PCP}]}{K_{\text{m}}^{\text{H}_2\text{O}_2}[\text{PCP}] + (K_{\text{m}}^{\text{PCP}} + [\text{PCP}])\left(1 + \frac{[\text{H}_2\text{O}_2]}{K_{\text{i}}}\right)[\text{H}_2\text{O}_2]} \tag{17.14}$$

where K_{i} is an inactivation constant that describes the inhibitory effect of H_2O_2. Equation 17.14 may be used to predict the effects of enzyme, H_2O_2, and PCP concentrations as well as the inhibitory effect of H_2O_2 concentration on the reaction rate, provided that the four constants K_{cat}, $K_{\text{m}}^{\text{H}_2\text{O}_2}$, $K_{\text{m}}^{\text{PCP}}$, and K_{i} are known. In the next section, we describe how these constants may be estimated by fitting Equation 17.14 to experimental data.

17.4 PARAMETER ESTIMATION AND MODEL VALIDATION

17.4.1 Experimental Data

To generate experimental data for parameter estimation, batch reaction experiments were conducted at 25°C using solutions containing equimolar concentrations of PCP and H_2O_2 (0.01 to 6 mM) in 100 mM sodium phosphate buffer (pH 6.5). The enzymatic reaction was initiated by adding a dose of HRP stock solution to the reaction mixture. Experiments were conducted at four different initial enzyme concentrations: 0.13, 0.148, 0.295, and 0.34 μM. Solution samples were taken at fixed time intervals and centrifuged to settle precipitated colloidal particles. The PCP concentration of the supernatant was determined using a UV spectrophotometer. Initial reaction rates were estimated from the initial slopes of PCP concentration versus time curves. Additional experiments were conducted to generate a new set of data for model validation. In these experiments, the initial enzyme and PCP concentrations were fixed at 0.72 μM and 1.5 mM, respectively, while the initial H_2O_2 concentration was varied in the range 0.01 to 12 mM.

17.4.2 Parameter Estimation

The four constants in Equation 17.14 may be estimated by fitting the equation to the measured initial reaction rate data presented in Figure 17.3. Because equimolar concentrations of the two substrates, PCP and H_2O_2, were used in the experiments, Equation 17.14 may be simplified as follows:

$$\begin{aligned} V &= \frac{K_{\text{cat}}[E_0][S]^2}{K_{\text{m}}^{\text{H}_2\text{O}_2}[S] + (K_{\text{m}}^{\text{PCP}} + [S])\left(1 + \frac{[S]}{K_{\text{i}}}\right)[S]} \\ &= \frac{K_{\text{cat}}[E_0][S]}{K_{\text{m}}^{\text{H}_2\text{O}_2} + K_{\text{m}}^{\text{PCP}} + \left(1 + \frac{K_{\text{m}}^{\text{PCP}}}{K_{\text{i}}}\right)[S] + \frac{1}{K_{\text{i}}}[S]^2} \end{aligned} \tag{17.15}$$

where $[S] = [\text{PCP}] = [\text{H}_2\text{O}_2]$. Fitting Equation 17.15 to the data shown in Figure 17.3 provides a simple way of estimating the four constants.

The best-fit values of the four constants were estimated by minimizing the error between experimental data and model calculations. The minimization algorithm is based on a genetic algorithm, which is a stochastic optimization technique patterned after the natural selection process taking place during biological evolution. It explores all regions of the solution space using a population of individuals. Each individual represents a set of the parameters to be optimized. Initially, a population of individuals is formed randomly. The fitness of each individual is evaluated using an objective function. Upon completion of the fitness evaluation, genetic operations such as mutation and cross-

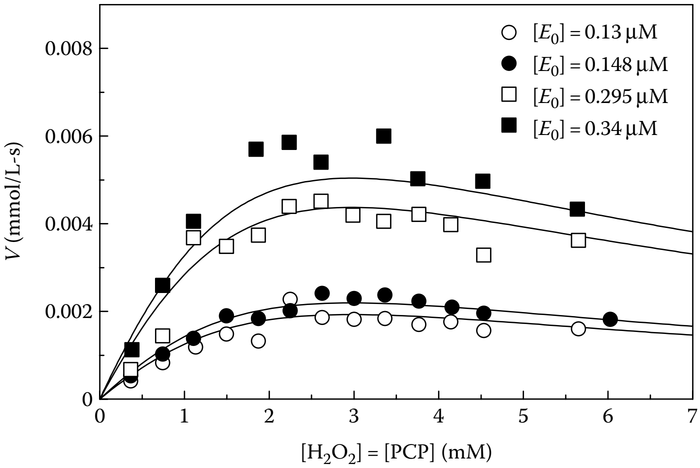


FIGURE 17.3 Experimental data (symbols) showing the variation of reaction rate V with equimolar substrate concentration ($[H_2O_2]$ = [PCP]) for different initial enzyme concentrations $[E_0]$. Also shown are the theoretical curves (lines) calculated according to Equation 17.15 with the constants of set A as given in Table 17.1.

over are applied to individuals selected according to their fitness to produce the next generation of individuals for fitness evaluation. This process continues until a near-optimum solution is found.

Because the genetic algorithm searches the entire input space in parallel, it is more robust than traditional deterministic methods and is more likely to converge to a unique global minimization. As with any artificial intelligence technique, the performance of a genetic algorithm is affected by a number of design parameters such as the initial population size, parent selection, crossover rate, mutation rate, and the number of generations. Some initial tests indicate that the genetic algorithm used in this work is robust to parameter variations, with the population size and the number of generations having the largest effect on performance. Using a population of 100, the solution successfully converged to the optimum values after 2000 to 3000 generations. All computations were conducted using the software package Matlab®. An excellent description of the implementation of genetic algorithms and their use as a problem-solving and optimization technique can be found in the book by Goldberg.[42]

Repetitive optimization runs reveal the existence of two distinct sets of best-fit values within the search space of 0 to 500 for each constant. These best-fit values are listed in Table 17.1. A comparison between the reaction rate profiles calculated from the two sets of constants (lines) and experimental data (symbols) is shown in Figure 17.3 and Figure 17.4. It is clear that there is generally good agreement, although at the highest $[E_0]$ examined the two theoretical curves underestimate the middle part of the experimentally measured reaction rate data. It is further observed that both sets of constants give congruent theoretical profiles. It can therefore be concluded that unique parameter estimates cannot be obtained for the simplified nonlinear model (Equation 17.15), because more than one combination of parameters can describe the same data set. In addition, the value of K_m^{PCP}

TABLE 17.1
Best–Fits Values of K_{cat}, $K_m^{H_2O_2}$, K_m^{PCP}, and K_i

Set	K_{cat} (s^{-1})	$K_m^{H_2O_2}$ (mM)	K_m^{PCP} (mM)	K_i (mM)
A	87.7	7.2	0.05	1.22
B	269.2	24.7	~0	0.34

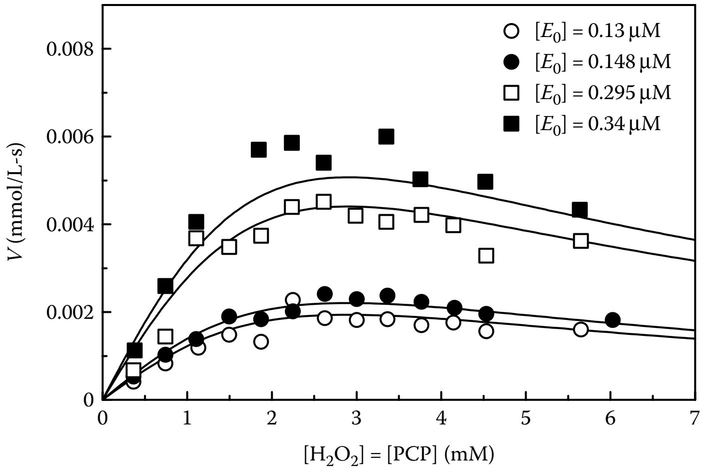


FIGURE 17.4 Experimental data (symbols) showing the variation of reaction rate V with equimolar substrate concentration ($[H_2O_2]$ = [PCP]) for different initial enzyme concentrations $[E_0]$. Also shown are the theoretical curves (lines) calculated according to Equation 17.15 with the constants of set B as given in Table 17.1.

identified by this multiparameter estimation routine is either zero or very close to zero, indicating that it is not a significant parameter. Simultaneous retrieval of unique estimates of the four constants may require fitting the original model equation (Equation 17.14) to data obtained from experiments with different combinations of $[E_0]$, [PCP], and $[H_2O_2]$. As the fitted parameters are able to capture the general trends of the experimental data, as shown in Figure 17.3 and Figure 17.4, the best-fit constants of set A are used in the simulation studies reported in Section 17.5.

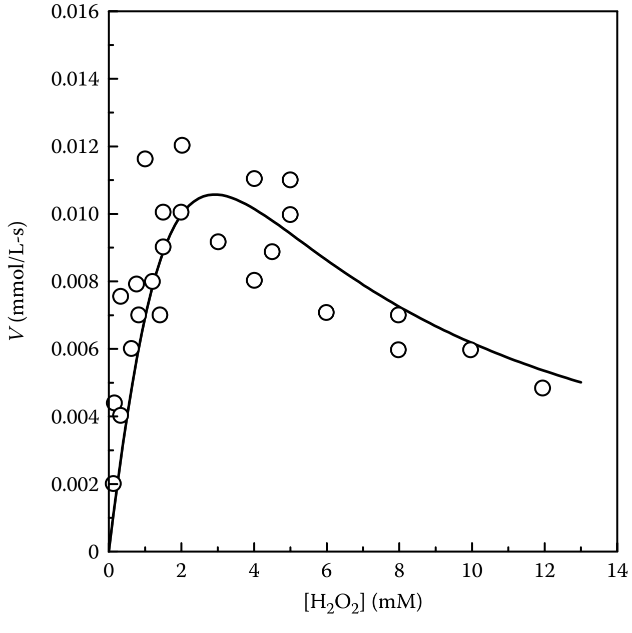


FIGURE 17.5 Experimental data (symbols) showing reaction rate V as a function of $[H_2O_2]$. The initial enzyme and PCP concentrations are $[E_0]$ = 0.72 μM and [PCP] = 1.5 mM, respectively. The theoretical curve (line) calculated from Equation 17.14 with the constants of set A (Table 17.1) is shown for comparison.

17.4.3 Model Validation

Because the constants identified by the parameter estimation approach described above are not unique, it is important to assess the predictive capability of the model equation before the model is used for simulation studies. The predictive capability of Equation 17.14 can be assessed by comparing its predictions with data obtained from experiments conducted at conditions that are different from those used to generate data for parameter estimation. A set of such data (symbols) is shown in Figure 17.5, together with the theoretical curve (line) calculated from Equation 17.14 with the constants of set A. As can be seen in Figure 17.5, although the simulation does not capture the measured reaction rate data accurately, it does predict the trend very well. Given that the experimentally measured data show some scatter, for all practical purposes the agreement achieved using the rate constants of set A is quite satisfactory. The results presented in Figure 17.5 clearly show that the reaction rate is inhibited when the H_2O_2 concentration is higher than ~3 to 4 mM. Having developed confidence in the theoretical model after matching the simulation results with the experimental observations, the model is used to examine the inhibitory effect of H_2O_2 in greater detail in the next section.

17.5 MODEL SIMULATION

17.5.1 Dependence of the Reaction Rate on PCP Concentration

We first examine the dependence of the reaction rate V on PCP concentration. Figure 17.6 and Figure 17.7 show the effect of PCP concentration on reaction rate for different initial enzyme and H_2O_2 concentrations, respectively. The reaction rate profiles shown in these two figures are calculated from Equation 17.14 with the constants of set A. Both figures show highly rectangular reaction rate profiles, indicating that the reaction rate reaches its maximum value at very low PCP concentrations (~0.1 to 0.2 mM) for a given initial enzyme or H_2O_2 concentration. The plateau of the profiles gives the maximum rate of reaction. The profiles shown in Figure 17.6 indicate that the maximum reaction rate increases if more enzyme is added. This is of course a typical feature of enzyme kinetics. On the other hand, the profiles in Figure 17.7 do not show a monotonic rise in maximum reaction rate with

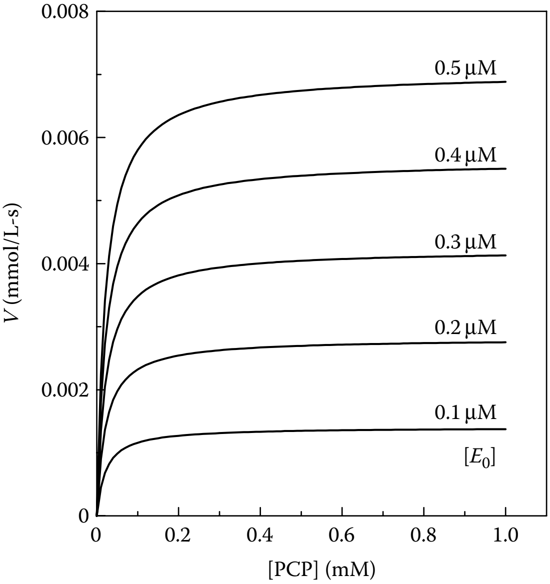


FIGURE 17.6 Theoretical profiles showing the variation of reaction rate V with [PCP] for different initial enzyme concentrations [E_0]. [H_2O_2] = 2 mM.

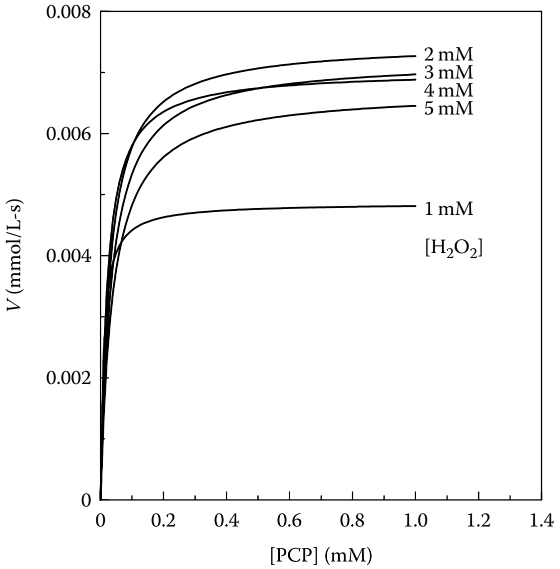


FIGURE 17.7 Theoretical profiles showing the variation of reaction rate *V* with [PCP] for different [H_2O_2]. The initial enzyme concentration is [E_0] = 0.5 μM.

H_2O_2 concentration. The simulation results suggest that the maximum reaction rate at first increases and then decreases with increasing H_2O_2 concentration, reflecting the inhibitory effect of H_2O_2.

17.5.2 DEPENDENCE OF THE REACTION RATE ON H_2O_2 CONCENTRATION

In this section, we describe the dependence of the reaction rate *V* on H_2O_2 concentration, as the reaction rate has been shown to be suppressed at high H_2O_2 concentrations (see Figure 17.5). Representative theoretical curves calculated according to Equation 17.14 with the constants of set A

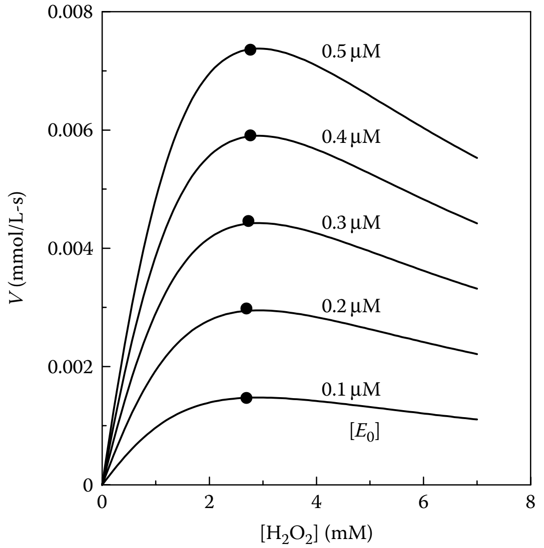


FIGURE 17.8 Theoretical profiles showing the variation of reaction rate *V* with [H_2O_2] for different initial enzyme concentrations [E_0]. [PCP] = 2 mM. The solid circles indicate the location of the maximum reaction rate.

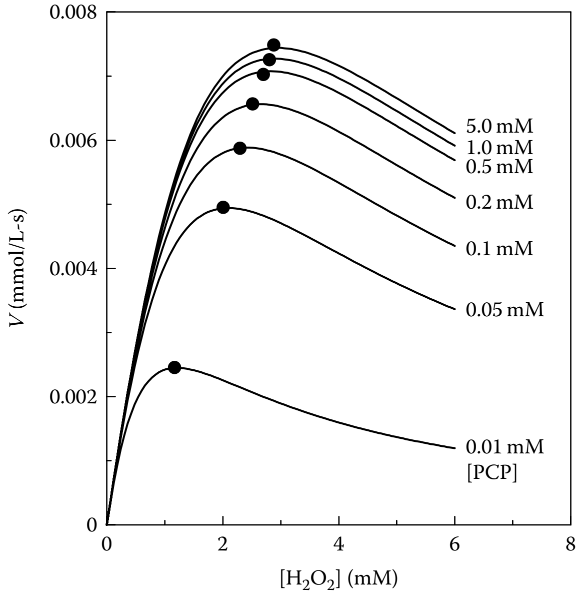


FIGURE 17.9 Theoretical profiles showing the variation of reaction rate *V* with $[H_2O_2]$ for different [PCP]. The initial enzyme concentration is $[E_0] = 0.5\ \mu M$. The solid circles indicate the location of the maximum reaction rate.

are shown in Figure 17.8 and Figure 17.9. As expected, the figures show that the reaction rate increases with increasing initial enzyme or PCP concentration at a given H_2O_2 concentration. Also, the reaction rate profiles in both figures have almost the same shape, although they differ in absolute values; they initially increase with increasing H_2O_2 concentration, reaching a maximum value before declining with a further increase in H_2O_2 concentration. This type of curve is commonly observed for systems in which the substrate is inhibiting.

However, two major differences between the two sets of profiles are observed. First, the variation in the shape of the profiles in Figure 17.8 is directly proportional to the enzyme concentration, but although the variation in Figure 17.9 is quite pronounced in the low PCP concentration region, at higher values of PCP concentration this is no longer true. The curves lie quite close together when the PCP concentration is >0.5 mM. Second, Figure 17.8 shows that the maximum reaction rate for each profile, as indicated by the solid circles, does not vary with H_2O_2 concentration and it appears to occur at a H_2O_2 concentration of ~3 mM. By contrast, Figure 17.9 shows that the occurrence of the maximum reaction rate is governed by the H_2O_2 concentration when the PCP concentration is varied from 0.01 to 5 mM. The simulation results presented in Figure 17.9 suggest that for a given PCP concentration an optimum H_2O_2 concentration exists that gives the maximum reaction rate. As it is desirable to run the enzymatic reaction at the maximum possible reaction rate, knowledge of the relationship between the optimum H_2O_2 concentration and PCP concentration is of great practical interest. The next section describes how this relationship may be derived from the model equation.

17.5.3 DETERMINATION OF OPTIMUM H_2O_2 CONCENTRATION

The relationship between the optimum H_2O_2 concentration and PCP concentration may be derived from Equation 17.14. Differentiating *V* with respect to the H_2O_2 concentration and setting the derivative to zero ($dV/d[H_2O_2] = 0$) yields the following equation:

$$\left[H_2O_2\right]_{\text{opt}} = \sqrt{\frac{K_m^{H_2O_2} K_i[\text{PCP}]}{K_m^{\text{PCP}} + [\text{PCP}]}} \qquad (17.16)$$

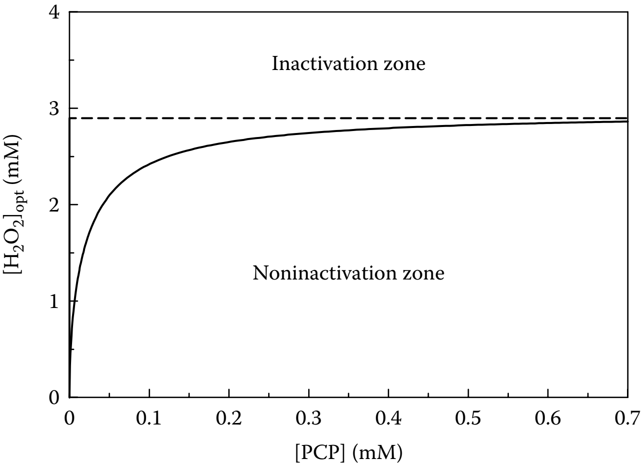


FIGURE 17.10 Theoretical profiles showing the variation of optimum $[H_2O_2]$ with [PCP] according to Equation 17.16. The solid and broken lines are calculated from Equation 17.16 with the constants of sets A and B, respectively (Table 17.1).

where $[H_2O_2]_{opt}$ is the optimum H_2O_2 concentration. The solid line in Figure 17.10 is a plot of Equation 17.16 using the constants of set A. This curve gives the optimum H_2O_2 concentration at which the maximum reaction rate occurs for a given PCP concentration. As can be seen in Figure 17.10, when the PCP concentration is <0.5 mM, the optimum H_2O_2 concentration increases nonlinearly with increasing PCP concentration. When the PCP concentration is >0.5 mM the optimum H_2O_2 concentration approaches an asymptote and becomes independent of the PCP concentration. Figure 17.10 therefore serves as a useful guide for selecting combinations of H_2O_2 and PCP concentrations that would avoid enzyme inactivation by H_2O_2. For example, the noninactivation zone is designated by the area below the solid line, and the area above the solid line depicts the inactivation zone where the inactivated form of the enzyme, E_{iii}, is formed in the presence of excess H_2O_2, leading to reduced reaction rates.

The low operational stability of HRP as a result of inactivation by H_2O_2 seriously impedes commercial applications of the enzyme in detoxification of waste streams and industrial organic synthesis. One approach to improving the operational stability of HRP is to maintain the concentration of H_2O_2 at a low level. This can be achieved using an appropriate method of H_2O_2 addition or generation. Examples of these methods include the stepwise addition of H_2O_2, feed-on-demand addition of H_2O_2, and *in situ* generation of H_2O_2.[43]

A different curve is observed when Equation 17.16 is plotted using the constants of set B. The optimum H_2O_2 concentration curve goes straight up from the origin to a certain H_2O_2 concentration and then extends horizontally from that point, as depicted by the broken line in Figure 17.10. This curve overestimates the optimum H_2O_2 concentration when the PCP concentration is <0.5 mM. Such a limiting form is a consequence of K_m^{PCP} being set to 0. As a result, we can see from Equation 17.16 that the optimum H_2O_2 concentration becomes independent of the PCP concentration. Nevertheless, from Figure 17.10 it is clear that both curves predict a limiting optimum H_2O_2 concentration of ~2.9 mM, even though the values of $K_m^{H_2O_2}$ and K_i used in generating the two curves are quite different, as may be seen from Table 17.1. This is evidently due to the fact that for high values of PCP concentration Equation 17.16 will approach the asymptote $\sqrt{K_m^{H_2O_2} K_i}$. The practically important conclusion from this analysis is that the effective use of mathematical models for simulation studies requires the development of sound methodologies to identify the key model parameters. It is essential to know whether the measured data are sufficient for identifying the unknown parameters and the conditions under which they are identifiable. The development of robust parameter estimation methodologies is beyond the scope of this chapter.

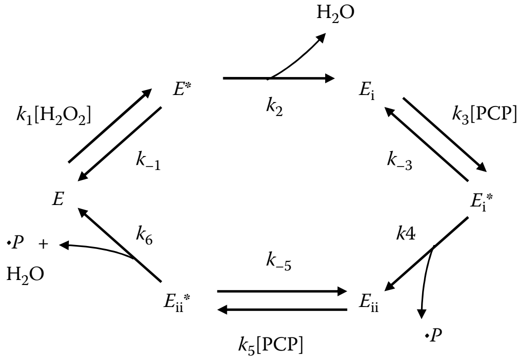
NOMENCLATURE

AH_2	Reducing substrate
E	Free enzyme
E^*	Enzyme–substrate complex
E_{i}	Compound I
E_{i}^*	Enzyme–substrate complex
E_{ii}	Compound II
E_{ii}^*	Enzyme–substrate complex
E_{iii}	Compound III
HRP	Horseradish peroxidase
k_1	Forward rate constant, L/mol-s
k_{-1}	Reverse rate constant, s^{-1}
k_2	Rate constant, s^{-1}
k_3	Forward rate constant, L/mol-s
k_{-3}	Reverse rate constant, s^{-1}
k_4	Rate constant, s^{-1}
k_5	Forward rate constant, L/mol-s
k_{-5}	Reverse rate constant, s^{-1}
k_6	Rate constant, s^{-1}
K_{cat}	Rate constant, s^{-1}
K_{i}	Inactivation constant, mM
$K_{\mathrm{m}}^{\mathrm{H_2O_2}}$	Constant, mM
$K_{\mathrm{m}}^{\mathrm{PCP}}$	Constant, mM
PCP	Pentachlorophenol
PPCHD	2,3,4,5,6-Pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone
V	Reaction rate, mol/L-s
$\bullet AH$	Radical product of AH_2
$\bullet P$	Radical product of PCP
$[A]$	Concentration of substrate, mM
$[B]$	Concentration of substrate, mM
$[E]$	Concentration of free enzyme, mM
$[E_0]$	Initial concentration of enzyme, mM
$[E^*]$	Concentration of enzyme–substrate complex, mM
$[E_{\mathrm{i}}]$	Concentration of compound I, mM
$[E_{\mathrm{i}}^*]$	Concentration of enzyme–substrate complex, mM
$[E_{\mathrm{ii}}]$	Concentration of compound II, mM
$[E_{\mathrm{ii}}^*]$	Concentration of enzyme–substrate complex, mM
$[E_{\mathrm{iii}}]$	Concentration of compound III, mM
$[\mathrm{H_2O_2}]$	Concentration of hydrogen peroxide, mM
$[\mathrm{H_2O_2}]_{\mathrm{opt}}$	Optimum concentration of hydrogen peroxide, mM
[PCP]	Concentration of pentachlorophenol, mM
$[S]$	Concentration of substrate, mM

APPENDIX

This appendix illustrates the steps involved in deriving the reaction rate equation (Equation 17.11) from the reaction scheme given in Section 17.3.2 using the King and Altman method.[41] This schematic method allows the derivation of a rate equation for essentially any enzyme mechanism in terms of the individual rate constants of the various steps in biocatalysis.

Step 1. An enzymatic reaction is considered as a cyclic process that displays all the interconversions among the various enzyme forms involved. For each step in the reaction a rate constant is defined in terms of the product of the actual rate constant for that step and the concentration of free substrate involved in the step. Hence, the cyclic form of the reaction scheme given in Equations 17.6, 17.7, and 17.8 is represented by



Because the enzyme serves as a catalyst and is not consumed, the conservation equation on the enzyme yields

$$[E_0] = [E] + [E^*] + [E_i] + [E_i^*] + [E_{ii}] + [E_{ii}^*] \tag{A17.1}$$

Step 2. Every reaction pathway in the reaction scheme involving five arrows, by which a particular enzyme species might be formed, is constructed. The concentration of a particular enzyme species is given by the sum of the rate constant products for that enzyme form. Consideration of the above cyclic reaction scheme yields the relationships given in Table A17.1.

Step 3. Equation 17.11 can now be derived from the overall reaction rate equation, Equation 17.10, using the expressions derived in Step 2 for the concentrations of the six enzyme species.

Dividing Equation 17.10 by $[E_0]$ gives

$$\frac{[E_0]}{V} = \frac{[E_0]}{k_6[E_{ii}^*]} \tag{A17.2}$$

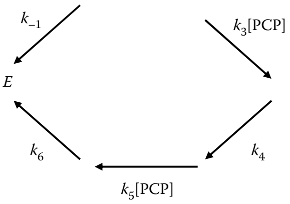
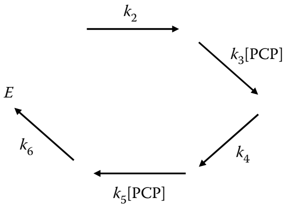
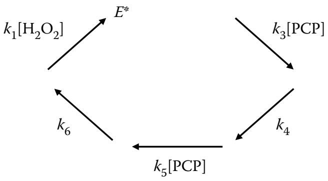
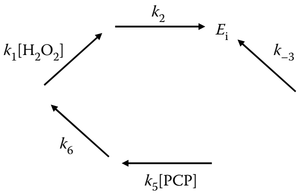
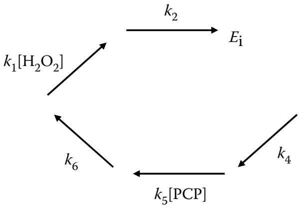
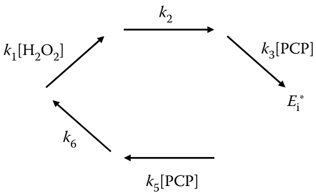
Substituting the enzyme conservation Equation A17.1 in the left-hand side of Equation A17.2 yields

$$\frac{[E_0]}{V} = \frac{[E] + [E^*] + [E_i] + [E_i^*] + [E_{ii}] + [E_{ii}^*]}{k_6[E_{ii}^*]} \tag{A17.3}$$

Substituting the expressions derived in Step 2 for the six enzyme species into Equation A17.3 gives

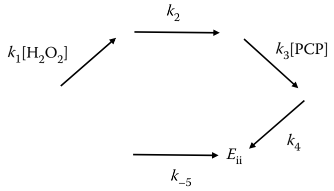
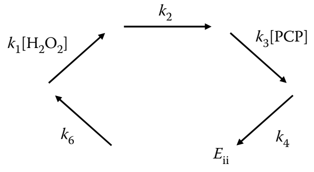
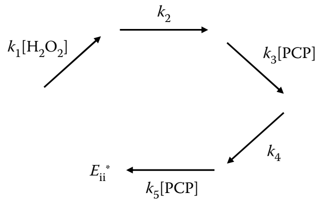
$$\frac{[E_0]}{V} = \frac{1}{k_6}\left\{\frac{(k_{-1}+k_2)k_6}{k_1k_2[H_2O_2]} + \frac{k_6}{k_2} + \frac{(k_{-3}+k_4)k_6}{k_3k_4[\text{PCP}]} + \frac{k_6}{k_4} + \frac{k_{-5}+k_6}{k_5[\text{PCP}]} + 1\right\} \tag{A17.4}$$

TABLE A17.1
King–Altman Relationships for the Various Enzyme Species

Enzyme Form	Pathways to Form	Sum of Rate Constant Products
E		$k_{-1}k_3k_4k_5k_6[\mathrm{PCP}]^2$
		$k_2k_3k_4k_5k_6[\mathrm{PCP}]^2$
		$[E] = (k_{-1} + k_2)k_3k_4k_5k_6[\mathrm{PCP}]^2$
E^*		$[E^*] = k_1k_3k_4k_5k_6[\mathrm{H_2O_2}][\mathrm{PCP}]^2$
E_i		$k_{-3}k_1k_2k_5k_6[\mathrm{H_2O_2}][\mathrm{PCP}]$
		$k_1k_2k_4k_5k_6[\mathrm{H_2O_2}][\mathrm{PCP}]$
		$[E_\mathrm{i}] = (k_{-3} + k_4)k_1k_2k_5k_6[\mathrm{H_2O_2}][\mathrm{PCP}]$
E_i^*		$[E_\mathrm{i}^*] = k_1k_2k_3k_5k_6[\mathrm{H_2O_2}][\mathrm{PCP}]^2$

Continued

TABLE A17.1 (continued)

Enzyme Form	**Pathways to Form**	**Sum of Rate Constant Products**
E_{ii}		$k_{-5}k_1k_2k_3k_4[H_2O_2][PCP]$
		$k_1k_2k_3k_4k_6[H_2O_2][PCP]$
		$[E_{ii}] = (k_{-5} + k_6)k_1k_2k_3k_4[H_2O_2][PCP]$
E_{ii}^*		$[E_{ii}^*] = k_1k_2k_3k_4k_5[H_2O_2][PCP]^2$

Solving Equation A17.4 for V we find

$$V = \frac{k_6[E_0][H_2O_2][PCP]}{\frac{(k_{-1}+k_2)k_6}{k_1k_2}[PCP] + \left\{\frac{(k_{-3}+k_4)k_6}{k_3k_4} + \frac{k_{-5}+k_6}{k_5}\right\}[H_2O_2] + \left\{+\frac{k_6}{k_2} + +\frac{k_6}{k_4} + 1\right\}[H_2O_2][PCP]} \tag{A17.5}$$

Rearranging the right-hand side of Equation A17.5 we obtain

$$V = \frac{\frac{1}{\frac{1}{k_2}+\frac{1}{k_4}+\frac{1}{k_6}}[E_0][H_2O_2][PCP]}{\frac{\frac{k_{-1}+k_2}{k_1k_2}}{\frac{1}{k_2}+\frac{1}{k_4}+\frac{1}{k_6}}[PCP] + \frac{\frac{k_{-3}+k_4}{k_3k_4}+\frac{k_{-5}+k_6}{k_5k_6}}{\frac{1}{k_2}+\frac{1}{k_4}+\frac{1}{k_6}}[H_2O_2] + [H_2O_2][PCP]} \tag{A17.6}$$

The above equation is formally identical to Equation 17.11.

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18 Remediation of Sites Contaminated by Underground Storage Tank Releases

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CONTENTS

18.1 INTRODUCTION

Underground storage tanks (USTs) comprise one or a combination of tanks (including the associated underground piping) that are used to contain substances regulated under the RCRA[1,2] (Resource Conservation and Recovery Act) or CERCLA[3,4] (Comprehensive Environmental Response, Compensation, and Liability Act—Superfund), the volume of which include 10% or more located below ground surface (bgs). Generally, this term does not encompass residential and farm tanks holding 4164 L (1100 gal) or less of motor fuel used for noncommercial purposes, tanks storing heating oil to be used on the premises where it is stored, tanks on or above the floor of an underground area, such as basements or tunnels, septic tanks, and systems for collecting wastewater and stormwater, flow-through process tanks, emergency spill and overfill tanks, and related pipeline facilities.[5–7]

When the UST program began, there were approximately 2.1 million regulated tanks in the U.S. Today there are far fewer, because many substandard UST systems have been closed.[8] According to the U.S. Environmental Protection Agency (U.S. EPA), less than 5% of the current number of UST tanks store hazardous substances.[6] The majority of these tanks are used to store petroleum products for retail and industrial purposes. of the regulated tanks, 80% are believed to be made of bare steel, which can quickly corrode, allowing the contaminants to seep into the ground, posing a significant threat to the environment. The greatest potential hazard from a leaking UST is that the petroleum or other hazardous substance may seep into the soil and contaminate groundwater, the source of drinking water for nearly half of all Americans.[8] A leaking UST can present other health and environmental risks, including the potential for fire and explosion.

Federal UST regulations[9,10] promulgated in September 1988 established the minimum requirements for the design, installation, operation, and testing of USTs in the U.S. Through the implementation of the Clean Water Act[11] (CWA) (including the regulations issued for oil pollution prevention) and the Occupational Safety and Health Administration[12] (OSHA) (incorporating underground motor fuel storage tanks in its regulations dealing with flammable and combustible liquids), the control of USTs has helped in the minimization of the adverse environmental impact caused by the leakage of products from underground tanks.

This chapter will discuss those USTs storing petroleum products, such as gasoline, fuel oil, kerosene, and crude oil, and the problems related to petroleum release. In this context, the term "oil" or "gasoline" will be used in the text. Accordingly, the sections on underground release and transport remedial technologies mainly deal with petroleum products. Most petroleum products are nonaqueous-phase liquids (NAPLs) that are immiscible with water and have a lower specific gravity. The remainder of NAPLs with specific gravities greater than water are called the dense nonaqueous-phase liquids (DNAPLs). DNAPLs constitute only a small percentage of the petroleum products stored in USTs.

18.2 LEGISLATIVE AND REGULATORY OVERVIEW

The consequences of the release of petroleum from leaking USTs include a loss of valuable fuel, contamination of drinking water supplies, and danger to human life, property, and the environment. The RCRA was enacted to regulate the generation, transportation, storage, treatment, and disposal of waste material that met the definition of hazardous waste. Subtitles I and J of the RCRA are specifically promulgated for the management of underground storage tanks.

18.2.1 SUBTITLE I OF THE RCRA

Subtitle I of RCRA was enacted to control and prevent leaks from underground storage tanks.[1,6] It regulates substances, including petroleum products and hazardous material. Tanks storing hazardous wastes, however, are regulated under Subtitle C, and are not the concern of this chapter.

On September 23, 1988, U.S. EPA issued the final technical performance standards and associated regulations for USTs.[13] On October 26, 1988, U.S. EPA issued the final regulations for financial responsibility for those USTs related mainly with petroleum products. The technical standards for USTs comprise eight components, as described in the following sections[13,14]:

18.2.1.1 Program Scope and Interim Prohibition

Both the program scope and the interim prohibition must be clearly identified and documented.

18.2.1.2 Design, Construction, Installation, and Notification Requirements

U.S. EPA has established standards for tanks and piping tightness tests. In lieu of the standards specified in the regulations, new USTs may be constructed using alternative standards as long as they are equally protective of human health and the environment. The cathodic protection systems of new USTs must be designed and installed in accordance with industry codes. Tank installation includes securing the tank, obtaining clean backfill, and ensuring that the substances to be stored are compatible with the tank system. Tanks must be properly installed following manufacturer specifications and certified by the state regulatory agency when installation is satisfactorily completed. USTs must also be fitted with equipment to prevent the spills and overfills that are the common causes of tank leakage. Existing USTs had to comply with all requirements for new tanks by December 22, 1998. Any UST systems that were unable to meet the deadline were closed.

18.2.1.3 General Operating Requirements

Four steps must be taken to meet the general operating requirements to prevent spills or overfills:

1. Ensuring that the capacity of the tank is greater than the volume of product to be transferred
2. Having someone present at all times during the transfer

3. Incorporating equipment that can prevent or severely limit spills, such as automatic shutoff devices that act when the tank is almost full
4. Following manufacturer recommendations regarding proper maintenance, including inspections, record keeping, periodic maintenance, and corrosion protection.

18.2.1.4 Release Detection

Release detection is one of the most important requirements of the UST program. The detection system should be capable of detecting a release from any part of the UST system. Detection methods will be discussed under Section 18.3.

18.2.1.5 Release Reporting, Investigation, and Confirmation

Any spill or overfill of over 95 L (25 gal) petroleum must be reported within 24 h. An amount less than 95 L (25 gal), that cannot be cleaned up within 24 h should also be reported.

18.2.1.6 Corrective Action Requirements

Following the immediate response activities (including release reporting, immediate containment, and monitoring of explosive hazards), the actions that the facility must implement as initial abatement measures include the following:

1. Further containing the regulated substance to prevent continued release
2. Preventing further migration of aboveground and underground release
3. Continuously monitoring and mitigating explosive hazards
4. Remedying hazards posed by excavated soils resulting from response activities
5. Performing a site check to evaluate the extent of the release
6. Determining the presence of free product on the water table
7. Compiling detailed corrective action plans if further corrective action is found to be required.

18.2.1.7 UST Closure

Unless permanently closed, all systems containing regulated substances must continue to comply with all the normal regulatory requirements. USTs closed for less than three months have no special requirements. USTs closed for between three and twelve months must leave vent lines open and cap all other lines. After 12 months out of service, USTs must be closed permanently. Before closing the UST system, the site must be assessed to ensure that no further release has occurred.

18.2.1.8 Financial Assurance

Under the new petroleum UST regulations, financial assurance (between ca. 0.5 and 1 million USD per occurrence or between 1 and 2 million USD for aggregate coverage) is required to cover both the cost of any required corrective action, and compensation for third-party liability from accidental release. State and federally owned facilities are exempt from these requirements.

As part of the amendments to Superfund, U.S. Congress created the Leaking Underground Storage Tank Trust Fund under RCRA Subtitle I. The Trust Fund is financed through a tax on gasoline, diesel, and aviation fuels and is used when the following conditions are met:

1. Cleanup costs exceed the coverage requirements of the financially responsible party.
2. The owner or operator refuses to comply with a corrective action order.
3. A solvent owner or operator cannot be found.

4. An emergency situation exists.
5. To cover the administrative and enforcement costs associated with a cleanup.

18.2.2 SUBTITLE J OF THE RCRA

In order to regulate USTs storing hazardous substances and to provide a second means of containing the substance should the tank fail, U.S. EPA revised Subtitle J of the RCRA, which regulates secondary containment systems. This secondary containment system would have the following features:

1. It will prevent waste or liquid from escaping to the soil or water for the life of the tank.
2. It will collect waste or leakage until the material is removed.
3. It will be constructed or lined with material compatible with the waste and with sufficient strength to prevent failure from pressure, climate, traffic, and daily use.
4. It will have an adequate base or foundation capable of resisting settlement compression and uplift.
5. It will have a system capable of detecting leaks within 24 h of occurrence.
6. It will have a slope or drain system to permit removal of leaks, spills, and precipitation, and contain provisions for such accumulation to be removed.
7. It will have 110% of the design capacity of the largest tank within the containment boundary.
8. It will prevent run-on or infiltration of precipitation unless the collection system has excess capacity (beyond the 110%) to hold precipitation consistent with the 25-yr, 24-h rainstorm prediction.

18.2.3 STATE AND LOCAL UST PROGRAMS

Several states already have, or are developing, regulatory programs for USTs. Subtitle I of the RCRA is designed to avoid interfering with those state programs and to encourage other states to press ahead with control programs.

According to the state program approval regulations (promulgated on September 23, 1989) U.S. EPA will evaluate various elements of the state program against the corresponding Federal requirements. U.S. EPA must determine that the state's requirements are "no less stringent" than the Federal program, and that there is provision for "adequate enforcement."

18.2.4 USTS CONTAINING OTHER HAZARDOUS CHEMICALS

The regulatory standards for leak detection in tank systems containing hazardous chemicals are more stringent than those for tanks containing petroleum motor fuels. Both above standards and those required in RCRA hazardous substances management should be met.

18.3 CAUSES OF LEAKS AND LEAK IDENTIFICATION METHODS

18.3.1 CAUSES OF TANK FAILURE

USTs release contaminants into the environment as a result of (1) corrosion, (2) faulty installation, (3) piping failure, and (4) overfills.[15–17]

Corrosion and poor installation are by far the most common causes of storage system leaks. The most common causes of release from bare-steel UST systems are galvanic corrosion and the breakdown of hard refined steel to its natural soft ore. Because older USTs are usually constructed from bare steel, corrosion is believed to be the leading factor contributing to release. The speed and severity of corrosion varies depending on site characteristics, such as soil conductivity, groundwater or soil water chemistry, and weather. Most commonly, part of a tank becomes negatively charged with respect to the surrounding area and acts as a battery. The negatively charged part of the steel UST starts to corrode at a rate proportional to the intensity of the current. Corrosion rate can be reduced significantly or eliminated if cathodic protection or other protection methods are used.

Faulty installation of USTs encompasses a wide variety of problems, for example, accidents from vehicles colliding with the storage system, or faulty installation arising from inadequate compaction of backfills and unsealing of joints. Therefore, precautions should be taken to ensure that poor construction or installation do not degrade the performance of the USTs.

Piping failure can be caused in several ways. A study by U.S. EPA[16] has shown that piping failure accounted for a substantial portion of releases at USTs. Spills and overfills are usually caused by human error. Repeated spill can also increase the corrosive nature of soils.

18.3.2 LEAK IDENTIFICATION METHODS

Three basic actions can be considered to identify leakage from USTs[5,18]: (1) direct observation (visual observation of losses or environmental and mechanical signs of leaks), (2) checking (inventory monitoring), and (3) testing (instrumental testing of tanks and piping for leaks). These are described in the following sections.

18.3.2.1 Visual Tank Inspection

Visual inspection may be carried out by entering the tank if it is large enough for a person to be able to enter and walk in the tank, or by inspection of the tank's outer walls following the removal of pads or backfill material.

18.3.2.2 Watching for Environmental Signs

There are at least five signs to look for:

1. The odor of motor fuel in the soil near the tank may be a sign of leakage.
2. The odor of motor fuel present in underground structures such as basements and sewers is also a sign of leakage.
3. Plants located on property near a UST may grow sluggishly, look sickly, or die.[5]
4. Motor fuels may be found in drinking water wells or rivers.
5. A higher than expected gain or loss of fuel in a tank may be caused by water infiltration or leakage of fuel through the tank wall.

18.3.2.3 Watching for Mechanical Signs

There are three phenomena to be monitored[5]:

1. Interruption in the delivery of motor fuel dispensed by the suction pump
2. A rattling sound and irregular fuel flow in the suction pumping system
3. Meter spin without motor fuel delivery

It should be noted that these can also be caused by other problems besides tank leakage, such as leaking valves, loose fittings, or other factors.

18.3.2.4 Checking Inventory

By carefully checking inventory records one is able to determine whether there is loss or gain of fuel in USTs. Inventory review is generally an inexpensive and relatively easy way to check for leakage.

This method is particularly useful for identifying large leaks, although small leaks may also be noticed, particularly in tanks with metered dispensing pumps. Interested readers can refer to U.S. EPA[5] and API (American Petroleum Institute)[20] for detailed procedures of inventory checking for tanks with metered or nonmetered pumps.

18.3.2.5 Environmental Tests with Instrumentation

Another method to examine tank leakage uses instrumentation. An instrumental test should be conducted if there is the suggestion of a leakage from various environmental or mechanical indicators or from an inventory review.

When the leaked motor fuel is at a deeper level or flows away from underground strata, there may be no visual sign, and instrumentation may be necessary to detect the leak. Such an instrumental test on the tank environment is called an external test, and is the counterpart of visual observation.

There are a number of methods for detecting the sign of leakage from external tanks. The most common method uses monitoring wells. Typically, the monitoring well reaches 2 ft below the bottom of the underground storage tank. Detection sticks are placed in the well, and indicate the existence of motor fuel within the well. Other methods include soil sampling, fuel vapor testing, ground penetrating radar, seismic methods, electromagnetic induction, resistivity, magnetometers, and X-ray fluorescence.

Tracer methods can also be used, in which tracers such as freon, fluorescent materials, and isotope-fuel are added to a tank, and are then detected externally. An analogy of tracer methods includes pressurizing the tank with a noble gas, then detecting the gas if it escapes from the tank through cracks or holes.

Some tanks are installed with permanent leak identification sensors, which can check for leaked fuel vapor or liquid as it comes into contact with the sensors.[21] However, these, as well as all the environmental sign tests (visual or instrumental) may be triggered by a spill instead of a leak. The success of external systems depends on the sensitivity of the sensor, the ability of the sensor to distinguish the stored chemical from other chemicals, the ambient background noise level of the stored chemical, the migration properties of the chemical, and the sampling network.

18.3.2.6 In-Tank Measurement with Instrumentation

In-tank measurement uses equipment that is placed inside the tank or pipes. Some tests can qualitatively determine whether a tank is leaking; others can establish the leakage rate. Most of the work can be performed within a time of 2 to 4 h, excluding setup time.[5,21] A common method measures the changes in the amount of fuel in the tank by measuring the fuel level or pressure. These tests may be influenced by several factors, including evaporation, condensation, and changes in temperature, changes in the shape of the tank due to changes in the fuel load, temperature air packets, vibrations from traffic, groundwater, or soil moisture.

Other devices and methods can also be applied, such as laser interferometry, which measures the change in the height of fuel in the tank using lasers, or acoustics methods that measure the sound of fluid escaping or entering the tank.

18.3.2.7 Direct Tank Tests with Instrumentation

An instrument can be used to test tank walls directly, for example, by using acoustics or sound waves to identify holes or cracks in the tank walls.[18]

18.3.2.8 Release Detection Approaches for Modern Tank Systems

Release detection is an important aspect of the management of USTs. U.S. EPA regulations required an upgrade of release detection during the 10-yr period between 1988 and 1998. The external or internal detection systems should be in compliance with the requirements for modern tank systems.

There are three methods of release detection that are associated with modern tank systems.[18,22] The first approach is to conduct an annual tank or line tightness test to detect small releases and to use more frequent monitoring by another method to detect large releases. All tank and line tightness tests must be performed at least once a year and must be able to detect leaks of 0.38 L/h (0.1 gal/h). In all cases where annual tightness tests are used, the regulation requires an additional form of leak detection in which tests on tanks are conducted at least monthly and those on pressurized lines at least hourly; this ensures the detection of excessively large releases. For tanks, daily inventory records must be reconciled monthly. for pressurized lines, leaks of up to 11.4 L/h (3 gal/h) must be reliably detected.

The second approach is to install an automatic tank gage or automatic line leak detector that is capable of detecting leaks of 0.76 L/h (0.2 gal/h); all monitoring tests must be done at least once a month. This option also requires that there be a system for detecting large leaks. The tank gage can be used to satisfy inventory control requirements, and most automatic line leak detectors are designed so as to be able to satisfy the 11.4 L/h (3 gal/h) test for pressurized piping.

The third approach is to install an external monitoring system that can detect the presence of the stored chemical in or on the groundwater or in the backfill and soil surrounding the tank system. In many instances both internal and external methods are used in conjunction as a way to increase the liability of detection.

18.4 UNDERGROUND CONDITIONS AND FACTORS AFFECTING TRANSPORT OF LIQUIDS IN THE SUBSURFACE

18.4.1 UNDERGROUND FORMATIONS

Subsurface formations can be divided into the overburden (unconsolidated) and bedrock according to its solidarity. The upper subsurface can be further divided into the unsaturated zone and the saturated zone depending on pore structure and moisture saturation. The saturated zone is the zone in which the voids in the rock or soil are filled with water at a pressure greater than atmospheric. The water table is at the top of a saturated zone in an unconfined aquifer. The unsaturated zone is the zone between the land surface and the water table, and is also called the zone of aeration or the vadose zone. The pore spaces contain water at less than atmospheric pressure, air, and other gases. This zone is unsaturated except during periods of heavy infiltration.

In the lower region of the unsaturated zone, immediately above the water table, is the capillary fringe, where water is drawn upward by capillary attraction. Above the capillary fringe, moisture coats the solid surfaces of the soil or rock particles. If the liquid coating becomes too thick to be held by surface tension, a droplet will pull away and be drawn downward by gravity. The fluid can also evaporate and move through the air space in the pores as water vapor.

The moisture in the upper unsaturated zone can be affected by plant transpiration and atmospheric conditions. Some scholars classify the unsaturated zone into subzones such as the soil water zone and the intermediate zone.[23]

18.4.2 GRAVITATIONAL FORCE AFFECTING UNDERGROUND LIQUID MOVEMENT

Soil water, like other bodies in nature, has two principal forms of energy, kinetic and potential. Kinetic energy is proportional to the square of velocity. As the velocity of groundwater is quite slow, the kinetic energy is usually negligible. Potential energy, due to position or internal conditions, determines the movement of water from a higher energy level to a lower energy level in soil formations. Accordingly, there are three forces related to potential energy:

1. Gravity (the weight of the fluid)
2. External pressure (atmosphere pressure)
3. Molecular attraction (surface tension, adsorptive, diffusive, and osmotic forces)

The forces resisting groundwater flow are shearing stress and normal stress due to viscosity, collision, and turbulence.

Gravity force can be measured by means of the mass of the water. The direction of the force is, obviously, downwards toward the Earth's center. The gravitational potential of soil water at each position is determined by the elevation of the position relative to some reference level. If we only consider the elevation potential and the related velocity energy, then a water body at a higher elevation will flow to a lower elevation, decreasing the elevation potential but increasing its velocity.

18.4.3 ATMOSPHERE PRESSURE AFFECTING UNDERGROUND LIQUID MOVEMENT

Atmospheric pressure is not obvious, because it is balanced in opposite directions. The combination of atmospheric pressure and the weight of the overlying water create the total pressure in the saturation zone.[24]

18.4.4 SURFACE TENSION AND CAPILLARY POTENTIAL AFFECTING UNDERGROUND LIQUID MOVEMENT

Tension in the free surface of a liquid is the cause of the tendency of a liquid surface to assume the form having a minimum area, as manifested in the shape of a bubble or a drop of liquid.[25] The tendency to contract is a special case of the general principle that potential energy tends toward a minimum value.

18.4.4.1 Wetting and Nonwetting

When a drop of liquid is placed on a solid surface, it will displace the gas and spread over the surface. If the contact angle is <90°, the liquid wets the solid (wetting, Figure 18.1a); if the contact angle is >90°, the liquid does not wet the solid (nonwetting, Figure 18.1b).

Whether a liquid wets or does not wet a solid surface depends on the affinity between the liquid and the solid. In the case of wetting, the smaller contact angle enables the liquid to enlarge the liquid–solid interface area (which has a lower surface energy than the liquid surface energy) and shrinks the liquid surface area (which has a greater surface energy), thus reducing the total energy. In the case of nonwetting, the greater contact angle enables the reduction of the liquid–solid

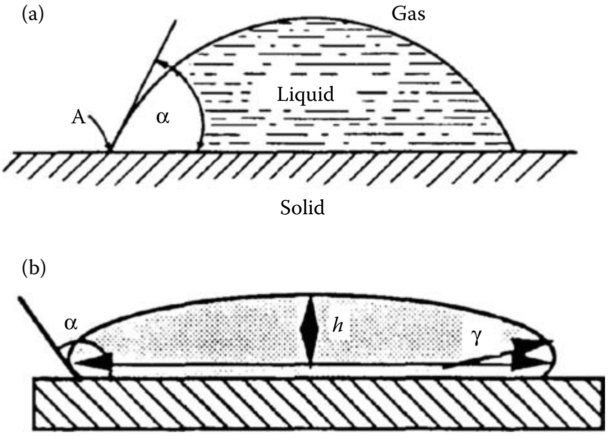


FIGURE 18.1 (a) Drop contact angle and (b) a sessile drop showing characteristic dimensions.

interface area (which has a higher surface energy than the liquid surface energy) and the enlargement of the liquid surface area (which has a lower surface energy), thus bringing about a reduction in the total energy.

18.4.4.2 Capillary Potential

A liquid–solid contact angle away from 90° induces the formation of a meniscus on the free surface of the liquid in a vertical tube (the solid phase). In the nonwetting case, the meniscus concaves upwards to the air. The upwards meniscus is the result of a downward surface tension at the liquid–tube interface, causing a capillary depression. In the wetting case, the meniscus has a concave-downward configuration. The downwards meniscus is the result of an upward surface tension at the liquid–tube interface, causing a capillary rise.

A typical profile of the pressure potential of soil moisture tested by a tensometer across the free-water surface shows a negative pressure (lower than atmosphere pressure) in the capillary zone (Figure 18.2). The negative pressure in the capillary zone indicates that the capillary zone belongs to the unsaturated zone.

Surface tension is independent of tube size. However, the extent of capillary rise or depression by surface tension is dependent on tube size. This can be seen from Equation 18.1 in Section 18.4.6.1. For example, in the case of a capillary rise, the greater the tension, the higher the water rises above the free-water surface. For the same amount of water, the smaller the tube is, the higher the water rises.

18.4.4.3 Relative Soil Wettability of Two Liquid Phases

The predominant form of released petroleum products is a liquid that is immiscible with water; this is called the free product (in this section it will be referred to as oil). The behavior of water and oil in soil depends on the interaction of the three phases water, oil, and soil. The affinity of water or oil with the soil can be estimated by establishing the contact angle of oil/water/soil triple line.

Note that the contact angle of the fluid 1/fluid 2/solid triple line is still largely unpredictable, even though the material properties of the three phases, taken separately, are known. It is difficult to compare the wettabilities of a solid with respect to two fluids that wet it perfectly, or, in other terms, to measure the fluids' spreading parameters, even on an ideal surface. There are several methods used for wettability evaluation. The AMOTT-IFP (E. Amott – Institut Français du Pétrole) test is probably the most widely accepted one. Other advanced methods for measuring wettability include the computerized automated tomographic X-ray scanner, magnetic resonance imagery,

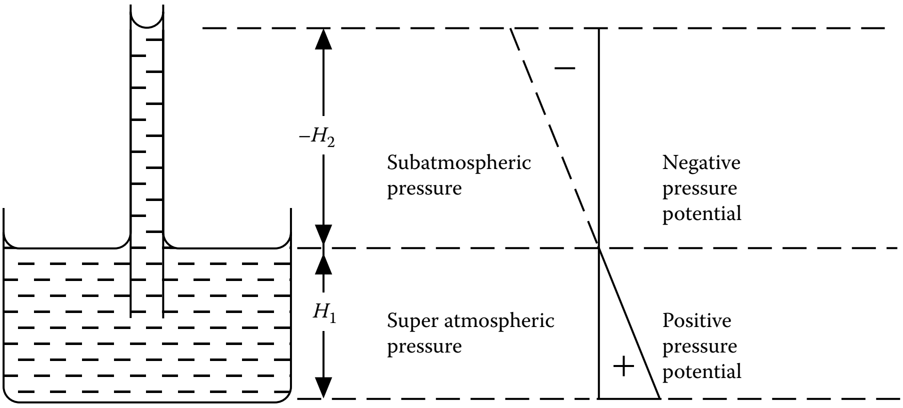


FIGURE 18.2 Superatmospheric and subatmospheric pressures below and above a free-water surface.

cryo-scanning electron microscopy, and nuclear magnetic resonance. For more information, see references 26 to 28.

Wettability measurements show that most soil constituents are water wettable or hydrophilic,[28] although calcium carbonates [calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$] are slightly hydrophobic; for example, the contact angle of water and heptane is 100 to 105°. Therefore, carbonaceous reservoirs are usually oil-wet.

In practice, evaluating the wettability of a soil is far more uncertain, because soil is a mixture of gravel, sand, silt, and clay particles, as well as other chemical precipitates. The mineral components of soil particles include quartz, feldspar, carbonates, and clay. These components have different wettability by water and oil. Therefore, the retention of oil or water in a soil matrix is heterogeneous and variable. The general wettability of soil or liquid retention in a soil is reported on a statistical basis.

The relative wettability of soil by oil and water determines the relative affinity of soil to oil and water, which in turn determines the level of retention of oil or water in the soil. A soil is hydrophilic (i.e., it has water affinity) if water has more affinity to the soil than the oil, although soil may also to a certain degree be somewhat wetted by oil. A soil is called hydrophobic if oil has more affinity to the soil than water.

When water-affinity soil that is originally saturated with oil is rinsed with water, most of the oil will be displaced by water; however, some oil will remain. This remaining amount of oil that can no longer be displaced by the flowing water is defined by the petroleum industry as the "residual oil saturation."[28] This term is used to measure the upper limit of the microscopic efficiency of the displacement of oil by water. There is no appreciable lower limit, as at a given pore level the wetting fluid should be spread over the mineral surface as a continuous wetting film, which might thin itself until the externally applied capillary pressure (or pressure difference across the wetting fluid/nonwetting fluid interface) is balanced by the thin film disjoining pressure.

If an open space of a water-affinity porous medium filled with oil is brought into contact with a reservoir of water, the oil will be spontaneously displaced by the water. Conceivably, a symmetric behavior can be observed if an oil-affinity medium at residual oil saturation is brought into contact with oil. The driving force for this spontaneous flow is the high initial capillary pressure (which equals the pressure in the nonwetting fluid minus the pressure in the wetting fluid) inside the medium compared to its value of zero outside, where the oil–water interface has no curvature at equilibrium. Capillary pressures, like relative permeabilities, are a function of saturations, the geometric properties of the porous medium, the fluid–fluid interfacial tension, and the wettability.[28] It is generally observed that if all other parameters of a system are maintained unchanged, but the wetting properties of the solid are changed, the nonwetting fluid will be displaced more easily by the wetting fluid than vice versa.

Surfactants are used to rinse oil from soil more effectively. Surfactants have higher soil affinity, and so reduce the interfacial tension between the oil and the soil. The replacement of the oil film by a surfactant solution is dependent on the contact angle between the oil–solution interface and the soil. As long as the contact angle (in the solution) is acute, the solution will tend to advance, displacing oil from the soil. Mechanical agitation would assist the spreading by compensating to some extent for the immobility of the molecules on the surface of the soil. Processes for the removal of surfactants in a contaminated liquid are described in works by Wang and colleagues[29] and Hrycyk and colleagues.[30]

18.4.5 ADSORPTIVE FORCE AFFECTING UNDERGROUND LIQUID MOVEMENT

Adsorption results from bonding forces between the solute and soil particles. These forces are generally electrostatic, although entropy generation and magnetic forces can be involved. Bonding forces range from relatively weak to strong with respect to bond formation.[31]

Adsorption can be attributed to the following interactions: van der Waals–London interactions, charge transfer/hydrogen bonding, ligand exchanges, ion exchange, direct and induced ion–dipole and dipole–dipole forces, chemisorption, hydrophobic bonding, and magnetic bonding. These interactions are the result of electrostatic magnetic or entropy-generating forces. Most often, physical adsorption is due to the electrostatic interactions between atoms, ions, and molecules resulting from instantaneous dipoles. Van der Waals force, charge transfer/hydrogen bonding, ligand exchange, ion exchange, direct and induced ion–dipole and dipole–dipole force, and chemisorption interactions are all the result of electrostatic forces, variation in energy level, and method of interaction. Hydrophobic bonding is due to entropy-generating forces, and magnetic bonding is due to magnetic forces.[31]

Van der Waals–London interactions are due to fluctuations in electron distribution as the electrons circulate within their orbits. These instantaneous dipoles are usually weak, but are, regardless, the most common interaction resulting in adsorption.[31] Stronger interactions result from charge transfer.

18.4.6 COMBINATION OF CAPILLARY AND ADSORPTIVE FORCES AFFECTING UNDERGROUND LIQUID MOVEMENT

Both adsorptive and capillary forces play an important part in soil–liquid interaction (see Figure 18.3). This is very important for unsaturated soil. The total force (i.e., the sum of capillary force and adsorptive force) is termed the matrix potential, which has a negative gage pressure relative to the external gas pressure on the soil water (more often the gage pressure is referred to as the atmospheric pressure).

In fact, an unsaturated soil has no pressure potential, only a matrix potential (expressible as a negative pressure). The negative pressure causes water to move toward the soil with a higher suction potential, in contrast to the saturated flow where water moves from a high pressure potential to a low pressure potential. For soils with the same properties but with different saturation, the less saturated soil has more excessive suction force, causing water to move towards it.

The presence of water in films as well as under concave menisci is most important in clayey soil and at high suctions, because clay minerals have high specific surface area and often have a

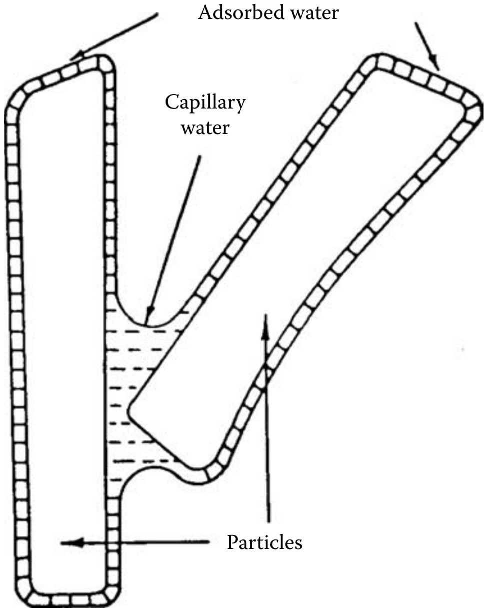


FIGURE 18.3 Water in an unsaturated soil is subject to capillarity and adsorption, which combine to produce a matric suction.

high cation exchange capacity. In sandy soil, adsorption is relatively unimportant and the capillary effect predominates. A combination of capillary effects and adsorption results in negative pressure potential.

18.4.6.1 Viscosity and Shearing Stress

Viscosity is the property of a fluid that offers resistance to the relative motion of fluid molecules. The energy loss due to friction in a flowing fluid is due to its viscosity.

As a fluid moves, shearing stress develops in it. The magnitude of the shearing stress depends on the viscosity of the fluid. Shearing stress can be defined as the force required to slide one unit area layer of a substance over another. Considering a fluid moving along a fixed surface, the velocity is highest along the moving surface, and zero at the fixed surface. The shearing stress in a fluid is directly proportional to the velocity gradient:

$$S_s = \mu(\mathrm{d}V_s/\mathrm{d}y) \tag{18.1}$$

where S_s = shearing stress (M/LT^2), y = distance (L) between the moving and fixed surfaces, V_s = the velocity along the surfaces (L/T), $\mathrm{d}V_s/\mathrm{d}y$ = velocity gradient across the surfaces, and μ = proportionality constant = dynamic viscosity (or absolute viscosity) of the fluid (M/LT).

Equation 18.1 is known as Newton's Law of Friction. In the SI system, the dynamic viscosity units are N-s/m^2, Pa-s, or kg/m-s. Here 1 Pa-s = 1 N-s/m^2 = 1 kg/m-s. The dynamic viscosity (or absolute viscosity) is also often expressed in the metric CGS (centimeter-gram-second) system as g/cm-s, dyne-s/cm^2, or poise (P) where 1 poise = 1 P = 1 dyne-s/cm^2 = 1 g/cm-s = 0.1 Pa-s = 100 centipoises = 100 cP. Water at 20.2°C (68.4°F) has a dynamic viscosity of 1 cP.

Kinematic viscosity is the ratio of dynamic viscosity and density, and can be obtained by dividing the dynamic viscosity of a fluid with its mass density, as shown by Equation 18.2:

$$\nu = \mu/\rho \tag{18.2}$$

where ν = kinematic viscosity (L^2/T), μ = dynamic viscosity (M/LT), and ρ = density (M/L^3).

In the SI system, the theoretical unit of ν is m^2/s or the commonly used Stoke (St) where 1 St = 0.0001 m^2/s = 100 cSt = 100 centiStoke. Similarly, 1 centiStoke = 1 cSt = 0.000001 m^2/s = 0.01 Stoke = 0.01 st. The specific gravity of water at 20.2°C (68.4°F) is almost 1. The kinematic viscosity of water at 20.2°C (68.4°F) is for all practical purposes equal to 1 cSt. For a liquid, the kinematic viscosity will decrease with higher temperature. For a gas, the kinematic viscosity will increase with higher temperature. Another commonly used kinematic viscosity unit is Saybolt universal seconds (SUS), which is the efflux time required for 60 mL of petroleum product to flow through the calibrated orifice of a Saybolt universal viscometer, as described by ASTM-D88. Therefore, the relationship between dynamic viscosity and kinematic viscosity can be expressed as

$$\nu = 4.63\ \mu/\mathrm{Sg} \tag{18.3}$$

where ν = kinematic viscosity (SUS), μ = dynamic or absolute viscosity (cP), and Sg = specific gravity (dimensionless).

The viscosities of water and gasoline increase with decreasing temperature. Gasoline has lower viscosity than water, and fuel and crude oil have a much higher viscosity that increases dramatically when temperature decreases.[32] The ease with which a fluid pours is an indication of its viscosity. It is observed that cold oil has a high viscosity and pours very slowly. The viscosity properties of various potential pollutants are discussed in Section 18.9.

18.4.6.2 Electrokinetic Effects

Flow movement also has a relationship with the electrokinetic phenomenon, which can promote or retard the motion of the fluid constituents. Electrokinetic effects can be described as when an electrical double layer exists at an interface between a mobile phase and a stationary phase. A relative movement of the two phases can be induced by applying an electric field and, conversely, an induced relative movement of the two will give rise to a measurable potential difference.[33]

Four phenomena are classified as electrokinetic effects:

1. Streaming potential
2. Electroosmosis
3. Sedimentation potential
4. Electrophoresis

The streaming potential (Dorn effect) relates to a movement of liquid that generates electric potential, and electroosmosis occurs when a direct electric potential causes movement of the liquid. The sedimentation potential relates to sedimentation (directed movement) of charged particles that generates electric potential, and electrophoresis occurs when a direct electric potential causes a movement of charged particles.

With regard to the movement of liquid versus particles under direct current, electrophoresis is the reverse of the effect of electroosmosis.[33] If particles move through a liquid that is stationary, this is called electrophoresis; conversely, if the liquid moves through particles that are stationary, that is called electroosmosis.

The potential governing these electrokinetic effects is clearly at the boundary (the face of shear) between the stationary phase (the fixed double layer) and the moving phase (the solution). This potential is called the electrokinetic potential or the zeta potential. An electrokinetic phenomenon in soil involves coupling between electrical, chemical, and hydraulic gradients.

Initially the electrical potential difference is distributed linearly across the specimen. The changing chemistry across the cell may result in variations in electrical potential difference in time and space.

It is suggested that the movement of the front by migration (electrical potential), diffusion (chemical potentials), and advection (hydraulic potentials) will cause desorption of cations and other species from clay surfaces and facilitate their release into the fluid.[34]

The relationship of electrokinetic phenomena and the movement of petroleum constituents is not of high importance; however, it can be important for the transport of some solutes related to a remedial technology such as electroosmosis remediation.

18.4.7 ENERGY CONSERVATION AFFECTING UNDERGROUND LIQUID MOVEMENT

Equation 18.4 describes the energy conservation when water moves between two points (1 and 2)

$$\frac{P_1}{\gamma} + Z_1 + \frac{v_1^2}{2g} + h_A - h_R - h_L = \frac{P_2}{\gamma} + Z_2 + \frac{v_2^2}{2g} \tag{18.4}$$

where P_1 = pressure at point 1 (M/L^2), P_2 = pressure at point 2 (M/L^2), P_1/γ = pressure head at point 1 (L), P_2/γ = pressure head at point 2 (L), γ = density of liquid (M/L^3), Z_1 = elevation of point 1 (L), Z_2 = elevation of point 2 (L), $v_1^2/2g$ = velocity head at point 1 (L), $v_2^2/2g$ = velocity head at point 2 (L), g = gravitational acceleration (L/T^2), h_A = the head added to the fluid with a mechanical device such as a pump (L), h_R = the head removed from the fluid with a mechanical device such as fluid motor (L), and h_L = the head losses from the system due to friction (L). Equation 18.4 reduces to the familiar Bernoulli's equation when there is no pump ($h_A = 0$), no motor ($h_R = 0$), and where the head loss (h_L) between the two points is negligible.

18.4.8 WATER MOVEMENT IN SATURATED ZONE OF SOIL FORMATION

Hydraulic conductivity is one of the characteristic properties of a soil relating to water flow. The movement of water in soil depends on the soil structure, in particular its porosity and pore size distribution. A soil containing more void space usually has a higher permeability. Most consolidated bedrocks are low in permeability. However, rock fractures could create a path for water movement.

Groundwater flowing through an aquifer is influenced by gravitational force, but the rate at which the groundwater moves can vary significantly. Depending on the permeability of an aquifer and the flow gradient, groundwater can move at a velocity varying from only a few meters per year to several meters per day.

The most important factor for movement in the saturated zone is the hydraulic gradient. The velocity head, which is generally more than ten orders of magnitude smaller than the pressure and gravitational head, may be neglected because of the slow water movement. Equation 18.4 can therefore be simplified to

$$\frac{P_1}{\gamma} + Z_1 + h_A - h_R - h_L = \frac{P_2}{\gamma} + Z_2 \tag{18.5}$$

The relative importance of pressure and gravitational heads depends on whether the water formation is in a free water table condition or in a confined aquifer condition.

18.4.8.1 Water Table Condition

When considering two points on a water table 1 and 2, P_1 can be regarded as equal to P_2, because the external pressure is the same as the atmospheric pressure. If there is neither addition nor loss of head by mechanical devices (i.e., $h_A = 0$ and $h_R = 0$), then Equation 18.5 reduces to

$$Z_1 - h_L = Z_2 \tag{18.6a}$$

and

$$Z_1 - Z_2 = h_L \tag{18.6b}$$

The cause of flow between these points is the difference in elevation head between them, that is, $(Z_1 - Z_2)$, denoted as d_h, which is contributed by the gravitational potential. If d_l is the distance between the two points on the water table, then the d_h/d_l ratio is known as the hydraulic gradient.

Comparing the results from the above paragraphs, it is apparent that the elevation difference d_h causes the flow between the two points and the energy is lost by friction (i.e., h_L) during the movement.

18.4.8.2 Confined Aquifer

For the confined aquifer, the pressure head becomes more important than the elevation head. As can usually be seen in an artesian aquifer condition, the groundwater may flow from a lower elevation to a higher elevation if the water pressure at the lower elevation is higher.

18.4.9 WATER MOVEMENT IN UNSATURATED ZONE OF SOIL FORMATION

In an unsaturated zone, the capillary force becomes predominant, and the pressure gradient becomes a suction gradient. Hydraulic conductivity is no longer constant, but is a function of the water content or suction, which is greatest in value when the soil is saturated and decreases in value steeply when the soil water suction increases and the soil loses moisture.

If we consider the water transport between two points, water movement would increase when suction increases and moisture decreases. That is, water tends to move from higher moisture to lower moisture points, because the point with lower moisture has a higher suction force.

Both vapor and liquid movement can be important where appreciable temperature gradients occur.

18.5 PROPERTIES OF GASOLINE AND ITS MOVEMENT IN SOIL

18.5.1 Properties of Gasoline and the Forms of Release Underground

Gasoline is a mixture of different compounds. A typical blend contains nearly 200 different hydrocarbons and additives such as antioxidants and antiknock agents. Thirteen of the chemicals commonly found in gasoline (nine hydrocarbons and four additives) are regulated as hazardous substances under CERCLA. Table 18.1 lists the chemicals along with the values of toxicity, water solubility, vapor pressure, and biodegradability.[19]

In general, there are four major forms of released gasoline underground:

1. Free product
2. Solutes dissolved in groundwater
3. Gases in the vapor phase in the soil void
4. Adsorbates adsorbed by the soil matrix

TABLE 18.1
Physical and Chemical Properties of Toxic Gasoline Components

	Mass		Prevalence	Fate and Transport			Toxicity
Compound	**% Volume in Gasoline**	**% Weight in Gasoline**	**% Gasolines Containing Chemical**	**Water Solubility at 20°C (mg/L)**	**Vapor Pressure (torr)[a]**	**Degree of Biogradability**	**Final RQ (kg)[b]**
Benzene	1–2	0.81	>99	1,780	75.0	Some	4.54
Toluene	4.0	12.02	>99	515	22.0	Some	454.00
Xylene-M	5–8	3.83	>99	175	5.0	Some	454.00
Xylene-O	5–8	1.93	>99	162	6.0	Some	454.00
Xylene-P	5–8	1.58	>99	198	6.5	Some	454.00
Ethylbenzene	2–5	1.70	>99	152	7.0	Some	454.00
Naphthalene	0.7	0.10	>90	31.1	1.0	Readily	45.40
Phenol	—	—	>90	66,667	0.5	Readily	454.00
EDB	0.01	0.024	<40	4,310	11.0	Some	4.54
EDC	0.01	<0.024	<40	8,690	61.0	Some	45.40
Tetraethyl lead	—	—	<40	0.08	0.2	Some	4.54
Dimethylamine	—	—	—	—	1,345.0	Readily	454.00
Cyclohexane	<0.7	0.17	—	66.5	77.0	Some	454.00

Source: U.S. EPA, Cleanups of Releases from Petroleum USTs: Selected Technologies, EPA/530/UST-88/00l, U.S. EPA, Washington, 1988.

EBD, ethylene dibromide; EDC, ethylene dichloride; RQ, reportable quantity.

[a] At 20°C.

[b] The lower the RQ value, the more toxic the chemical is in pure product form.

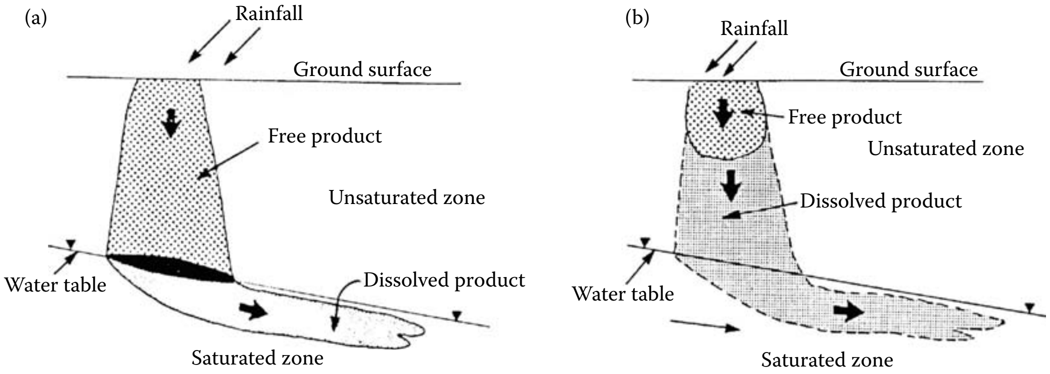


FIGURE 18.4 Schematic of contaminant plumes showing methods by which groundwater can be contaminated.

Figure 18.4 shows schematically the methods by which groundwater can be contaminated. Most of the gasoline components are immiscible with water—these are called the free product. The density of gasoline free product ranges from 0.72 to 0.78 g/mL with a viscosity less than that of water. Gasoline free product floats on and moves faster than groundwater. The density of crude oil and fuel oil ranges from 0.86 to 0.97 g/mL, with a viscosity greater than that of water.

There are many components of gasoline that readily dissolve in water and are transported as solutes in the groundwater. Most gasoline products are volatile and can release gas into the soil void in gaseous form, particularly in the unsaturated zone. Besides these three forms, gasoline components can be adsorbed by the soil matrix and exist in the soil as adsorbates.

Some gasoline constituents, particularly those that are highly volatile or soluble, are readily biodegraded in the presence of soil bacteria and oxygen. Gasoline constituents underground, specifically in the unsaturated zone, belong to the four forms or phases mentioned above. The released gasoline can be transported in the soil matrix in three forms: gas, liquid (free product), or solute. The distribution among these forms may change due to adsorption by soil, desorption from soil, and the extent of degradation.

18.5.2 Fates of Gasoline Underground: Adsorption and Degradation of Gasoline and the Effect on Gasoline Movement

18.5.2.1 Adsorption of Gasoline by Soil

The forces associated with adsorption of gasoline by the soil are the same as those for adsorption of water by soil. The difference is in the adsorptive strengths of gasoline and water, because gasoline and water have different affinity to soil. Moreover, different gasoline constituents may also have different extents of adsorption by soil. For example, tetraethyl lead and naphthalene have relatively low mobility values and are likely to be adsorbed to the soil. Toluene, xylenes, benzene, and phenol have high mobility values and are therefore more likely to appear in either the dissolved or gaseous phases than being adsorbed. Table 18.2 lists the adsorption coefficients for common gasoline compounds.

The soil above the water table in a gasoline release site is most likely to have the highest concentration of adsorbed gasoline. The soil may be flushed by groundwater when the level of the water table fluctuates, or by infiltrating water, thus changing the adsorbed concentration. In gasoline movement, the gasoline constituent will transfer between the moving phases and the soil adsorptive sites. The extent of transfer depends on the concentration of gasoline in these phases and the distribution coefficient among these phases. Generally, in the release case, gasoline will be adsorbed more by the soil matrix when passing through a pristine soil. During remediation, the gasoline

TABLE 18.2
Adsorption Coefficients for Gasoline Compounds

Chemical	K_{oc} Value (mL/g)
Tetraethyl lead[a]	4900
(n) Heptane	2361
(n) Hexane	1097
Naphthalene[b]	976
(n) Pentane	568
Ethylbenzene[b]	565
Toluene[b]	339
1-Pentane	280
(o) Xylene[b]	255
Benzene[b]	50
Phenol[b]	50
Ethylene dibromide	44

Source: U.S. EPA, Cleanups of Releases from Petroleum USTs: Selected Technologies, EPA/530/UST-88/00l, U.S. EPA, Washington, 1988.

[a] K_{oc} is a measure of the tendency for organic compounds to be adsorbed by soil. The higher the K_{oc} value for each compound, the lower the mobility and the higher the adsorption potential.

[b] Toxic compound.

constituents will be released from the soil, because the condition is manipulated to have a lower concentration than the previously partitioned concentration.

18.5.2.2 Degradation of Gasoline

Gasoline compounds are also subjected to chemical and biological processes.[19] Biodegradation and biotransformation are two basic biotic processes. Biodegradation is the decomposition of gasoline by microorganisms. The end products are water, carbon dioxide, and energy. Biotransformation is partial biodegradation. Gasoline compounds are partially degraded to simpler compounds that may be more or less soluble or toxic than the original compounds. Most of the biotic processes occur under aerobic conditions.

Abiotic chemical transformation is the reduction of chemical concentrations by degrading the chemicals into other products. The most important chemical transformations are hydrolysis and oxidation/reduction reactions.

Degradation is often the result of the combined effect of chemical transformation and biodegradation. For example, the oxidation/reduction of complex hydrocarbons can produce simple compounds such as peroxides, primary alcohols, and monocarbocylic acids. These compounds can then be further degraded by bacteria, leading to the formation of carbon dioxide, water, and new bacterial biomass.[19,35]

18.5.2.3 Movement of Gasoline Free Product

Most gasoline constituents are immiscible with water, and thus form free product of gasoline from water and usually float on groundwater.

The movement of free product is dependent on soil permeability and moisture. The released gasoline first infiltrates downward vertically, mainly governed by the gravity force, into and through the unsaturated zone, then reaches the water table. If there is an impermeable layer above the water table, the free product will be purged and may not reach the water table directly. In the unsaturated zone, gasoline can be retained by capillary forces and adsorbed onto soil particles. The capillary action in the unsaturated zone also enhances the extent of evaporation of both gasoline and groundwater.

As oil has a lighter specific gravity and lower viscosity than groundwater, the free product floats on the groundwater surface and moves at a faster rate than the groundwater. This horizontal movement is mainly governed by the hydraulic gradient. In the process, gasoline components are also partly adsorbed by the soil, evaporated into the soil void, and dissolved in the groundwater.

18.5.2.4 Movement of Gas-Phase Gasoline

Most gasoline constituents are volatile organics. Volatilization depends on the potential volatility of the compounds and on the soil and environmental conditions, which modify the vapor pressure of the chemicals. Factors affecting volatility are water content, clay content, surface area, temperature, surface wind speed, evaporation rate, and precipitation.

For vapor to move in the unsaturated zone, the soil formations must be sufficiently dry to permit the interconnection of air passages among the soil pores. Vapor concentration and vapor flow govern its movement. Vapor can move by diffusion from areas of higher concentration to areas of lower concentration and ultimately to the atmosphere. Therefore, the transportation of the vapor phase of gasoline components in the unsaturated zone can pose a significant health and safety threat because of inhalation and explosion potential.

Vapor can also move due to pressure gradient, as effected by a barometric-pumping-imposed pressure gradient, and due to density differences. If there is an impermeable layer above the rising vapors, such as a paved road, building, or a frozen ground surface, the vapors are able to move only by lateral underground travel; thus, migration can occur over relatively long distances.

The level of vapor movement in the unsaturated zone is much less important than transport in liquid form. However, this might not be true if the water content of the soil is very low or if there is a strong temperature gradient. The movement of vapor through the unsaturated zone is a function of temperature, humidity gradients, and molecular diffusion coefficients for water vapor in the soil.

18.5.2.5 Movement of Gasoline Solutes

Solubility causes gasoline compounds to be more mobile in association with the movement of groundwater. Dissolved gasoline compounds reach the saturated zone in several ways:

1. From groundwater flow that already has dissolved solute
2. From infiltrating water that has extracted solute from the soil or free product in its path due to the extraction of solute directly from soil adsorbates
3. From free product by the contacting groundwater

Dissolution of gasoline compounds to soil water is a function of each compound's solubility. A highly soluble gasoline substance often has a relatively low adsorption coefficient and also tends to be more readily degradable by microorganisms,[19] as shown in Table 18.1.

The most soluble gasoline compound is methyl tertiary-butyl ether (MTBE) (43,000 mg/L). In addition, MTBE in solution has a cosolvent effect, causing some of the other compounds in gasoline to solubilize at higher concentrations than they normally would in clean water.

18.5.3 MULTIPHASE MOVEMENT OF GASOLINE COMPOUNDS

Because gasoline is composed of some highly volatile and soluble hydrocarbon fractions, its components can move in the subsurface in three states: vapor, solute, and liquid. The form of its components in the soil are vapor, solute, free product, and adsorbate. The multiphase flow of gasoline is further complicated due to the various characteristics of the undersurface formation. The partition coefficients of the gasoline constituents in the gasoline free product, groundwater, soil particles, and soil gas determine the transformation of the gasoline forms.

The fate of gasoline in the subsurface is dependent on its interaction with soil and groundwater, volatilization, chemical reaction, biodegradability, and its movement, which in turn depends on the properties of both gasoline and the underground structure.

Soil moisture may greatly affect the movement of gasoline constituents. The adsorptive sites in a soil saturated with moisture are less available than those in a less saturated soil, so an unsaturated condition may promote adsorption of gasoline and retard the movement of gasoline away from a drier soil. Water makes gasoline less able to "wet" the soil, thus promoting the movement of gasoline as long as the pore space of soil is not fully occupied with water.

The extent of soil adsorption and suction forces varies depending on soil components. For example, clay has a much greater adsorption capacity and suction force than sand. The depth of gasoline penetrating the subsurface depends on the volume release, and the adsorption capacity and permeability of the soil. Gravitational force causes downward vertical migration. Suction can cause both vertical movement and horizontal movement. A higher suction force may cause a wider dispersion of gasoline away from the contaminated area.

In different soil zones, the effect of the forces is different, so the movement of gasoline should be considered separately in each zone. Based on the above discussion, the reader should be able to determine the fate and movement of a gasoline compound in different soil zones. The following gives a brief summary:

1. In the saturated zone, the most important phase of gasoline is its free product above the groundwater, then the gasoline as adsorbate in the soil; the gasoline as solute in the groundwater is less important.
2. In the upper unsaturated zone (above the capillary fringe), multiphase movement and transformation are typical. Vapor-phase gasoline becomes more important; gasoline adsorption by soil, dissolution in pore water, and free product in the pore space can also be significant.
3. In the capillary fringe, movement by suction occurs in all directions. Transport in the capillary fringe is also governed by multiphase flow. The increased water content in the capillary zone affects the rates of volatilization and dissolution. As soil water content increases, volatilization and vapor transport generally decrease and dissolution and solute transport generally increase. Free product migration occurs on top of the water table; the free product continues to spread and is held by capillary forces in the soil matrix. When the free product is exhausted, migration stops and residual saturation is reached.

Note that the heterogeneity of underground conditions would favor the flow along the path of least resistance, which is another factor controlling flow besides control by the hydraulic or concentration gradients.

18.6 MANAGEMENT OF TANKS AND THE ENVIRONMENT AS REMEDIAL ACTIONS

Immediate response for release is required, including release reporting, immediate containment, monitoring of explosive hazards, performing a site check to evaluate the extent of release, determining the presence of free product on the water table, and remedying hazards posed by excavated soils. Further corrective actions may be required such as removing the released free product, soil gas, and contaminated groundwater and soils, as well as removal and replacement of tanks. Detailed correction action plans are required if such further corrective actions are needed.[36,37]

An underground storage system that is found to leak or likely to leak should be abandoned, repaired, or replaced. Removal and cleaning of the tank are usually carried out before repair.

18.6.1 TANK REMOVAL

Removal of a leaking storage tank can limit liability and environmental damage. The following steps may be followed[38,39]:

1. Analyzing the tank content according to the U.S. EPA hazardous waste characterization process to determine the proper disposal procedure for the contents
2. Emptying the tank
3. Cleaning the tank interior with high-pressure water, steam, or solvent
4. Purging vapors from the tank using air, carbon dioxide, or nitrogen
5. Removing the tank from the ground
6. Rendering the tank to ensure it will not be reused any further, then disposing of it
7. Examining soil around the excavation for contamination
8. Removing and disposing of obviously contaminated soil (note that groundwater analyses are usually not required when a tank is removed)
9. Obtaining soil samples in the cleaned area for analysis, and documenting the effectiveness of the cleanup effort
10. Backfilling the excavation
11. Documenting the removal and disposal of the tank and soils; filing a report with the controlling government agencies and with the tank's owner, if any spills occurred during the work

Tanks should be removed only by contractors familiar with pertinent government regulations and knowledgeable about the safeguards necessary to prevent environmental harm so as to limit potential liability to the owner of the storage system.

18.6.2 TANK REPAIR

Some tanks, after repair, may stay in service to store gasoline. Most steel tank repairs are done by lining the interior of the tank with epoxy-based resins or some other coating that is compatible with fuel products.[5] Before the tank can be repaired, all free products must be emptied, and all vapors must be removed completely. The tank should be cleaned thoroughly to ensure the lining material adheres to the interior surface of the tank. Before putting the tank back into service, the tank should be tested and examined to be sure that all leaks are repaired, and whether or not additional work needs to be done. For example, recoating the tank, reinforcing the tank area, and lining or relining can all extend a tank's life.

18.6.3 TANK REPLACEMENT

There are cases in which tanks should be replaced rather than repaired. For instance, the American Petroleum Institute (API) does not recommend the lining of a tank that has open seams more than 3 in. long, perforations larger than about 1.5 in. in diameter, more than five perforations per square foot of surface area, or more than 20 perforations per 500 square feet of surface area.[40] Some localities have certain restrictions on repairing tanks.[5] It is also recommended to replace an unsecured underground storage system with a new one.

Compared to earlier tanks, current underground storage systems have two advantages:

1. Minimization of leaks
2. Leak monitoring devices

Leaking is minimized in new tank systems by including corrosion protection and using a double-walled tank construction. Corrosion protection is achieved by coating, by using cathodic protection, or by using fiberglass-enforced plastic tanks. In double-walled construction, the outer wall protects the erosion of the inner wall and contains any leakage that may occur.

New tank systems are also equipped with leak monitoring devices that take advantage of the double-walled construction. Leakage can be reported in real time and more accurately using these detection devices, which include water- or product-sensitive probes, or pressure detection devices if the space between the two walls is designed to remain under vacuum.

18.6.4 ALTERNATIVES FOR TANK ABANDONMENT AND REPLACEMENT

There are two alternatives to tank abandonment and replacement:

1. Abandonment in place
2. Installation of an aboveground storage tank

Although it is more desirable to remove unreliable underground tanks, a tank may be abandoned in place, for example, when it is indoors, under a building, beneath a foundation, or barricaded with other constructions.

Before a tank is abandoned in place, the following measures should be taken into consideration[38,39]:

1. Assessment of the tank's integrity, knowing that a tank may be abandoned in place only if it has never leaked; otherwise, a broader remediation effort might be required if it has leaked and contaminated the soil and groundwater
2. Removal of all liquids
3. Removal and disposal of sludge and residues
4. Cleaning of the tank and disposal of the cleaning residue
5. Filling of the tank with inert material such as sand, gravel, or concrete
6. Disconnection of piping, and plugging it with concrete or nonshrinkable grout or removing all piping.

The second alternative is to construct an aboveground tank, whenever it is feasible, in order to avoid the liability of uncontrolled USTs. This alternative is being chosen by many tank owners for new storage. However, the aboveground storage system has the following disadvantages compared with underground storage:

1. There are more strict fire regulations.
2. Space is needed for installation.
3. It is more likely to be exposed to accidental damage.
4. It is more exposed to local building codes, which usually do not favor aboveground tank systems.

18.7 CONTROL OF CONTAMINANTS MIGRATION AS REMEDIAL ACTIONS

18.7.1 GAS CONTROL

Gas control is required, because the vapor phase of gasoline components in an unsaturated zone can pose a significant health and safety threat. The gas control and safety concern are discussed in another chapter. Some of the remedial technologies presented in subsequent sections of this chapter can also act as gas control measures.

18.7.2 CONTROL OF PLUME MIGRATION

Migration of the gasoline free product and the contaminated groundwater plumes should be controlled. The containment of a plume prevents its further migration and the enlargement of contaminated areas. The most effective method is to pump so as to cause a depression of the water

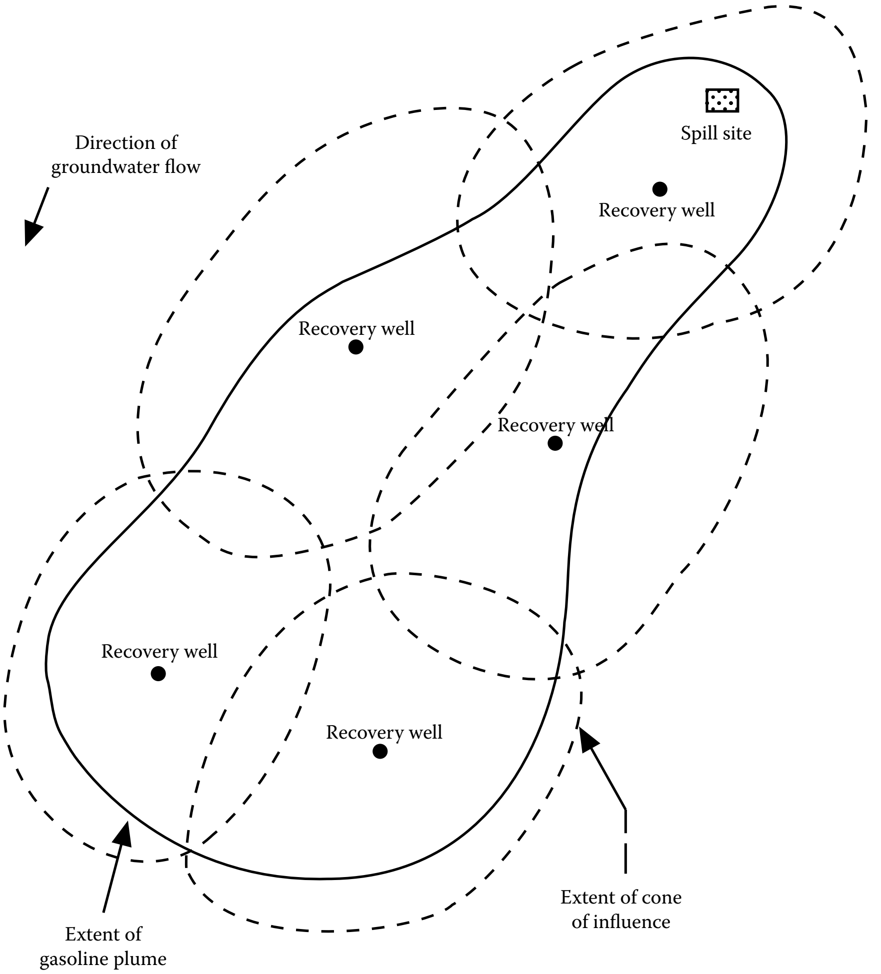


FIGURE 18.5 Using overlapping cones of influence to contain a gasoline plume.

table, which modifies and controls the flow direction of groundwater (Figure 18.5). The trench method can also intercept the plume and prevent it from further migration.

These two methods, which are used as an emergency action, can also be utilized for the cleaning of plumes. Containment methods can often be extended to plume treatment by using the trench or well pumping to recover the free product.

There are other methods for containment such as slurry walls and piling sheets, which are only used as methods for containment but not for treatment.

18.8 REMOVAL OF CONTAMINANTS AS REMEDIAL ACTIONS

18.8.1 Removal and Recovery of Free Product

Recovering free product comprises the following major steps[41]:

1. Establishing gasoline plume containment
2. Gathering and extracting (associated with gasoline/water separators) the contained plume from underground
3. Recovering gasoline

18.8.1.1 Gasoline Plume Containment and Extraction

Trench method

The trench method uses an excavator to dig a trench down to the water table to intercept the flow of the floating gasoline. The trench should be dug deep enough to pond groundwater and the floating gasoline. Pumping out the water in the trench can increase the hydraulic gradient and increase the movement of gasoline to the trench.

Groundwater flow direction should be predetermined. An impermeable membrane is placed on the downgradient side of the trench to ensure that the gasoline in the trench does not escape back into the soil. A better practice is to install an upgradient membrane that can allow more gasoline but less water to enter the trench, and a downgradient membrane to prevent gasoline from moving into the soil while allowing water to pass out to the soil on the downgradient side.

The ponded gasoline in the trench is removed separately from the water for recovery. Special equipment has been used for this purpose, including skimmers and filter separators that are automatically activated when gasoline is present in the trench to separate and remove the gasoline from the water.[19] It is inevitable that a gasoline and water mixture will be pumped out. Gasoline will then be recovered using methods (detailed later) for the treatment of pumped contaminated groundwater.

The trench method is applicable only when the water table is relatively shallow, less than 10 to 15 ft below the ground surface. For a deeper water table, the cost of the trench method becomes more expensive than other methods such as pump systems. Another limitation of the trench method is the soil structure. The soil above the water table has to be firm and well aggregated to allow for the trench to be self-supporting. Otherwise, embankment enforcement or screening would be needed. A third limitation is that continuous pumping and skimming is required to maintain a flow gradient towards the trench. Otherwise, the free product will move back and reenter the soil.

Pumping well method

The pumping well method is more suitable for a water table that is too deep for the trench method. Pumps draw water, forming a cone of depression in the water table to control the movement of floating gasoline. The gasoline is then pumped out. The pumps can be either single- or a dual-pump systems.

Groundwater models and other analytic techniques are available to assist in proper pump siting, choosing pump capacities, and calculating the movement of the contaminant plume. The characteristics of the aquifer, the flow of groundwater, and the size of the plume should be known.

In the single-pump system both gasoline and water are recovered through a single pipeline to aboveground storage tanks or oil/water separators (Figure 18.6a). There are two problems encountered with this single-pump system:

1. During pumping, gasoline and water are mixed, which complicates aboveground separation.
2. Large volumes of contaminated water must be stored, treated, and disposed of.

Therefore, the single-pump method is commonly used only for smaller spills when the gasoline–water recovery rates are relatively low (e.g., less than 1892 L/h or 500 gal/h).

The dual-pump system is used when a large amount of gasoline is to be recovered. Separate gasoline and water pumps are used. The dual-pump system significantly reduces the amount of water that must be treated. Water pumps are placed at a depth lower than the water table to be able to establish a cone of depression, and the gasoline pumps draw out the gasoline that floats into the depression on the top of distorted water table for product recovery (Figure 18.6b).

Dual-pump systems are better able to control a constant cone of depression than the single-pump system. It is important to maintain a nearly constant cone of depression to prevent the migration of the gasoline plume. If a constant cone of depression is not maintained, the water table and

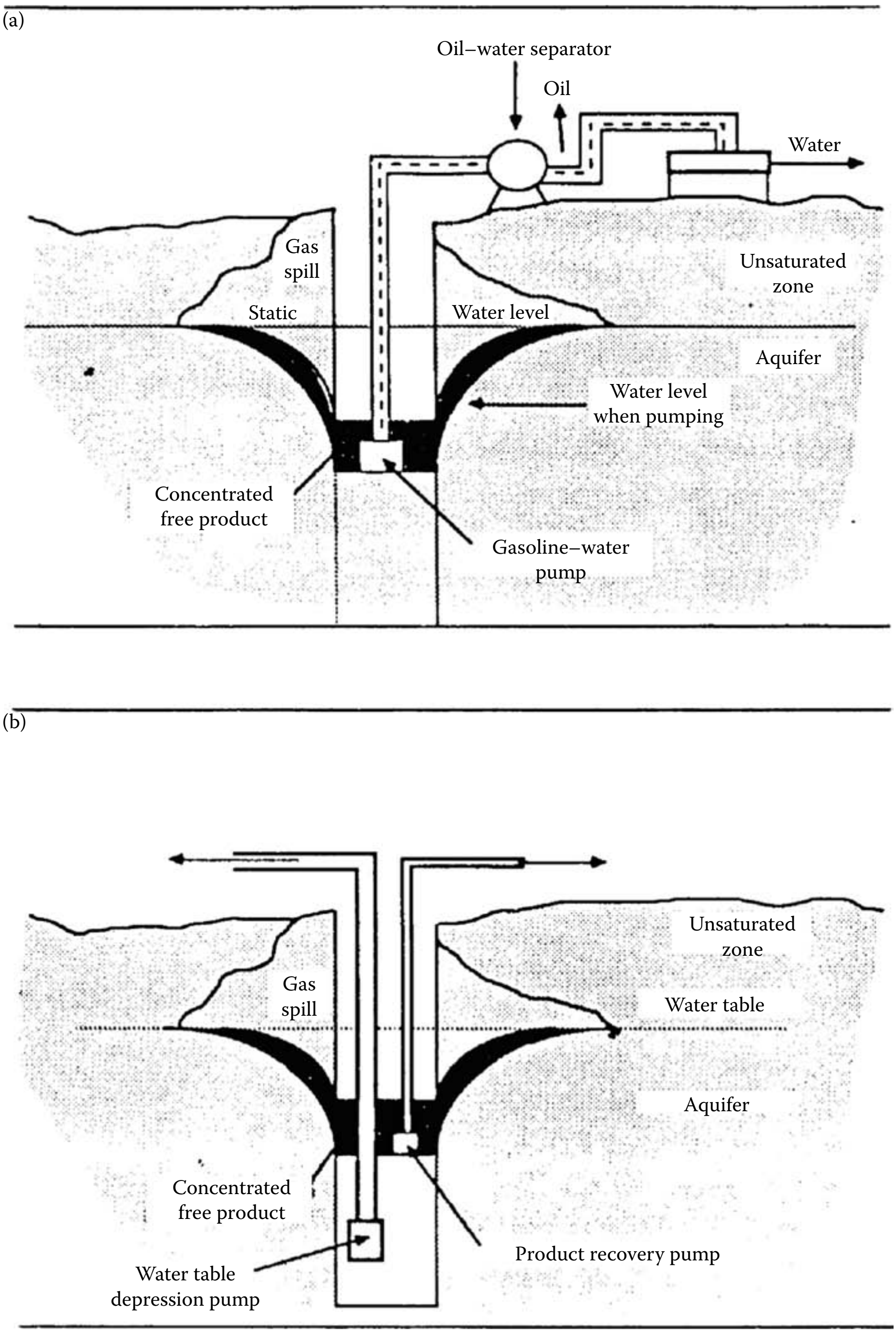


FIGURE 18.6 (a) Single-pump and (b) dual-pump gasoline recovery systems.

the gasoline plume will rise, and gasoline droplets may adhere to soil particles and consequently remain in the soil.

The cone of depression in a dual-pump system is controlled by a detection probe. Initially, the probe is set in the well at the depth of the proposed cone of depression of the gasoline–water interface. The water pump draws the water table down, reaching the pump probe. The water pump ceases when the pump probe detects gasoline. The depressed water table will rise slightly. As soon as the probe detects water again, the water pump resumes, thus maintaining a constant cone of depression. Gasoline will accumulate in the depression. The product pump, both inlet and probe of which are placed a few inches above the water probe, draws gasoline aboveground.

Installation of the pumping well is more time consuming than digging a trench. There is a lag period between the start of pumping, the formation of the depression cone, and containment of the plume. This limits its use as a rapid containment measure. The water table depression must be kept constant; otherwise, if the water table is allowed to fluctuate, gasoline droplets may adhere to soil particles and get trapped below the water table, especially when the depth of the cone of depression gets lower.

The pumped free product is usually accompanied by water. Hence, it is necessary to separate water from the oil, which is usually performed aboveground, although recently a subsurface recovery system has been developed.

18.8.1.2 Subsurface Gasoline Recovery

Subsurface gasoline recovery is analogous to *in situ* oil–water separation. The main advantage of this technique is that the pumped gasoline, which moves with the groundwater gradient, can be intercepted and recovered with minimum energy input.[19] The plume is trapped and directed to the separator influent nozzle. Other advantages are that it reduces the likelihood of water being frozen in the separator in cold weather, it eliminates the evaporation of potentially dangerous volatile organic compounds, and it saves aboveground space for other uses.

The disadvantages of subsurface gasoline recovery are as follows:

1. It is difficult to excavate a hole large enough and deep enough to install the separator at the water table.
2. Installation is time consuming and may not be completed quickly enough to contain the migration of a rapidly moving plume.
3. The separator effluent usually contains a residual dissolved gasoline concentration of 15 mg/L.
4. Treatment of separated gasoline is also needed if the reuse of gasoline is desired. In such a case, an aboveground advanced gasoline–water separator is needed.

18.8.1.3 Aboveground Gasoline Recovery

Aboveground separators are typically large tanks whose function is to slow down the flow of the incoming water; this allows gravity separation of the less dense gasoline emulsions.[19,41] Separators are composed of two or more chambers. The first chamber is used for the deposition of settleable solids, and the second is used for the separation of liquids of dissimilar specific gravities and the removal of the lighter liquid.

In the preseparation chamber, the less dense oil droplets rise, collide, and fuse with adjacent droplets. According to Stoke's law, the larger the diameter of a particle, the faster is its rate of rise. Thus, as small droplets coalesce to form larger droplets, their upward vertical velocity increases. Coalescing tubes or plates are designed to enhance the separation of oil–water emulsions. The emulsion free water is directed away from the tubes or plates and enters the separation section. Some separators are built with an outlet zone for the discharge of clarified water.

Under optimum conditions, an oil–water separator can reduce the hydrocarbon emulsion in water down to 15 mg/L. The separator is most effective when the gasoline plume is relatively small and the rate of water flow is slow enough to allow for complete separation.

If it is desirable to reuse the oil, then more efficient oil–water separators utilizing heating and nebulization techniques will be needed. U.S. patents issued to Weber and colleagues[42] and Wang and colleagues[43] make use of such techniques.

18.8.1.4 Recovered Gasoline

Recovered gasoline can either be disposed of by incineration or reused. If the gasoline is to be reused, it must be refined or mixed with other gasoline as it gets degraded while in the soil. There are three processes that affect the degradation of gasoline:

1. Aromatic hydrocarbons such as benzene, toluene, and xylene become oxidized in the presence of oxygen.
2. Gasoline constituents are metabolized by soil microbes.
3. Water particles may coalesce with the hydrocarbons.

18.8.1.5 Recovered Water

Recovered water that contains a small amount of floating free product and dissolved constituent is usually passed through an oleophilic–hydrophobic adsorbent filter to remove the remaining free product.[19]

If the remedial action involves the treatment of contaminated water (such as pump-treatment for groundwater recovery or soil-washing for soil recovery, which will be discussed in Section 18.8.2), then the preliminarily recovered water can be combined with a treatment stream for further treatment.

There are many options for the disposal of the filter-treated water and dissolved hydrocarbons:

1. The aquifer may be recharged with the recovered water in order to flush out the remaining pockets of free gasoline. A drawback to this technique is that the recharging water contains dissolved constituents.
2. The water may be discharged to a natural water course where dilution and exposure to oxygen will reduce the hazards of its dissolved gasoline constituents. In such a case, a National Pollutant Discharge Elimination System permit and a State Pollutant Discharge Elimination System permit must be obtained.
3. The water may be sent through a wastewater treatment plant where the remaining dissolved constituents can be removed.
4. The water may be treated with on-site air strippers and carbon adsorption filtration systems.

18.8.2 *IN SITU* BIOLOGICAL TREATMENT OF GROUNDWATER DECONTAMINATION

Several methods are available to remove gasoline constituents from water, such as air stripping, biorestoration, activated carbon adsorption, reverse osmosis, ozonation, oxidation, resin adsorption, oxidation with hydrogen peroxide, ultraviolet irradiation, flotation, and land treatment.

Biological *in situ* treatment is based on the concept of stimulating microflora to decompose the contaminants in place, resulting in the breakdown and detoxification of those contaminants. Biological degradation or biological remediation is generally considered a cost-effective method for the removal of organic compounds, although it is site-specific for *in situ* biological degradation. For removing volatile organic compounds (VOCs), on the other hand, cost-efficiency may be achieved by using the technologies involving volatization (such as air-stripping), as well as other technologies. In fact, about 95% of cases that involve removing a gasoline plume dissolved in groundwater use air stripping and filtration through GAC.[19] Biological treatment is not widely applied in the field, although it is cost-effective and promising for coarse-grained soils.

18.8.2.1 Classification of Biological Treatment

Bacteria can grow in two main environments, aerobic and anaerobic. In aerobic treatment, aerobic and facultative bacteria use molecular oxygen as their terminal electron acceptor. The treatment occurs in the presence of a molecular oxygen supply. In anaerobic treatment, anaerobic and facultative bacteria use some other compound as their terminal electron acceptor, for example, carbon dioxide, sulfate, or nitrate, in the absence of molecular oxygen. In fact, there is another type of biological treatment called the fermentative and methanogenic process, which is carried out by what is referred to as a methanogenic consortium.[44,45]

So far, only aerobic processes have proved to be effective for *in situ* removal of organic waste in groundwater and soil.

18.8.2.2 Characteristics and Factors Affecting Aerobic Biological Treatment

In the aerobic process, organic contaminants such as gasoline releases are broken down by bacteria to produce new biomass (bacteria) and other byproducts:

$$\text{Bacteria} + \text{organics} + \text{oxygen} + \text{nutrients (N, P)} \longrightarrow \text{more bacteria} + \text{byproducts} \tag{18.7}$$

The organics contaminants, whose concentration is usually expressed in terms of biochemical oxygen demand (BOD), are utilized as food for the bacteria. Besides oxygen, nutrients (nitrogen and phosphorus) are also needed by the bacteria for its metabolism. The concentrations of oxygen, bacteria, organic contaminants, and nutrients, as well as other factors, have an affect on the biological treatment rate.

Dissolved oxygen (DO) in a bioreactor should be maintained above a critical concentration in order to maintain good aerobic biological activity. The minimum required DO concentration ranges between 0.2 and 2.0 mg/L with 0.5 mg/L being the most reported value.

Significant and active microbial populations are usually found in the subsurface soil and groundwater. However, if there is a lack of required microorganisms, then bacteria can be injected *in situ*. An optimum food/microorganisms (F/M) ratio should be maintained for effective removal of organic contaminants.

An equally important factor is the biomass/oxygen ratio. If oxygen is deficient, then the biomass cannot be sustained under aerobic conditions. Thus, control of the oxygen supply becomes important. In fact, in bioremediation the most important part of the design is the provision of an appropriate level of oxygen supply to maintain an efficient process.

Another important factor is the food/nutrient ratio. Many of the necessary nutrients may already be present in the aquifer, such as K, Mg, Ca, S, Na, Mn, Fe, and trace elements; however, N and P may be deficient and need to be added. The optimum ratio of BOD : N : P is 100 : 5 : 1. It is not a good practice to inject a large quantity of nutrients in the aquifer at one go. They should be fed at the required usage rate throughout the cleanup process. Both the organic contaminants and the nutrients should be completely exhausted by the end of the *in situ* remediation of an aquifer.

pH should be maintained near neutral, between 6 and 8. Generally, the optimal value is slightly higher than 7.

The optimal temperature for bacterial growth is between 20 and 37°C. For every 10°C decrease in temperature, bacterial activity is approximately halved. Temperature in deep groundwater is rather constant. However, for shallow soil and water, in cold weather the rate of biodegradation becomes depressed compared to in warmer weather, and therefore warm water may need to be injected into the subsurface.

Other factors affecting performance include the presence of toxic material, the redox potential, salinity of the groundwater, light intensity, hydraulic conductivity of the soil, and osmotic potential. The rate of biological treatment is higher for more permeable soils or aquifers. Bioremediation is not applicable to soils with very low permeability, because it would take a long time for the cleanup process unless many more wells were installed, thus raising the cost.

Clogging of aquifers by the growth of biomass is an operational problem. The permeability of an aquifer could be reduced due to the precipitation of biomass sludges and chemicals, or due to clay dispersion.

18.8.2.3 Design of an *In Situ* Bioremediation System

The concentration of biomass is important for the degradation of organic contaminants. Designers can utilize the available microbial population in the soil and groundwater. However, the biomass grows slowly, and remediation requires an accelerated growth rate. This can be realized by a delivery and recovery system. The delivery directs oxygen and nutrients to the underground formations; the recovery stage recovers the spent treatment solution. Circulation of groundwater is very important. A complete delivery and recovery system will do the following:

1. Deliver a high concentration of oxygen and supply additional nutrients or commercially available bacteria if bacteria and nutrients are deficient
2. Provide adequate contact between the biomass and contaminants
3. Prevent the clogging of the soil voids to ensure a sufficient groundwater flow
4. Flush the groundwater
5. Provide hydrologic control of treatment agents and contaminants to prevent their migration beyond the treatment area
6. Provide for complete recovery of the spent treatment solution or contaminants where necessary

As bioremediation proceeds, the bacterial population increases due to the growth of the biomass. Thus, although bacteria may be deficient at the beginning they do not usually need to be added after the startup.

The following design example of an injection and extraction system (Figure 18.7) illustrates the bioremediation process. Both the soil and groundwater are contaminated. Groundwater is extracted downgradient and reinjected upgradient of the zone of contamination. Water is also injected to flush the soil.

There are two methods for the injection of oxygen: *in situ* and in line. In an *in situ* oxygen supply, oxygen is supplied directly from the aeration well to the contaminated plume. A mechanical aeration unit produces sufficient mixing of oxygen and bacteria with the leachate plumes. In an in-line oxygen supply, oxygen is added together with nutrients or bacteria to the mixing tanks (Figure 18.7b).

The most common sources as oxygen supply are air, pure oxygen, hydrogen peroxide, or possibly ozone. Table 18.3 summarizes the advantages and disadvantages of these oxygen supply alternatives.

Using air is economical. However, an in-line method using air may not provide adequate oxygen supply because the maximum oxygen supply is approximately 10 mg/L O_2, which is sufficient for the degradation of only about 5 mg/L of hydrocarbons. Even when using pressurized air or pure oxygen, an in-line supply of oxygen can only degrade low levels of contaminants, less than 5 to 25 mg/L of hydrocarbons.

Pure oxygen can also be used. The injection method can be the same as for air injection. The advantage of using pure oxygen over conventional aeration is that higher oxygen transfer to the biomass can be attained. The in-line injection of pure oxygen will provide sufficient dissolved oxygen to degrade 20 to 30 mg/L of organic material.

Using hydrogen peroxide (H_2O_2) has the following advantages:

1. Greater oxygen concentrations can be delivered to the subsurface.
2. Less equipment is required.
3. Hydrogen peroxide can be added in-line along with the nutrient solution, and aeration wells are not necessary.
4. Hydrogen peroxide keeps the well free of heavy biological growth, thus reducing clogging problems.

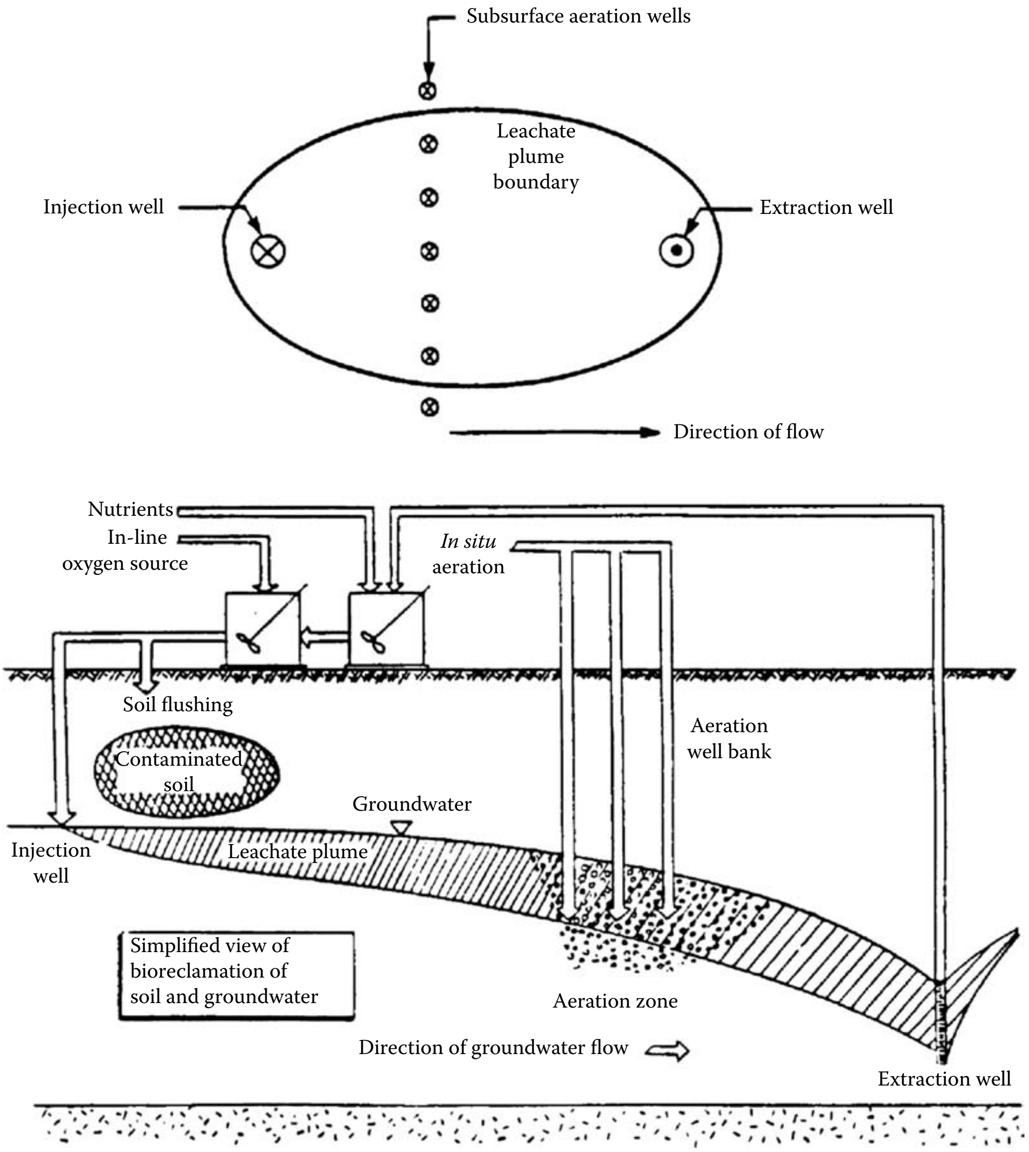


FIGURE 18.7 Simplified view of groundwater bioreclamation.

Ozone is not widely used, because of its high cost and the possibility of some toxicity to bacteria if used at high dosage for low BOD concentrations (higher than 1 mg/L of ozone per mg/L total organic carbon).

In situ oxygen supply requires aeration wells for the injection of oxygen. The criteria are that the aeration well zone must be wide enough to allow the total plume to pass through, and the flow of air must be sufficient to produce a substantial radius of aeration while small enough so as not to create an air barrier to groundwater flow. The required residence time t_r for aeration can be calculated from Darcy's law as a function of the groundwater head and hydraulic conductivity:

$$t_r = \frac{L_a^2}{K(h_1 - h_2)} \tag{18.8}$$

TABLE 18.3
Oxygen Supply Alternatives

Substance	Application Method	Advantages	Disadvantages
Air	In-line	Most economical	Not practical except for trace contamination <10 mg/L COD
	In situ wells	Constant supply of oxygen possible	Wells subject to blow out
Oxygen-enriched air or pure oxygen	In-line	Provides considerably higher O_2 solubility than does aeration	Not practical except for low levels of contamination <25 mg/L COD
	In situ wells	Constant supply of oxygen possible	Very expensive Wells subject to blow out
Hydrogen peroxide	In-line	Moderate cost Intimate mixing with groundwater Greater O_2 concentrations can be supplied to the subsurface (100 mg/L) H_2O_2 provides 50 mg/L O_2) Helps to keep wells free of heavy biogrowth	H_2O_2 decomposes rapidly upon contact with soil, and oxygen may bubble out prematurely unless properly stabilized
Ozone	In-line	Chemical oxidation will occur, rendering compounds more biodegradable	Ozone generation is expensive Toxic to microorganisms except at low concentrations May require additional aeration

Source: U.S. EPA, Cleanups of Releases from Petroleum USTs: Selected Technologies, EPA/530/UST-88/00l, U.S. EPA, Washington, 1988.

where t_r = residence time (T), L_a = length of aerated zone (L), h_1 = groundwater elevation at beginning of aerated zone (L), h_2 = groundwater elevation at the end of the aerated zone (L), K = hydraulic conductivity (L/T).

The design conditions for the injection and extraction system are as follows:

1. The groundwater injection rate should be determined by a field testing program.
2. All injected groundwater and associated elements are to be kept within the site boundary to prevent the transport of contaminants to adjacent areas.
3. The distance between the injection-pumping wells should be such that approximately six injection-pumping cycles can be completed within a six-month period.
4. Aquifer flow rate should be sufficiently high so that the aquifer is flushed several times over the period of operation.
5. Flow and recycle rates should not be high enough to cause excessive pumping costs or loss of hydraulic containment efficiency due to turbulent conditions, corrosion, flooding, or well blow out.

18.8.2.4 Case History of *In Situ* Bioremediation

A bioremediation system described by U.S. EPA[19] consists of a downgradient dewatering trench and well, two mobile biological activating tanks, two mobile settling tanks, and two upgradient

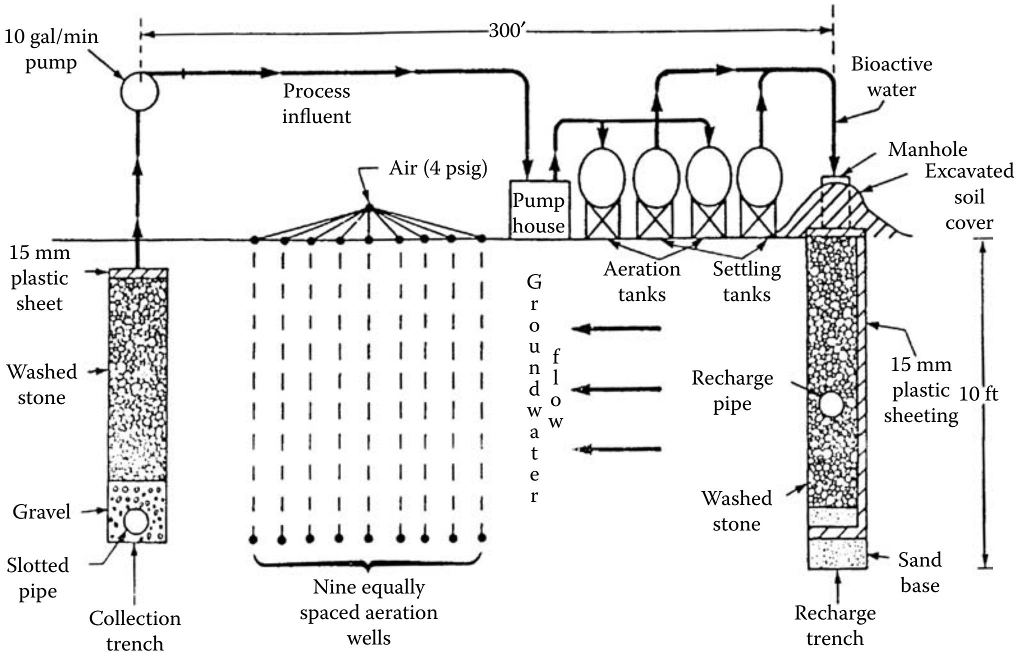


FIGURE 18.8 Flow diagram of Biocraft biorestoration.

reinjection trenches (Figure 18.8). The system was used to treat between 53,000 and 76,000 L/d (14,000 and 20,000 gal/d) of groundwater that had been contaminated with 114 m^3 (30,000 gal) of organics that leaked from USTs. The reduction of contaminant mass ranged from 88 to 98% for methylene chloride, acetone, and n-butyl alcohol, and 64% removal for dimethylaniline. Most of the contaminants in the groundwater (over 95%) had been removed during its operation from 1981 to 1985.[46]

There are several advantages of using *in situ* bioremediation[47–49]:

1. Cost-effectiveness
2. Minimal disturbance to an existing site
3. On-site destruction of contaminants
4. Continuous treatment after shutdown of the project
5. Permanent solution
6. Possibility of simultaneous cleanup for both groundwater and soil

Most contaminations of aquifers are a result of material being released above the saturated zone. The contaminant pumping method is limited to the cleanup of the saturated zone. Contaminants in the unsaturated zone can still be a source of future contamination. *In situ* bioremediation techniques can also be designed to clean up the unsaturated zone simultaneously.

The limitations of *in situ* bioremediation are as follows:

1. It is not suitable for short-term projects (it usually needs two to eight weeks of startup period to have the bacteria grown to a sufficient concentration in order to effectively remove the contaminants).
2. It is not suitable for low-permeability and high-salinity areas, as well as areas with extreme pH levels.

3. It is not suitable for the removal of nonbiodegradable organics, toxic material, or material whose concentration is too high and thus toxic to bacteria.
4. It requires continuous operation (a biological treatment system cannot be turned on and off frequently).

18.8.3 PUMP-AND-TREAT PROCESSES FOR GROUNDWATER DECONTAMINATION

18.8.3.1 Air Stripping

Air stripping is an effective and widely used method to remove VOCs from water. It is the most cost-effective option for removal of gasoline from groundwater.[19]

The basic principle of air stripping is to provide contact between air and water to allow the volatile substances to diffuse from the liquid to the gaseous phase. Mass transfer occurs across the air–water interface. The theory of air stripping is related to Henry's law. At a given temperature, the partition of VOCs in the contacting air and water follows Henry's law:

$$P_a = HX_a \tag{18.9}$$

where P_a = particle vapor pressure of VOC (atm), H = Henry's law constant (atm), and X_a = mole fraction of VOC in water (mol/mol).

The Henry's law constant can be regarded as the partitioning coefficient of VOCs between air and water. Molecules of VOCs can pass freely between gaseous and liquid phases. At equilibrium, the same numbers of molecules move in both directions through a unit area in a unit of time. Departure from equilibrium provides the driving force for mass transfer. This can be affected by a change of temperature or by driving the VOC out of the air phase. Air stripping can be regarded as a "controlled disequilibrium".[19,50] Removal of a VOC from the contacting air–water system leads to it being at a decreased concentration in the water. The eventual outcome is the removal of the VOC from water.

Types of air stripping facilities

There are many methods to introduce fresh air for air stripping, including diffused aeration, tray aerators, spray basins, and packed-towers methods.

In the air diffusion method, compressed air is injected into the water through diffusers or sparging devices that produce fine air bubbles.[51] Mass transfer occurs across the air–water interface of the bubbles. Consequently, contaminants are removed from the wastewater. Mass transfer rates can be improved by producing fine bubbles, increasing the air/water ratio, improving basin geometry, using a turbine to increase turbulence, or increasing the depth of the aeration tanks. Reported removal of organics by air diffusion is between 70 and 90%.[52]

The tray aeration method is a simple, low-maintenance method of aeration that does not use forced air.[19] Water is allowed to cascade through several layers of slat trays to increase the exposed surface area for contact with air (Figure 18.9). Tray aeration is capable of removing 10 to 90% of some VOCs, with a usual efficiency of between 40 and 60%.[53] This method cannot be used where low effluent concentrations are required, but could be a cost-effective method for reducing a certain amount of VOC concentration prior to activated carbon treatment.

The spray aeration method comprises a grid network of piping and nozzles over a pond or basin. Contaminated water is simply sprayed through the nozzles and into the air to form droplets. Mass transfer of the contaminant takes place across the air–water surface of the droplets. Mass transfer efficiency can be increased by multiple passing of the water through the nozzles. This method has three disadvantages:

1. A large land area is necessary for the spray pond.
2. Mist is formed, which could be carried into nearby residential areas.

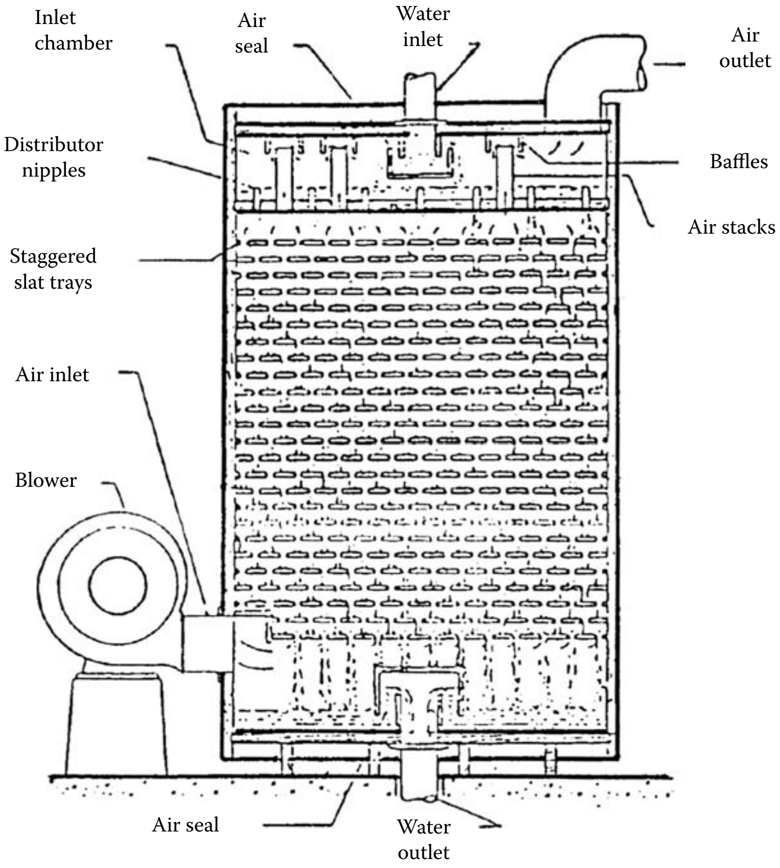


FIGURE 18.9 Schematic diagram of Redwood slatted tray aerator.

3. There is the possibility of ice formation, which lowers the usefulness of the technique in colder climates.

The packed-tower method involves passing water down through a column of packing material while pumping countercurrent air up through the packing (Figure 18.10). The packing material breaks the water into small droplets, causing a large surface area across which mass transfer takes place. The towers are very effective in removing VOCs. Typical removal efficiencies are between 90 and 99%, although 100% (i.e., down to nondetectable levels) removal has been reported. These countercurrent packed towers are the most common of the air-stripping methods. The air emission problems associated with air stripping units have been eliminated from the units developed in the early 1990s by Wang and colleagues[29] and Hrycyk and colleagues.[30]

Henry's law constant

Henry's law constant (H) is usually expressed as follows:

$$H = P_{\text{atm}}(M_{\text{w}}/M_{\text{c}}) \tag{18.10}$$

where P_{atm} = pressure (atm) (here 1 atm = 760 mmHg), M_{w} = weight of water (mol), and M_{c} = weight of contaminant (mol).

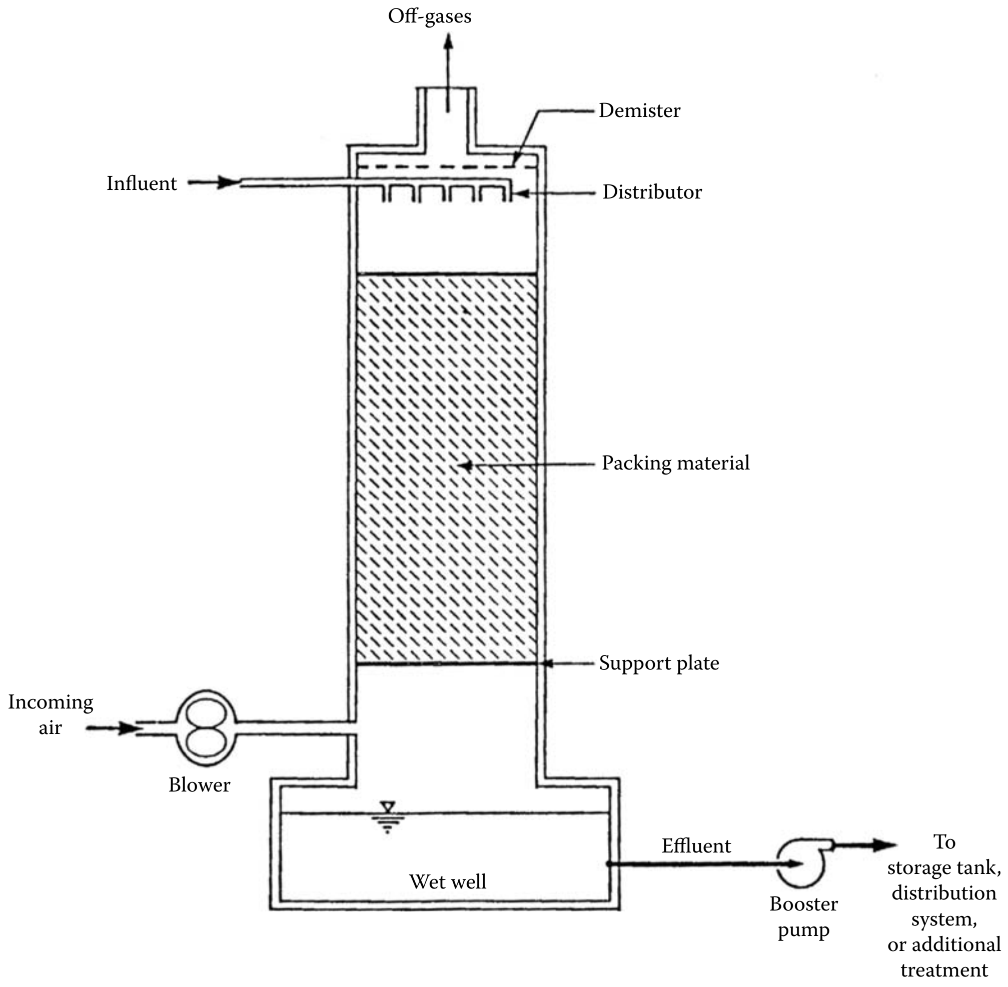


FIGURE 18.10 Schematic diagram of packed tower aerator.

Dimensionless units are also used that are valid only for systems that operate at standard pressure (P_{atm} = 1). The actual units are as follows:

$$H = P_{atm}(V_w/V_c) \tag{18.11a}$$

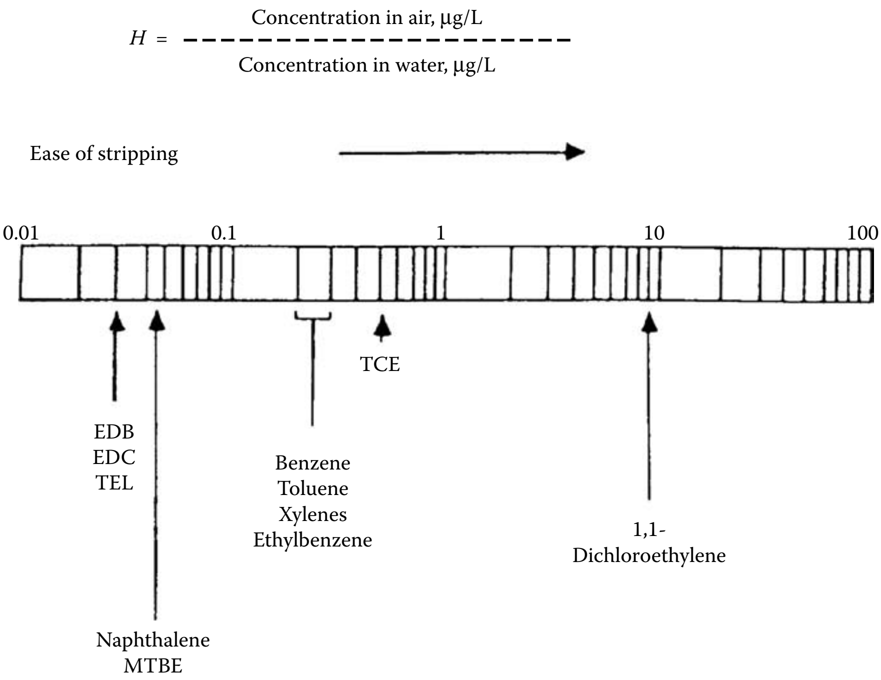
and

$$H = (V_w/V_c) \tag{18.11b}$$

where P_{atm} = 1 (standard pressure), V_w = volume of water (m^3), and V_c = volume of contaminant (m^3).

Typical values of H for gasoline components range between 20 and 500 atm (0.03 to 0.30 in dimensionless units at the standard condition [P_{atm} = 1]).

Henry's law constants for most of the compounds of interest can be found in the literature.[54] Figure 18.11 shows Henry's law constants for TCE, EDC and several gasoline compounds.[19] These data are derived from water solubility data and the equilibrium vapor pressure of pure liquids at certain temperatures, and may be extrapolated correctly to field design work. Temperature has a major effect on Henry's constant and on stripper performance. Each rise of 10°C in temperature



EDB = Ethylene dibromide (1,2-dibromoethane)
EDC = Ethylene dichloride (1,2-dichloroethane)
TEL = Tetraethyl lead
MTBE = Methyl tertiary butyl ether
TCE = Trichloroethylene

FIGURE 18.11 A comparison of stripping rates for TCE and gasoline compounds.

may cause an increase of Henry's constant by a factor of about 1.6.[55] Consequently, warmer temperatures can achieve higher rates of stripping.

Mass balance and air/water ratio

Contaminant mass transport in an air stripper is schematically shown in Figure 18.12. The removal process can be described mathematically by a mass balance for the contaminant assuming that there is no change in the accumulated contaminant in the stripper under steady-state conditions:

$$L(X_{\text{in}} - X_{\text{out}}) = G(Y_{\text{out}} - Y_{\text{in}}) \tag{18.12}$$

where L = volumetric rate of contaminated groundwater (L^3/T), G = volumetric rate of air (L^3/T), X_{in} = influent contaminant concentration in water (M/L^3), X_{out} = effluent contaminant concentration in water (M/L^3), Y_{in} = influent contaminant concentration in air (M/L^3), and Y_{out} = effluent contaminant concentration in air (M/L^3).

For a further application of the mass balance equation to removal processes, four basic assumptions are made:

1. Influent air is free of VOCs (i.e., $Y_{\text{in}} = 0$).
2. Differential flow holds for air and water.
3. Changes of liquid and air volumes during mass transfer are negligible.
4. Henry's law holds for these conditions.

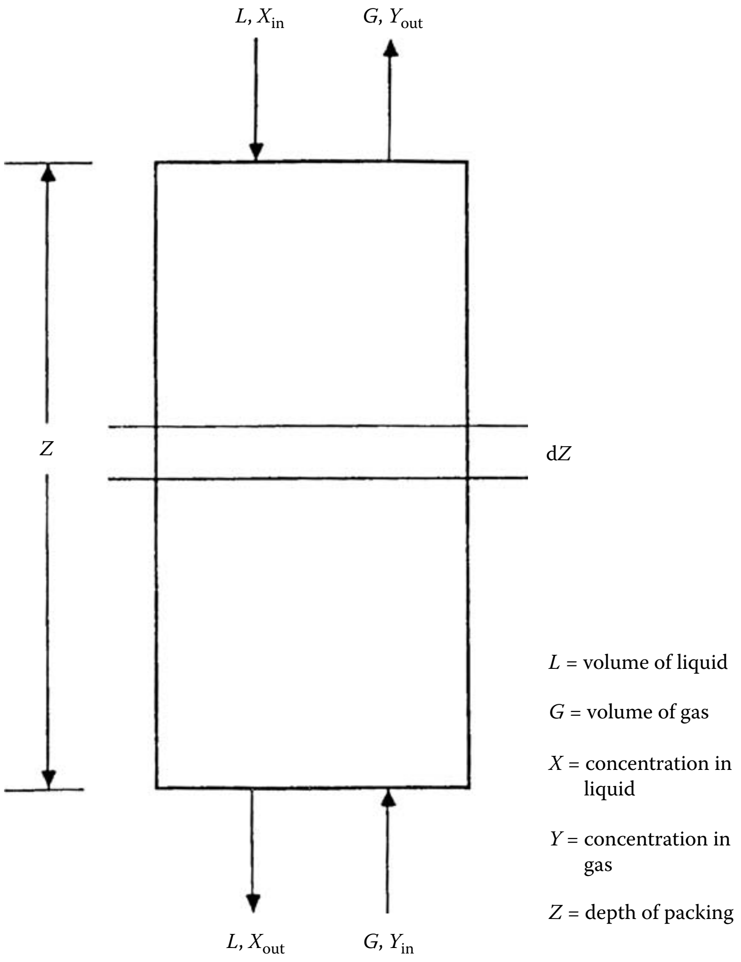


FIGURE 18.12 Differential element for an air stripping tower.

Applying the first assumption, $Y_{in} = 0$, Equation 18.12 can be rearranged as

$$G(Y_{out}) = L(X_{in} - X_{out}) \tag{18.13}$$

and

$$\frac{G}{L} = \frac{X_{in} - X_{out}}{Y_{out}} \tag{18.14}$$

Applying Henry's law at the point that air leaves the stripper (i.e., the contaminated water enters stripper) and assuming that equilibrium for mass transfer holds between air and water at that point, Equation 18.9 becomes

$$Y_{out} = HX_{in} \tag{18.15}$$

Substituting Equation 18.15 into Equation 18.14 yields

$$\frac{G}{L} = \frac{X_{in} - X_{out}}{HX_{in}} \tag{18.16}$$

where H = Henry's constant (dimensionless).

Note that $(X_{\text{in}} - X_{\text{out}})/X_{\text{in}}$ is the removal efficiency of a stripper, denoted as f. Then Equation 18.16 becomes

$$\frac{G}{L} = \frac{f}{H} \tag{18.17a}$$

G/L in Equation 18.17a is the theoretical air/water ratio required for the removal efficiency f for a specific contaminant following Henry's law. In this context, the G/L is denoted $(G/L)_{\text{theory}}$, indicating the theoretical air/water ratio. This also means that a minimum amount of air must be brought into contact with the water for a certain length of detention time, the sparging size of the water droplets also affects the mass transfer, as does the air pressure.

Stripping factor

Theoretically, the required air/water ratio for a specific removal can be determined by the mass balance in the stripper:

$$\left(\frac{G}{L}\right)_{\text{theory}} = \frac{f}{H} \tag{18.17b}$$

This air/water ratio is the theoretical or minimum air/water ratio for a given removal. However, in practice, the contaminant mass transfer is a long way from being at ideal equilibrium. A higher air/water ratio, denoted as $(G/L)_{\text{actual}}$, the actual air/water ratio, is required for that removal.

The stripping factor R is used to describe the ratio of the actual operating air/water ratio to the theoretical minimum ratio:

$$R = \frac{\left(\frac{G}{L}\right)_{\text{actual}}}{\left(\frac{G}{L}\right)_{\text{theory}}} \tag{18.18}$$

The air stripping factor is directly related to the air/water ratio, and is in turn related to the gas pressure drop through the stripper.

Gas pressure drop

The gas pressure drop is a function of the gas and liquid flow rates and the size and type of packing. It relates to the overall cost of the air stripper and to its performance. The gas pressure drop through a stripping unit can be determined from the pressure drop curve.

A stripper operating at a high pressure drop will require a smaller volume than a similar stripper at a lower pressure drop. This reduces the capital cost for the tower, but increases the blower cost. Towers designed and built to operate at a low pressure drop have the flexibility to increase the gas flow rate and hence the air/water ratio, should the future influent concentration increase or the effluent limitation decrease. Towers designed for high pressure drops do not have this flexibility in operation and would need to decrease the liquid loading to increase the air/water ratio.

Applicability to air stripping

The removal effectiveness of air stripping depends on the following factors:

1. *Physical properties of the contaminants*. Physical properties, particularly Henry's constant, determine the ease of air stripping. The higher the value of Henry's constant, the higher is the removal efficiency.

2. *Temperature.* The temperature of contaminated water significantly influences the removal efficiency because Henry's constant increases with temperature.
3. *VOC concentration in water.* The higher the concentration of a target component in the contaminated water, the higher is its removal efficiency, because the driving force for the target compound to transfer from the contaminated water to the gas is greater when its concentration is higher than at equilibrium.
4. *Air/water ratio.* Increasing the air/water ratio will increase the removal efficiency.
5. *Packing material.* Packing materials are usually designed to be less susceptible to biological and mineral fouling in order to maintain a high surface area and a high void volume, both of which are necessary for maintaining a high operating efficiency.

There are several factors that may limit the use of conventional air stripping for the removal of dissolved gasoline from groundwater:

1. Applicability of air-stripping methods with respect to the type of groundwater contaminants is the most important factor. The major constituents of interest, such as benzene, toluene, xylene, and ethylbenzene, are all fairly volatile and thus are easily removed by this technique. Compounds with low volatility such as 1,2-dichloroethane (DCE) cannot be readily removed.
2. The air pollution impact of the stripping tower is significant, because the air-stripping treatment does not destroy the contaminant; it simply transfers it from the liquid to the gaseous phase. The stripper off-gas, after dilution in the tower, usually mixes with the ambient air in the atmosphere that would further lower the contaminant concentration to values below unsafe levels. Some states have regulated the limit of discharge of volatiles to the atmosphere. In New Jersey, the limit of discharge including benzene is 0.1 lb/h. Off-gas air pollution control is required if a stripper exceeds this limit. Most commonly, GAC adsorption is used to treat the vapor-phase contaminant.[56]
3. High concentrations of iron and magnesium or suspended solids in the influent will limit the efficiency of air stripping, because iron and manganese facilitate the growth of bacteria on the packing, causing decreased mass transfer rates and higher gas pressure drop (suspended solids can cause a similar problem if they are trapped by the packing).
4. High noise levels associated with tower operation may limit air stripping.

Air stripping processes[29,30] and air flotation process[57–59] introduced in the 1990s have solved some of the abovementioned problems.

18.8.3.2 Activated Carbon Adsorption

Applications

Many case studies[19,60,61] have demonstrated the ability of activated carbon to remove a variety of compounds in gasoline from contaminated water to nondetectable levels (99.99+% removal). GAC is more widely used than powdered activated carbon (PAC). Activated carbon adsorption, in general, is not cost-effective in removal of highly concentrated gasoline compounds in water, where the air-stripping method or biological treatment method may be applied. Thus, GAC is widely used for removing low concentrations of complex pollutants, in particular in polishing effluent or in point-of-entry treatment for drinking water.

The main limitation of GAC in removing gasoline compounds is its cost and the disposal of the generated spent carbon. However, the problem of spent carbon's regeneration has been solved, at least in part.[29]

The compounds MTBE and disopropyl ether (DIPE) are sometimes found as additives in gasoline. Both have very high carbon usage rates; thus, the costs of removing these compounds are prohibitive, especially if the influent concentrations are substantial. Therefore, the presence or absence of highly soluble compounds such as MTBE or DIPE or other additives may determine the appropriateness of using GAC for a particular gasoline spill.

Petroleum hydrocarbons (benzene, toluene, ethylbenzene, and xylenes—collectively BTEX), particularly benzene, are believed to pose significant health concerns, especially as they are contained in over 99% of all gasoline. However, additives such as MTBE and DIPE, which have high carbon usage rates, are not found in all gasolines and hence pose less significant health concerns. Thus, GAC is generally applicable for the removal of BTEX.

As mentioned, a major potential limitation of GAC use is the disposal of the spent carbon. The spent GAC can be regenerated or disposed of using sanitary landfills or incineration. GAC regeneration is possible and highly feasible by heating the carbon to very high temperatures (e.g., in a kiln) to remove the volatiles and incinerate them. However, on-site regeneration is economical only in very large projects, not in UST sites. Off-site regeneration, on the other hand, may be acceptable at a central regeneration facility. However, U.S. highways authorities consider any carbon with a flash point below 200°F to be hazardous and cannot therefore be transported on the highways. Under RCRA rules, many contaminant-laden carbons are considered hazardous materials, necessitating disposal in a permitted landfill.

Iron and manganese levels in the influent water may also limit the use of GAC. They will precipitate onto the carbon during treatment. If this happens, head losses will increase rapidly, the removal of organics will be hindered, and the carbon filter may eventually get clogged, making it ineffective and increasing cost substantially, or impractical due to space constraints. If these elements are present at concentration levels above 5 mg/L, they must be removed prior to GAC treatment.

Design of GAC systems for groundwater decontamination

An isotherm test can determine whether or not a particular contaminant can be adsorbed effectively by activated carbon. In very dilute solutions, such as contaminated groundwater, a logarithmic isotherm plot usually yields a straight line represented by the Freundlich equation[62,63]:

$$\log\frac{X}{W} = \log k + \frac{1}{n}\log C \tag{18.19}$$

where X = amount of contaminant adsorbed (M), W = weight of activated carbon (M), k = constant, n = constant, C = unabsorbed concentration of contaminant left in solution (M/L^3), and $1/n$ = represents the slope of the straight-line isotherm. The above equation also indicates the approximate capacity of activated carbon for groundwater decontamination and provides a rough estimate of the activated carbon dosage required.

For the design of a GAC system, the following interrelated parameters should be taken into consideration:

1. Influent flow
2. Carbon contact time
3. Dosage
4. Bed depth
5. Pretreatment requirements
6. Carbon breakthrough characteristics
7. Headloss characteristics
8. On-stream cycle time of carbon (i.e., the time between carbon regenerations)

In general, influent flow and contact time determine the carbon bed depth and size, which in turn determine the breakthrough characteristics of the carbon bed for the influent water, thereby deciding the actual carbon dosage. The carbon dosage determines the volume of influent water that can be treated, which sets the on-stream cycle time of the carbon. These operating variables are related by the following equations:

$$B_m = (Q_m)(t)(d_m) \tag{18.20a}$$

where B_m = carbon bed (kg), Q_m = influent rate (m^3/min), t = contact time (min), and d_m = carbon density (kg/m^3),

$$B = \frac{Q}{7.48} td \tag{18.20b}$$

where, B = carbon bed (lb), Q = influent rate (gal/min), t = contact time (min), and d = carbon density (lb/ft^3),

$$B_m = Q_m(C_{cm})\ (1440\ \mathrm{T}) \tag{18.21a}$$

where C_{cm} = actual carbon dosage (kg/m^3), T = on-stream cycle time (d), and Q_m = influent rate (m^3/min),

$$B = Q\frac{C_c}{1000}(1440\ \mathrm{T}) \tag{18.21b}$$

where C_c = actual carbon dosage (lb/1000 gal), T = on-stream cycle time (d), Q = influent rate (gal/min), and d = 25 (lb/ft^3), and

$$P_{dm} = (55{,}922)\frac{\mu K_c Q_m B_{hm}}{D_p^2 D_{cm}} \tag{18.22a}$$

where P_{dm} = pressure drop (mmHg), μ = dynamic viscosity (centipoise), Q_m = influent flow rate (m^3/min), B_{hm} = carbon bed depth (m), D_p = mean carbon particle diameter (mm), D_{cm} = carbon column diameter (cm), and K_c = carbon adsorption coefficient.

$$P_d = \frac{\mu K_c Q B_h}{D_p^2 D_c} \tag{18.22b}$$

where P_d = pressure drop (in.Hg), μ = dynamic viscosity (centipoise), Q = influent flow rate (gal/min), B_h = carbon bed depth (ft), D_p = mean carbon particle diameter (mm), D_c = carbon column diameter (in.), and K_c = carbon adsorption coefficient.

Gravity flow in downflow carbon beds is usually controlled at hydraulic loadings less than 9.78 m^3/h/m^2 (4 gal/min/ft^2). Upflow carbon beds with bed expansion should be considered when headloss is expected. It should be noted that TSS will break through an upflow carbon bed at about 10% bed expansion.

18.8.3.3 Air Stripping and Activated Carbon Combination

Activated carbon is more suitable for an influent with low VOC concentration, and air stripping is more suitable for treating high VOC concentrations, but yields a relatively higher effluent concentration in comparison to GAC treatment. The cost of air stripping may be doubled if one tries to yield an effluent concentration to be as low as in activated carbon treatment. This is because it would require a taller tower, a higher air/water ratio, or higher air pressure. The combination of air stripping and activated carbon can complement each other and avoid such a high cost.

Many cases have demonstrated that the combination of activated carbon adsorption and air stripping is one of the most common methods for the removal of dissolved gasoline compounds in groundwater. In this case, air stripping lowers the high concentration in the influent, and the GAC further polishes the effluent to a very low concentration. Generally, this method also reduces operation and maintenance costs. O'Brien and Stenzel[64] reported that, when using air stripping, a wastewater containing 1000 μg/L TEC was reduced to 200 μg/L. This 80% removal of TEC resulted in 58% reduction in the consumption of activated carbon.

Another process involving the use of both air stripping and activated carbon adsorption has been developed by Wang and colleagues.[29] This process purifies and recycles the emitted gas, thus not creating an air pollution problem. Also, the spent GAC can be automatically regenerated for reuse.

18.8.3.4 Integrated Vapor Extraction and Steam Vacuum Stripping

Integrated vapor extraction and steam vacuum stripping can simultaneously treat groundwater and soil contaminated with VOCs. The system developed by AWD Technologies consists of two basic processes: a vacuum stripping tower that uses low-pressure steam to treat contaminated groundwater; and a soil gas vapor extraction/reinjection process to treat contaminated soil. The two processes form a closed-loop system that provides simultaneous *in situ* remediation of contaminated groundwater and soil with no air emission.

The vacuum stripping tower is a high-efficiency countercurrent stripping technology. A single-stage unit typically reduces VOCs in water by up to 99.99%. The soil vacuum extraction system uses vacuum to treat a VOC-contaminated soil mass, with a flow of air through the soil that removes vapor-phase VOCs with the extracted soil gas. The soil gas is then treated by carbon beds to remove the VOCs. The two systems share a single GAC unit. Noncondensable vapor from the stripping system is combined with the vapor from the soil vacuum system and decontaminated by the GAC unit. Byproducts of the system are a free-phase recyclable product and the treated water. The granulated carbon will have to be replaced and the used carbon disposed of every three years.

18.8.3.5 *Ex Situ* Biological Treatment for Groundwater Decontamination

The processes of *ex situ* biological treatment for pumped contaminated groundwater is similar to the processes used in biological wastewater treatment plants. These include activated sludge, waste stabilization ponds and lagoons, trickling filters, rotating biological contactors, and land application.[44,45]

The immobilized cell bioreactor system developed by Allied Signal is an aerobic fixed-film bioreactor system (Figure 18.13). The system offers improved treatment efficiency through the use of a unique proprietary reactor that maximizes the biological activity, and a proprietary design that maximizes contact between the biofilm and the contaminants. The advantages include a fast and complete degradation of target contaminants to carbon dioxide, water, and biomass; high treatment capacity; compact system design; and reduced operation and maintenance cost resulting from simplified operation and slow sludge production.[65]

After further polishing, such as clarifying and filtering, if necessary, the biologically treated groundwater may be reinjected into the aquifer in an operation similar to deep well injection.[66]

The advantage of *ex situ* biological treatment is the ability to control the effluent quality. The use of air for aerobic treatment is easier to control and costs less. Nutrient can be added more effectively and the temperature can be controlled.

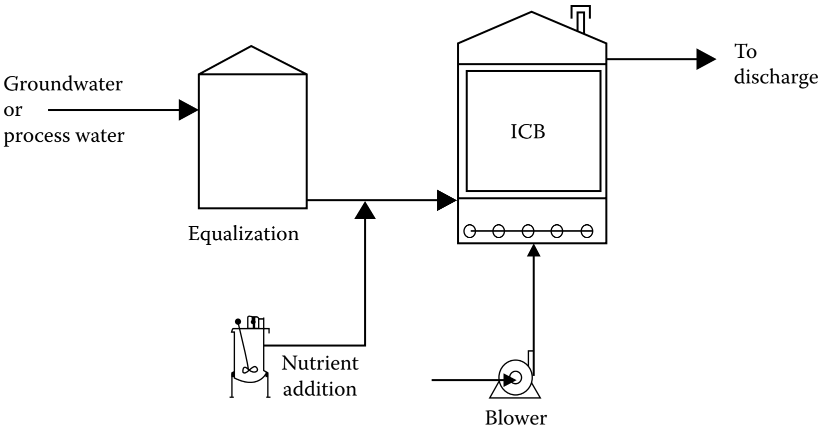


FIGURE 18.13 Allied Signal Immobilized Cell Bioreactor (ICB).

The disadvantages of *ex situ* biological treatment in comparison to *in situ* biological treatment are as follows:

1. After shutting off the system, biological treatment cannot continue in the contaminated site.
2. The contaminants in places where they are strongly adsorbed or where permeability is locally low, or where microcracks are developed in rocks, cannot be efficiently drawn out with water using the pumping method.
3. The emitted gas containing VOCs may cause air pollution problems.

A biological process developed by Wang and colleagues[57] does not cause air pollution problems and is highly efficient for the biodegradation of organics present in water.

18.8.3.6 Oxidation

Oxidation is a means of decontamination. There are several methods that can facilitate oxidation to treat contaminated groundwater. In the following we describe two examples of such technologies.

The perox-pure system developed by Peroxidation Systems is designed to destroy dissolved organic contaminants in groundwater or wastewater through an advanced chemical oxidation process using ultraviolet (UV) radiation and hydrogen peroxide. Hydrogen peroxide is added to the contaminated water, and the mixture is then fed into the treatment system. The treatment system contains four or more compartments in the oxidation chamber. Each compartment contains one high-intensity lamp mounted in a quartz sleeve. The contaminated water flows in the space between the chamber wall and the quartz tube in which each UV lamp is mounted. UV light catalyzes the chemical oxidation of the organic contaminants in water by its combined effect upon the organics and its reaction with hydrogen peroxide. This technology can treat water contaminated with chlorinated solvents, pesticides, polychlorinated biphenyls, phenolics, fuel hydrocarbons, and other toxic compounds at concentrations ranging from a few thousand mg/L to 1 μg/L. For higher organic concentrations, UV light combined with other processes such as air stripping, steam stripping, biological treatment, or air flotation may be more cost effective.[29,58,59]

Chemical Waste Management have developed a technique using evaporation and catalytic oxidation to treat contaminated water.[65] Contaminated water is concentrated in an evaporator by boiling off most of the water and the volatile contaminants, both organic and inorganic. Air or oxygen is added to the vapor, and the mixture is forced through a catalyst bed, where the organic and inorganic compounds are oxidized. This stream, composed mainly of steam, passes through a scrubber, if necessary, to remove any acid gases formed during oxidation. The stream is then condensed or vented to the atmosphere. Suitable wastes include leachates, contaminated groundwater, and process waters. This technique can also be used to treat complex wastewaters that contain volatile and nonvolatile organic compounds, salts, metals, and volatile inorganic compounds.

18.8.3.7 Solvent Extraction

Solvent extraction uses an organic solvent to extract toxic substances from contaminated liquid or solid.[67] Examples can be found in the section dealing with the treatment of contaminated soil.

18.8.3.8 Dissolved Air Flotation (DAF)

Perhaps the most efficient but least recognized process for groundwater decontamination is dissolved gas flotation, also known as dissolved air flotation (DAF), in which air is used for the generation of extremely fine air bubbles having diameters less than 80 μm.

DAF is used to remove suspended solids by decreasing their apparent density; they then rise and float on the water surface. DAF is also used to remove soluble iron, VOCs, oils, and surface active agents by oxidation, air stripping, and surface adsorption. The flotation technology is becoming one of the most important technologies for groundwater decontamination, industrial effluent treatment, and water purification.[58–61,70]

A typical DAF process consists of saturating a portion or all of the influent feed, or a portion of recycled effluent with air at a pressure of 1.76 to 6.33 kg/cm^2 (25 to 90 psi). The pressurized influent is held at this pressure for 0.2 to 3 min in a pressure vessel and then released to atmospheric pressure in a flotation chamber. A controlled reduction in pressure results in the release of microscopic air bubbles, which oxidize the soluble ferrous iron (Fe^{2+}) to form insoluble ferric iron (Fe^{3+}) and attach themselves to VOCs, surfactants, oil, and suspended particles in the influent water in the flotation chamber. This results in agglomeration, air stripping, and surface adsorption due to the generated air bubbles. The VOCs are removed by air stripping and discharged to a gas-phase GAC adsorber for purification. The floated material (oil, surfactants, TSS) rises to the surface with vertical rise rates ranging between 0.15 and 0.6 m/min (0.5 to 2.0 ft/min) and forms a floating scum layer. Specially designed sludge scoops, flight scrapers, and other skimming devices continuously remove the floating scum. The clarified effluent water that is almost free of suspended solids and oil is discharged near the bottom of the flotation chamber. The retention time in the flotation chamber used to be about 20 to 60 min but has been reduced to 3 to 15 min by innovative design.

The effectiveness of DAF depends upon efficient air oxidation and the attachment of bubbles to the oil, VOCs, surfactants, and other particles that are to be removed from the influent water stream. Flotation can be induced in at least three ways:

1. Air bubbles adhering to the insoluble solids by electrical attraction
2. Air bubbles becoming physically trapped in the insoluble solids original or flocculated structure
3. Air bubbles being chemically adsorbed to the insoluble solids in their original form or their flocculated structure

The attraction between the air bubble and contaminants is believed to be primarily a result of particle surface charges and bubble size distribution. The more uniform the distribution of water and microbubbles, the shallower the flotation chamber can be. Generally, the depth of effective flotation chambers is between 0.9 and 2.7 m (3 and 9 ft). Flotation units can be round, square, or rectangular. Gases other than air can be used. The petroleum industry has used nitrogen, with closed vessels, to reduce the possibilities of fire. Ozone can be fed through with air for more efficient reduction of soluble iron, VOCs, and so on.[57] Ozone-UV flotation is another alternative for groundwater decontamination.

Several high-rate air flotation clarifiers (both DAF and dispersed air flotation) with less than 15 min of detention times have been developed for groundwater decontamination, industrial effluent treatment, resources recovery, and water reclamation. Both insoluble and soluble impurities such as

VOCs, activated sludge, fibers, free oil and grease, emulsified oil, lignin, protein, humic acid, tannin, algae, BOD, TOC, iron ions, manganese ions, hardness, titanium dioxide, phosphate, and heavy metals can be separated from a target water stream. Addition of flotation aids to a flotation clarifier is required. Flotation aids include, but are not limited to, aluminum sulfate, ferric chloride, organic polymer, poly aluminum chloride, calcium chloride, ferrous sulfate, calcium hydroxide, ferric sulfate, powdered activated carbon, sodium aluminate, surfactants, and pH adjustment chemicals. Design equations and examples of high-rate DAF clarifiers can be found in the literature.[58,59,69,71]

Toxic organic compounds commonly found in groundwater are presented in Table 18.4. Other toxic organic compounds (representing 1% of cases) include PCBs (polychlorinated biphenyls), 2,4-D, 2,4,5-TP (silvex), toxaphene, methoxychlor, lindane, and endrin, of which 2,4-D and silvex are commonly used for killing aquatic and land weeds. Inorganic toxic substances commonly found in

TABLE 18.4
Toxic Organic Compounds Commonly Found in U.S. Groundwater

Organic Compounds in Groundwater	Percent of Occurrences	Concentration Range
Carbon tetrachloride	5	130 μg/L–10 mg/L
Chloroform	7	20 μg/L–3.4 mg/L
Dibromochloropropane	1	2.5 mg/L
DDD	1	1 μg/L
DDE	1	1 μg/L
DDT	1	4 μg/L
cis-1,2-Dichloroethylene	11	5 μg/L–4 mg/L
Dichloropentadiene	1	450 μg/L
Diisopropyl ether	3	20–34 μg/L
Tertiary methyl butylether	1	33 μg/L
Diisopropyl methyl phosphonate	1	1250 μg/L
1,3-Dichloropropene	1	10 μg/L
Dichloroethyl ether	1	1.1 mg/L
Dichlorosopropyl ether	1	0.8 mg/L
Benzene	3	0.4 μg/L–4.11 mg/L
Acetone	1	10–100 μg/L
Ethyl acrylate	1	200 mg/L
Trichlorotrifluoroethane	1	6 mg/L
Methylene chloride	3	1.21 mg/L
Phenol	3	63 mg/L
Orthochlorophenol	1	100 mg/L
Tetrachloroethylene	13	5 μg/L–70 mg/L
Trichloroethylene	20	5 μg/L–16 mg/L
1,1,1-Trichloroethane	8	60 μg/L–25 mg/L
Vinylidiene chloride	3	5 μg/L–4 mg/L
Toluene	1	5.7 mg/L
Xylenes	4	0.2–10 mg/L
EDB	1	10 μg/L
Others	1	Not available

Source: Wang, L.K. and Wang, M.H.S., Decontamination of groundwater and hazardous industrial effluents by high-rate air flotation process, *Proc. Great Lakes Conf.*, Hazardous Materials Control Research Institute, Silver Springs, MD, September 1990. With permission.

DDD, Dichlorodiphenyl dichloroethane; DDE, dichlorodiphenyl dichloroethylene; DDT, dichlorodiphenyl trichloroethane; EDB, ethylene dibromide.

groundwater include lead, arsenic, copper, cadmium, barium, chromium, mercury, selenium, silver, and nitrate. In a typical groundwater decontamination project, additional industries that are nontoxic but require pretreatment for their removal include iron, manganese, total dissolved solids, and color.

Innovative air flotation technologies have been developed for more cost-effective groundwater decontamination in comparison with the state-of-the-art technologies.[68,69] DAF is very efficient and cost-effective for decontamination of groundwater in which heavy metals, color, TDS, iron, manganese, coliforms, and hardness can all be significantly removed, aiming at not only the decontamination of groundwater but also elimination of biological and chemical fouling for subsequent processes. Furthermore, many VOCs can also be removed by DAF. Table 18.5 represents the U.S. EPA's removal data for DAF processes. The capability of DAF for the treatment of various liquid streams has been well established.[58,59,69] However, its application for the decontamination of groundwater is comparatively new.

Special chemicals may be required for the groundwater decontamination process. For instance, PAC may be dosed into a DAF system for enhancement of contaminant removal efficiency. In such a case, the process is called adsorption flotation (PAC-DAF process). In a pilot plant study, a system consisting of adsorption flotation and sand filtration has proved to be feasible for groundwater decontamination.[70] PAC was added as an adsorbent for the removal of color, odor, EDB (ethylenedibromide), TTHM (total trihalomethane), and other toxic substances from groundwater. Next, the spent PAC was flocculated by coagulants and floated to the water surface by DAF. Finally, the flotation clarified water was polished using the automatic backwash filtration (ABF) process. The results of both bench-scale and pilot plant studies have indicated that using 250 mg/L of PAC at 15 min of detention time can remove color by 100% (from 25 CU [color units]), iron by 100% (from 25 μg/L), humic acid by 98% (from 3200 μg/L), EDB by 100% (from 1.2 μg/L), TTHM by 98% (from 1265 μg/L), odor by 99.6% (from 500 TON [threshold odor numbers]), mercaptans by 100% (from 730 μg/L S), lead by 100% (from 6 μg/L), and arsenic by 100% (from 1000 μg/L). The plant was operated at 40 L/min (10.6 gal/min) for the separation of 250 mg/L of spent PAC. Nearly 100% of spent PAC (from 250 mg/L) and total coliform (from 3/100 mL) and over 95% of turbidity (from 4.5 NTU [nephelometric turbidity units]) were removed by the addition of 1.5 mg/L of anionic polymer and 2.5 mg/L of coagulant. The process was operated at 30% recycle flow rate and 0.014 m^3/h (0.5 ft^3/h) air flow. The sand filter consisted of 28 cm (11 in.) of quartz sand (E = 0.36 mm, U = 1.65) and operated at 102 L/min/m^2 (2.5 gal/min/ft^2).

A DAF-GAC system involving the use of DAF and GAC has also proved to be equally effective for complete groundwater decontamination for the same influent water mentioned above.

For the treatment of a contaminated groundwater source containing a high concentration of hardness, DAF filtration is also an excellent pretreatment process system for the reduction of scale formation in subsequent processes. In a study, groundwater having 12 units of color, 13 NTU of turbidity, and 417 mg/L of carbon hardness as $CaCO_3$ was successfully treated by a continuous DAF filtration plant consisting of hydraulic flocculation, a DAF clarifier, a recarbonation facility, and three sand filters. The added chemicals were 42 mg/L of magnesium carbonate as a coagulant and a small amount of lime for pH adjustment (to pH 11.3). The plant's treatment efficiency in terms of removal had the following values: color, 100%; turbidity, 98%; total hardness, 62%. Recarbonation with CO_2 maintained the effluent pH at 7.2. This plant's operational conditions included a flocculation detention time of 5.6 min, DAF detention time of 3.0 min, flotation clarification rate of 102 L/min/m^2 (2.5 gal/min/ft^2), sand depth of 28 cm (11 in.), influent water flow rate of 45.5 L/min (12 gal/min), recycle water flow rate of 11.4 L/min (3 gal/min), air flow rate of 0.028 m^3/h (1 ft^3/h) at 6.33 kg/cm^2 (90 psig) pressure. Soda ash (Na_2CO_3) may be needed only if permanent hardness ($CaSO_4$) is present. The chemical reactions are as follows:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3 + H_2O + MgCO_3$$

TABLE 18.5
Control Technology Summary for Dissolved Air Flotation

Pollutant	**Effluent Concentration**		**% Removal**
	Range	**Median**	
Classical Pollutants (mg/L)			
BOD (5-day)	140–1000	250	68
COD	18–3200	1,200	66
TSS	18–740	82	88
Total phosphorus	<0.05–12	0.66	98
Total phenols	>0.001–23	0.66	12
Oil & grease	16–220	84	79
Toxic Pollutants (μg/L)			
Antimony	ND–2300	20	76
Arsenic	ND–18	<10	45
Xylene	ND–1,000	200	97
Cadmium	BDL–<72	BDL	98
Chromium	2–620	200	52
Copper	5–960	180	75
Cyanide	<10–2300	54	10
Lead	ND–1000	70	98
Mercury	BDL–2	BDL	75
Nickel	ND–270	41	73
Selenium	BDL–8.5	2	NM
Silver	BDL–66	19	45
Zinc	ND–53,000	200	89
Bis (2-ethylhexyl)phthalate	30–1100	100	72
Butyl benzyl phthalate	ND–42	ND	>99
Carbon tetrachloride	BDL–210	36	75
Chloroform	ND–24	9	58
Dichlorobromomethane		ND	>99
Di-*n*-butyl phthalate	ND–300	20	97
Diethyl phthalate		ND	>99
Di-*n*-octyl phthalate	ND–33	11	78
N-nitrosodiphenylamine		620	66
2,4-Dimethylphenol	ND–28	14	>99
Pentachlorophenol	5–30	13	19
Phenol	9–2400	71	57
Dichlorobenzene	18–260	140	76
Ethylbenzene	ND–970	44	65
Toluene	ND–2100	580	39
Naphthalene	ND–840	96	77
Anthracene/phenanthrene	0.2–600	10	81

Source: Wang, L.K. and Wang, M.H.S., Decontamination of groundwater and hazardous industrial effluents by high-rate air flotation process, *Proc. Great Lakes Conf.*, Hazardous Materials Control Research Institute, Silver Springs, MD, September 1990. With permission.

ND, non-detectable; BDL, below detection limit; NM, not measured.

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$$

$$CaSO_4 + MgCO_3 = CaCO_3 + MgSO_4$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$

$$CO_2 + Mg(OH)_2 = MgCO_3 + H_2O \text{ (coagulant regeneration)}$$

DAF is controlled under laminar hydraulic flow conditions using a very small volume of air flow amounting to about 1 to 3% of the influent groundwater flow. DAF only requires 3 to 5 min of detention time; therefore it is a low-cost process for the decontamination of groundwater.

18.8.3.9 Dispersed or Induced Air Flotation (IAF)

Another innovative process, induced air flotation (IAF), operates under turbulent hydraulic flow conditions by using a large volume of air flow amounting to 400% of the influent groundwater flow. The air bubbles are coarse and large, similar to the air bubbles used in an activated sludge aeration basin. IAF requires only 4 to 10 min of detention time, so it is also a very cost-effective process.[58,59] Unlike DAF, IAF is not an effective pretreatment process for the removal of heavy metals, color, turbidity, TDS, hardness, and coliforms, but it is as efficient as conventional air-sparging and air-stripping processes for the removal of iron, manganese, surfactants, and VOCs.

IAF itself is an aeration process, so soluble iron and manganese ions may be oxidized to form insoluble suspended particles that can be separated easily from the liquid phase. The aeration efficiency of IAF is higher than that of DAF. If groundwater's soluble ferrous iron content is 8 mg/L or below, DAF alone using conventional coagulants will be able to remove the soluble iron.[69] When groundwater's soluble ferrous iron is higher than 8 mg/L, either IAF or an oxidizing agent (ozone, hydrogen peroxide, oxygen, potassium permanganate, and so on) will be required for iron removal.

In the conventional air-stripping process, groundwater is introduced into a gas phase for stripping VOCs; in IAF, air bubbles are injected into the groundwater. An air-stripping tower is over 3 m (10 ft) tall, and an IAF cell can be as shallow as 1 m (3 ft). An important feature of an enclosed IAF cell for VOC reduction is its capability of recycling and reusing its purified air streaming, thus eliminating any possibility of air pollution.[29,30]

In summation, both DAF and IAF are good innovative processes for more efficient and more cost-effective groundwater decontamination.

18.8.4 REMOVAL OF GASOLINE FROM CONTAMINATED SOIL

18.8.4.1 *In Situ* Soil Vapor Extraction

The technologies for *in situ* treatment for groundwater can usually be applied to *in situ* soil remediation, although some of the technologies may have varying suitability for soil. As soil contamination involves a more contaminated phase, the vapor phase, thus vapor extraction is uniquely developed for soil vapor remediation. The decreasing of soil vapor pressure by extraction would cause the free gasoline product to vaporize, so the vapor extraction method also plays a role in the remediation of the liquid phase of VOCs. Based on these observations, the technologies presented in the following discussion will focus mainly on the SVE systems, although other technologies, such as *in situ* soil flushing and *in situ* biological treatment, will also be addressed.

SVE has been an effective technique for removing VOCs such as TCE and some petroleum compounds from the vadose zone of contaminated soil.[72] The following presents some of the newly developed technologies.

Vacuum extraction

The vacuum extraction process involves using vapor extraction wells alone or in combination with air injection wells. Vacuum blowers are used to create the movement of air through the soil. The air flow strips the VOCs from the soil and carries them to the surface. Figure 18.14 shows the flow diagram for such a process. During extraction, water may also be extracted along with vapor. The mixture should be sent to a liquid–vapor separator. The separation process results in both liquid and vapor residuals that require further treatment. Carbon adsorption is used to treat the vapor and water streams, leaving clean water and air for release, and spent GAC for reuse or disposal. Air emissions from the system are typically controlled by adsorption of the volatiles onto activated carbon, by thermal destruction, or by condensation.

The vacuum extraction method has been effectively applied to removing VOCs with low organic carbon content from well-drained soil, although it may also be effective for finer and wetter soils, but with comparatively slower removal rates. There are generally significant differences in the air permeability of various strata, which can influence process performance. Contaminants with low vapor pressure or high water solubilities are difficult to remove.

Soil vacuum extraction is cost-effective if the volume of contaminated soil exceeds 382 m^3 (500 yd^3), and if the contaminated area is more than 6 m (20 ft) deep; otherwise, soil excavation and

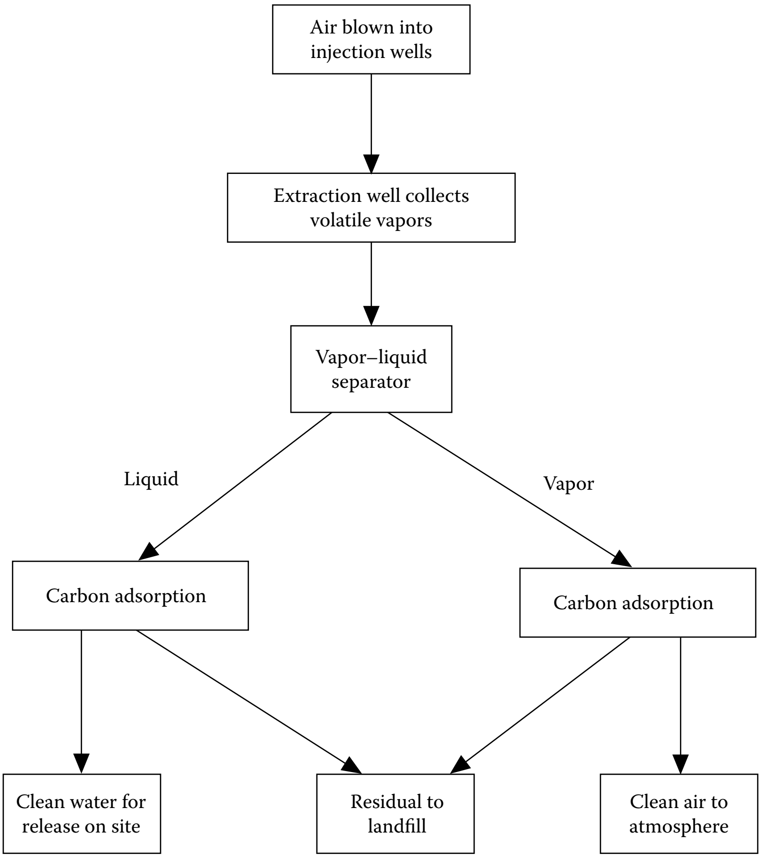


FIGURE 18.14 *In situ* soil vapor extraction.

treatment may be more cost-effective. The level of the groundwater is also important. Rising of the water table that occurs as a result of vacuum extraction wells has to be controlled to avoid water entering the contaminated vadose zone. The water infiltration rate can be controlled by placing an impermeable cap over the site, and a pump may be required to draw the water table down and allow efficient vapor venting. Usually, soil washing follows vapor extraction of volatile contaminants.

In an example, as a result of an impending property transfer that necessitated rapid remediation of diesel-affected soil at a former service station, thermal-enhanced SVE (TESVE) was used to accelerate remediation. The recovery system included a network of TESVE units and injection wells that were separately connected to two regenerative blowers. The recovered vapors were treated in a thermal incinerator, an oxidizing unit to destroy the recovered hydrocarbons. Treated air at a temperature of 1800°F was passed through a heat exchanger and ambient air was simultaneously pumped through the heat exchanger, which increased the temperature of the ambient air to 350°F. The heated ambient air was then injected into the affected soil through a network of four carbon steel injection wells using a regenerative blower.[73]

Soil venting

Soil venting is a technique that removes contaminant vapors from unsaturated soil without excavation. A vacuum extraction system usually consists of gravel packs extending to the soil surface, and a slotted or unslotted well casing that allows gases to move out of the soil. Passive systems consist of vents that are open to the atmosphere and do not require energy for extraction of the gases. Active systems use pressure or vacuum pumps to accelerate the removal of gasoline vapors from the soil. With venting, the vapors are either discharged to the atmosphere or treated before discharge depending on vapor concentrations and regulatory requirements.

Enhanced volatilization

The enhanced volatilization process is operated by putting contaminated soil in contact with clean air in order to transfer the contaminants from the soil into an air stream. The air stream is further treated through the use of carbon canisters, water scrubbers or afterburners to reduce air emission impacts. Four methods are available that can achieve this effect[19]:

1. Mechanical rototilling
2. An enclosed mechanical aeration system
3. A low-temperature thermal stripping system
4. A pneumatic conveyer system

The mechanical rototilling method involves turning over soils to a depth of about 0.30 m (1 ft) below the surface to increase the rate of volatilization. Following treatment, the topsoil is moved to a nearby pile and rototilling is performed on the next 0.30 m (1 ft) of soil. The effectiveness of this mechanical rototilling method is highly dependent on weather conditions. High-speed rototillers and soil shredders can enhance the rate of volatilization.

For effective volatilization using an enclosed mechanical aeration system, contaminated soil is mixed in a pug mill or rotary drum. The gasoline components are released from the soil matrix by the churning action of the air/soil contact. The induced airflow within the chamber captures the gasoline emissions and passes them through an air pollution control device (e.g., a water scrubber or vapor-phase carbon adsorption system) before they are discharged through a properly sized stack.

The configuration of a low-temperature thermal stripping system is similar to the enclosed mechanical aeration system except that additional heat transfer surfaces allow the soil to heat by coming into contact with a screw auger device or rotary drum system. The induced airflow conveys the desorbed volatile organics/air mixture through an afterburner where organic contaminants are destroyed. The over air stream is then discharged through a properly sized stack.

A pneumatic conveyer system consists of a long tube or duct to carry air at high velocities, an induced draft fan to propel the air, a suitable feeder for addition and dispersion of particulate solids into the air stream, and a cyclone collector or other separation equipment for final recovery of the solids from the gas stream. Several such units heat the inlet air to 300°F to induce volatilization of organic contaminants. Pneumatic conveyers are primarily used in the manufacturing industry for drying solids with up to 90% initial moisture content.

Of the four enhanced volatilization methods described above, documentation exists to support the contention that the low-temperature thermal stripping system has the greatest ability to successfully remove contaminants that are similar to gasoline constituents (i.e., compounds with high vapor pressures) from soil. The limitations of some enhanced volatization techniques can be attributed to the following:

1. Associated soil characteristics that inhibit the mobility of gasoline vapors from the soil to the air
2. Contaminant concentrations that may cause an explosion or fire
3. The need to control dust and organic vapor emissions

Some integrated techniques may be more economical if they can be used simultaneously for soil and groundwater treatment, such as integrated vapor extraction and steam vacuum stripping.

18.8.4.2 *In Situ* Soil Flushing

Soil flushing treatment is a technique that removes gasoline constituents from the soil matrix by actively leaching the contaminants from the soil into a leaching medium. The most common washing medium is water, which may contain additives such as acids, alkalis, and detergents. The washing fluid can also be composed of pure organic solvents such as hexane and triethylamine.

The washing media are recharged into soil using a spray recharge system or injection wells. Withdraw wells convey the after-washing liquid to an aboveground treatment facility. The after-washing liquid is treated using biological treatment or physical-chemical methods such as air stripping.

Surfactants have been widely used to reduce the interfacial tension between oil and soil, thus enhancing the efficiency of rinsing oil from soil. Numerous environmentally safe and relatively inexpensive surfactants are commercially available. Table 18.6 lists some surfactants and their chemical properties.[74] The data in Table 18.6 are based on laboratory experimentation; therefore, before selection, further field testing on their performance is recommended. The Texas Research Institute[75] demonstrated that a mixture of anionic and nonionic surfactants resulted in contaminant recovery of up to 40%. A laboratory study showed that crude oil recovery was increased from less than 1% to 86%, and PCB recovery was increased from less than 1% to 68% when soil columns were flushed with an aqueous surfactant solution.[74,76]

Contained recovery of an oily waste process has been developed by the Western Research Institute.[65] It uses steam and hot water (through injection wells) to displace oily waste from the soil, which is then conveyed (by production wells) aboveground for treatment (Figure 18.15). Low-quality steam is injected below the deepest penetration of organic fluids. The steam condenses, causing rising hot water to dislodge and sweep the buoyant organic fluid upward into more permeable soil regions. Hot water is injected above the impermeable soil regions to heat and mobilize the oily waste accumulations, which are recovered by hot water displacement. When oily wastes are displaced, the organic fluid saturation in the subsurface pore space increases, forming an oil bank. The oil saturation is reduced to an immobile residual saturation in the subsurface pore space. The produced oil and water are treated for reuse or discharge. In the process, contaminants are contained laterally by groundwater isolation, and vertically by organic fluid flotation.

The contained recovery method is claimed to have the following advantages:

1. It removes large portions of oily waste accumulations.
2. It stops the downward migration of organic contaminants.
3. It immobilizes any residual saturation of oily wastes.

TABLE 18.6
Surfactants Characteristics

Surfactant Type		Selected Properties and Uses	Solubility	Reactivity
Anionic	Carboxylic acid salts	Good detergency	Generally water-soluble	Electrolyte-tolerant
	Sulfuric acid ester salts	Good wetting agents		Electrolyte-sensitive
	Phosphoric and polyphosphoric acid esters	Strong surface tension reducers	Soluble in polar organics	Resistant to biodegradation
	Perfluorinated anionics			High chemical stability
	Sulfonic acid salts	Good oil in water emulsifiers		Resistant to acid and alkaline hydrolysis
Cationic	Long-chain amines	Emulsifying agents	Low or varying water solubility	Acid stable
	Diamines and polyamines	Corrosion inhibitor	Water-soluble	Surface adsorption to silicaeous materials
	Quaternary ammonium salts			
	Polyoxyethylenated long-chain amines			
Nonionic	Polyoxyethylenated alkyl-phenols, alkylphenol ethoxylates	Emulsifying agents	Generally water-soluble	Good chemical stability
	Polyoxyethylenated straight-chain alcohols and alcohol ethoxylates	Detergents	Water insoluble formulations	Resistant to biodegradation
	Polyoxyethylenated poly-oxypropylene glycols	Wetting agents		Relatively nontoxic
	Polyoxyethylenated mercaptans			
	Long-chain carboxylic acid esters	Dispersents		
	Alkylolamine condensates, alkanolamides	Foam control		Subject to acid and alkaline hydrolysis
	Tertiary acetylenic glycols			
Amphoterics	pH-sensitive	Solublizing agents	Varied (pH-dependent)	Nontoxic
	pH-insensitive	Wetting agents		Electrolyte-tolerant Adsorption to negatively charged surfaces

Source: U.S. EPA, Remedial Action at Waste Disposal Sites, EPA/625/6-85/006, U.S. EPA, Washington, 1985.

4. It reduces the volume, mobility, and toxicity of oily wastes.
5. It can be used for both shallow and deep contaminated areas.
6. It uses the same mobile equipment required for conventional petroleum production technology.

18.8.4.3 *In Situ* Biological Soil Treatment

The technology for *in situ* biological treatment for soil is similar to that for *in situ* biological groundwater treatment. The following sections present three newly developed techniques.

Deep in situ *bioremediation process*

This technique was developed by In-Situ Fixation Company for increasing the efficiency and rate of biodegradation in deep contaminated soils using a dual-auger system. Mixtures of microorganism and required nutrients are injected into the contaminated soils without any excavation. The injection and mixing effectively break down fluid and soil strata barriers and eliminate pockets of

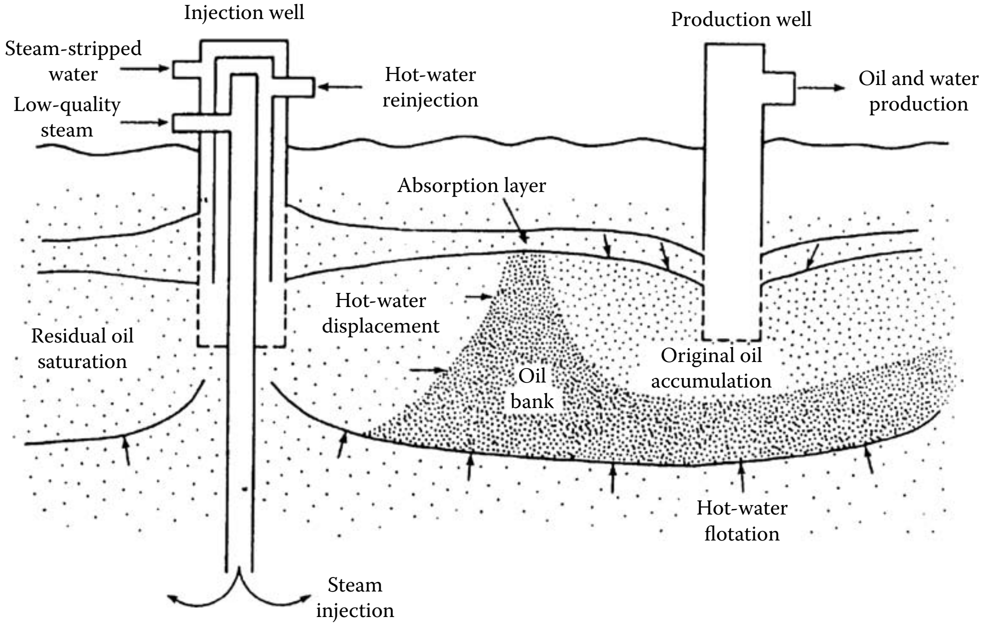


FIGURE 18.15 CROWTM subsurface development.

contaminated soil that would otherwise remain untreated. The drilling is carried out in an overlapping manner to ensure complete treatment of all contaminated soil. The mixing action is continued as the augers are withdrawn. The treatment depth may exceed 30 m (100 ft).[65]

In situ *geolock and biodrain treatment platform*

This system consists of an *in situ* polyethylene tank, an application system, and a bottom water recovery system.[65] An underlying, permeable, water-bearing zone facilitates the creation of ingradient water flow conditions. The tank defines the treatment area, minimizes the potential for release of bacterial cultures to the aquifer, and maintains contaminant concentration levels that facilitate treatment. The ingradient conditions facilitate reverse leaching or soil washing and minimize the potential for outmigration of contaminants.

The application system, called the biodrain, is installed within the treatment area. The biodrain aerates the soil column and any standing water. This cerates an aerobic environment in the pore spaces of the soil. Other gas mixtures can also be introduced to the soil column, such as the air/methane mixtures used in the biodegradation of chlorinated organics. The treatment platforms can be placed in very dense configurations. International Environmental Technology claims that the cost of installation is low.

The bottom water recovery system uses existing wells or new wells to create the water recovery system for removal of the water used to wash the contaminated soil. Reverse leaching or soil washing can be conducted by controlling the water levels within the tank. This design minimizes the volume of clean *ex situ* water entering the system for treatment. Extremely dense clays may be difficult to treat with this technology.

In situ *bioventing technology*

Bioventing technology was developed by the U.S. EPA Risk Reduction Engineering Laboratory to treat soil contaminated by numerous industrial wastes, which is subjected to aerobic microbial degradation, especially to promote the degradation of polycyclic aromatic hydrocarbons.[65] It uses a series of air injection probes, each of which is attached to a low-pressure air pump. The air pump operates at extremely low pressures to allow the inflow of oxygen without volatilization of contaminants. Additional additives such as ozone or nutrients may also be supplied to stimulate microbial growth.[77]

18.8.4.4 *Ex Situ* Soil Treatment

All *ex situ* soil treatment methods involve a two-step approach: soil excavation and aboveground treatment of the excavated soil. The differences in the various *ex situ* excavation/treatment methods for soil remediation lie only in the methods of soil treatment aboveground, such as soil washing plus extraction, and slurry biodegradation.

Soil washing technology

The excavated soil is removed from the site and screened to remove large solid objects. The screened soil is washed and the washing water is treated.[78] Clearly, the washing media used in *in situ* soil-flushing treatment can be used here. The most common washing medium is water. Surfactants are used to reduce the affinity of contaminants to the soil.

Several unit processes can be used in the washing process. The soil is mixed with washing agents and extraction agents that remove the contaminants from the soil and transfer them to the extraction fluid. The soil and washwater are then separated. The soil can be further rinsed with clean water. The soil is removed as clean product, ready to put back into the original excavation, and the washwater is ready to be treated by conventional wastewater treatment processes as addressed in the next subsection.

The big difference in application from the *in situ* flushing method is that this *ex situ* method can apply to soils with lower permeability, because soil is excavated and can be sufficiently washed. The following presents two *ex situ* soil washing processes for organic contaminants: the BioGenesis soil cleaning process and the BioTrol soil washing system.

The BioTrol soil washing system developed by BioTrol, Inc., is shown in Figure 18.16. After debris is removed, the excavated soil mixed with water and is subjected to various unit operations common to the mineral processing industry. Process steps include mixing units, pug mills, vibrating screens, froth flotation or induced air flotation (IAF) cells, scrubbing machines, hydrocyclones, screw classifiers, and various dewatering operations. The core of the system is a multistage, countercurrent, intensive scrubbing circuit with interstage classification. The scrubbing action disintegrates soil aggregates, freeing contaminated fine particles from the coarser sand and gravel. In addition, superficial contamination is removed from the coarse fraction by the abrasive scouring action of the particles themselves. Contaminants may also be solubilized, as dictated by solubility characteristics or partition coefficients. This technology is a water-based volume reduction process for treating excavated soil. Soil washing may be applied to contaminants concentrated in the fine-size fraction of soil (silt, clay, and soil organic matter) and the superficial contamination associated with the coarse soil fraction. This technology can be applied to soils contaminated with PAH (polycyclic aromatic hydrocarbons) and PCP (pentachlorophenol), PCB (polychlorinated biphenyl), petroleum hydrocarbons, and pesticides.[65,78]

The BioGenesis soil cleaning process developed by BioVersal USA, Inc., uses a specialized truck, water, and a complex surfactant (a light alkaline mixture of natural and organic materials containing no hazardous ingredients) to clean contaminated soil. Ancillary equipment includes gravity oil/water separators, coalescing filters, and a bioreactor. Figure 18.17 shows the soil washing procedure. After washing, the extracted oil is reclaimed, the wash water is recycled or treated, and the soil is dumped for refill. Hazardous organics are extracted in the same manner and then further treated. It was shown that the clean rate is ca. 25 t/h for 5000 mg/L oil contamination and lower rates for more contaminated soils. One single wash removes 95 to 99% of hydrocarbon contamination levels up to 15,000 mg/L. The main advantages of the process are as follows[65]:

1. Treatment is applicable to soils containing both volatile and nonvolatile oils.
2. Soil containing clay may be treated.
3. The process rate is high.
4. Contaminants are transformed into reusable oil, treatable water, and soil suitable for on-site treatment.
5. There is no air pollution, except during excavation.

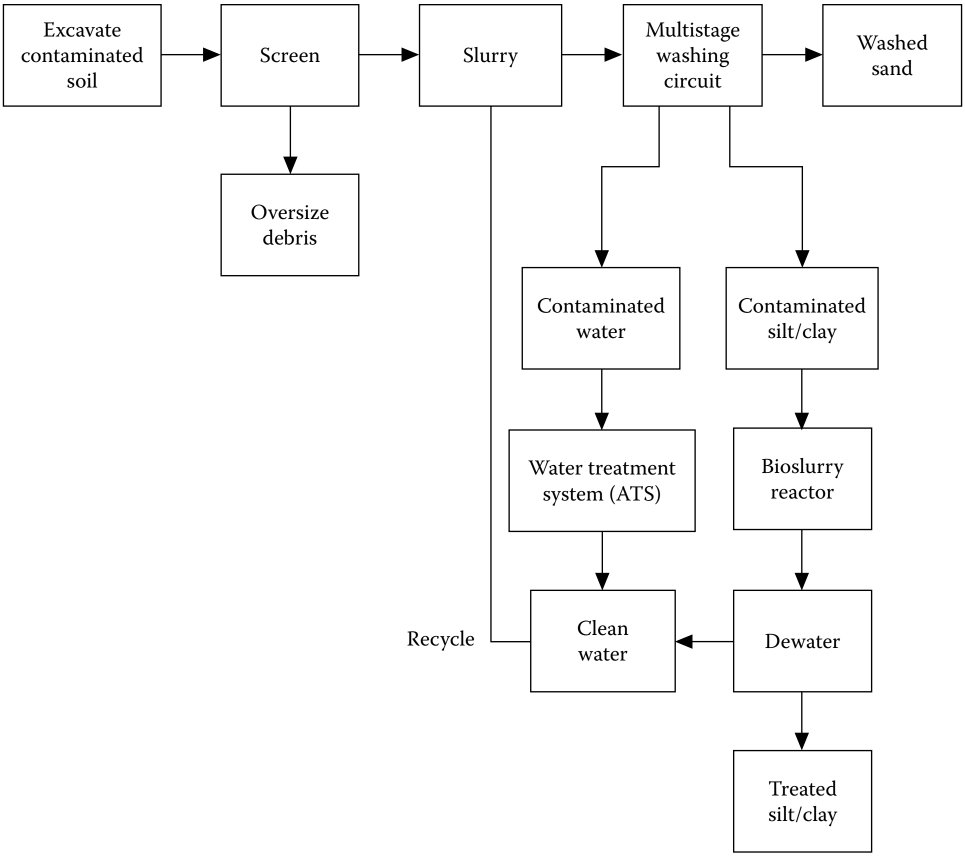


FIGURE 18.16 BioTrol soil washing system process diagram.

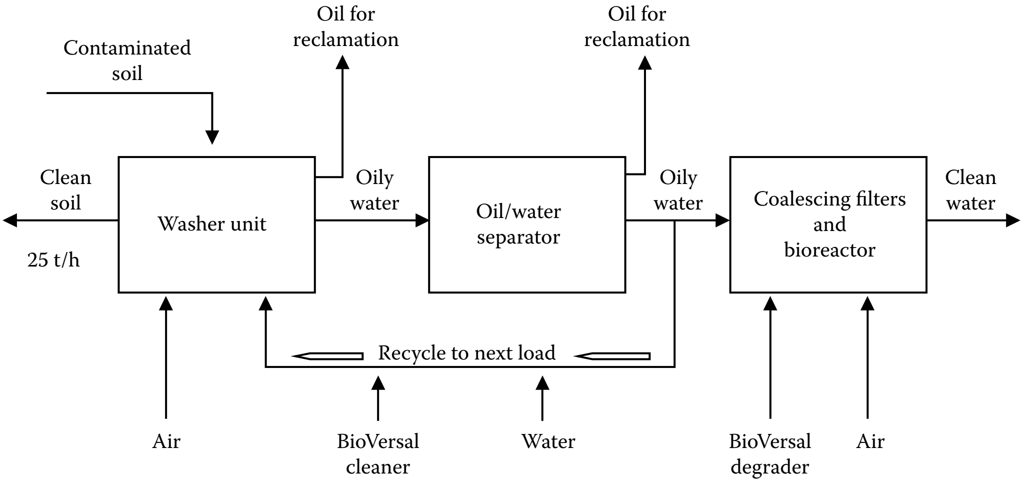


FIGURE 18.17 Soil washing procedure.

A solvent extraction technology developed by CF System Corporation uses liquefied gases as solvent to extract organics (such as PCB, dioxins, PCP, petroleum wastes) from sludges, contaminated soils, and wastewater.[65,79] Propane is the solvent most typically used for contaminated soils, and carbon dioxide is used for wastewater streams. The system is available as either a continuous flow unit for liquid wastes or a batch system for soils. Contaminated soils, slurries, or wastewaters are fed into an extractor along with the solvent. Typically, more than 99% of organics are extracted from the feed. Following phase separation of the solvent and organics, treated water is removed from the extractor while the mixture of solvent and organics passes to the solvent recovery system. In the solvent recovery system, the solvent is vaporized and recycled as a fresh solvent. The organics are drawn out and either reused or disposed of.

Treatment technologies for washing water

Washing fluid can be separated from soil by conventional techniques such as sedimentation, flotation, and filtration.[69] Slurry of soil can be dewatered. The treated soils can then be returned into the original excavation or sent to a sanitary landfill. Treatment of washing water is similar to the treatment of pumped contaminated groundwater, including air stripping of the volatile organics or biological treatment.

18.8.4.5 *Ex Situ* Biological Treatment on Excavated Soil by Slurry Biodegradation

The procedure for slurry biodegradation is not different from conventional biological treatment. The first step is cleaning the soil and separating it from the washing liquid, which is followed by separate biological treatment for the liquid and the soil slurry. The treated soil is then separated from the slurry. Figure 18.18 shows the slurry biodegradation steps in processing the soil.[80]

Waste preparation for slurry biodegradation

Several preparation steps after soil excavation are required to achieve the optimum inlet feed characteristics for maximum contaminant removal:

1. Screening of the soil to remove large objects
2. Size reduction for large particles
3. Water addition
4. pH and temperature adjustments

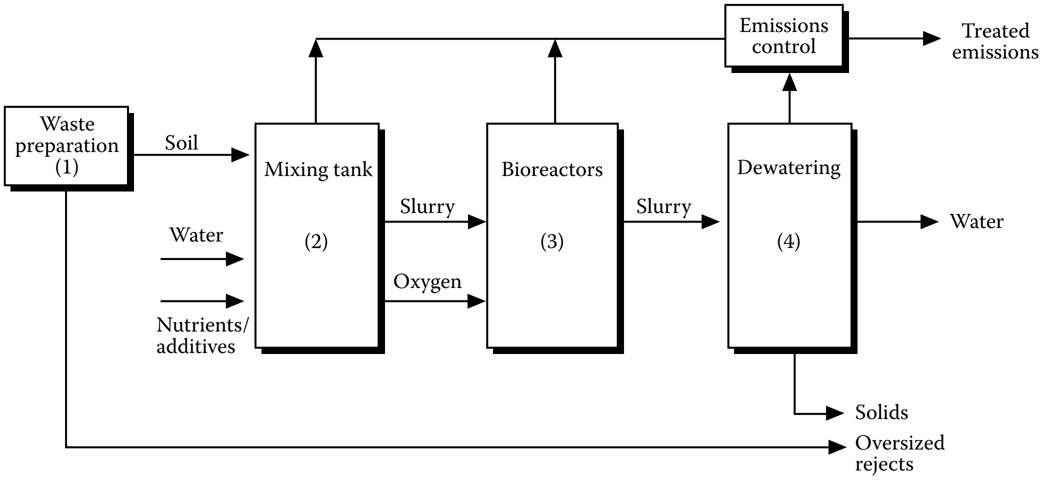


FIGURE 18.18 Slurry biodegradation process.

Treatment by slurry biodegradation

The pretreated soil is mixed with water in a tank to form a slurry. Sufficient mixing is necessary to ensure contact between the contaminants and the microorganisms to facilitate mass transfer from the contaminants to the microorganisms. The well-mixed slurry is conveyed to a bioreactor or a lined lagoon where the aerobic process takes place. Aeration is provided by either floating or submerged aerators. Once the biodegradation of the contaminants is completed, the treated slurry is sent to a dewatering system to separate the soil phase from the aqueous phase of the slurry. Figure 18.19 shows the process for a slurry bioreactor developed by ECOVA Corporation.[65]

U.S. EPA has shown that 90% of process water can be recycled to the front end of the system for slurry preparation, and the rest must be treated on site or transported to an off-site facility.[80] During the aerobic process, some contaminated air may be formed and emitted from the reactor. Depending on the air characteristics, a compatible air pollution control device may be used, such as activated carbon. Slurry biodegradation has been shown to be successful in treating soils contaminated with soluble organics, PAHs, and petroleum waste. The process has been most effective with contaminant concentrations ranging from 2500 mg/kg to 250,000 mg/kg.

The slurry bioreactor developed by ECOVA Corporation[65] showed a 93.4% reduction in PAHs over a 12-week treatment period with an initial 89.3% reduction in the first two weeks.

18.8.4.6 *Ex Situ* Soil Desorption

In situ SVE methods can be used for desorption of VOC from excavated soils. The excavated soil has the advantage that assist technologies may be applied to enhance vaporization, for example, through venting and heating.

One of the desorption technologies, the anaerobic thermal process, is a thermal desorption process. In this process, heating and mixing of the contaminated soils, sludges, and liquids take place in a special rotary kiln that uses indirect heat for processing.[65] The SoilTech anaerobic thermal process is designed to both desorb and treat organic contaminants in soil. The kiln portion of the system contains four separate internal thermal zones: preheat, retort, combustion, and cooling. From the preheat zone, the hot granular solids and unvaporized hydrocarbons pass through a sand seal to the retort zone. Heavy soils vaporize in the retort zone and thermal cracking of the

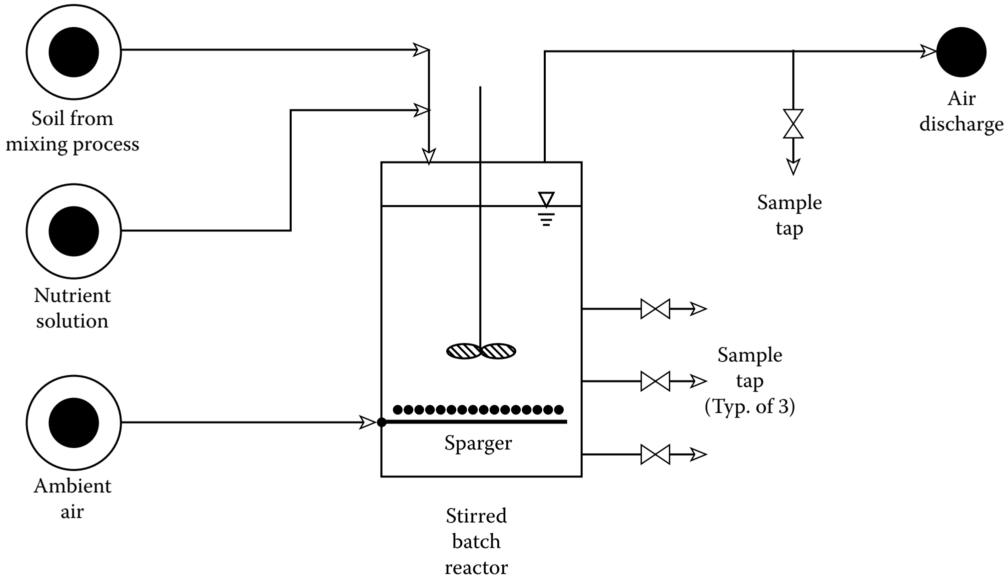


FIGURE 18.19 Process flow diagram.

hydrocarbons forms coke and low-molecular-weight gases. The vaporized contaminants are removed by vacuum to a retort gas-handling system. After cyclones remove the dust from the gases, the gases are cooled, and condensed, and the oil is separated into its various fractions. The coke (with the coked soil) is burned, and the hot soil is either recycled back to the retort zone or sent to the cooling zone. Flue gases from the combustion zone are treated prior to discharge in a cyclone and a baghouse for particle removal, wet scrubber for removal of acid gases, and carbon adsorption bed for removal of trace organic compounds.

The unit desorbs, collects, and recondenses hydrocarbons from the solids. The unit can also be used in conjunction with a dehalogenation process to destroy halogenated hydrocarbons through a thermal chemical process. The technology can be used for oil recovery from tar sands and shales, dechlorination of PCBs and chlorinated pesticides in soil and sludges, separation of oils and water from refinery wastes and spills, and general removal of hazardous organic compound from soils and sludges.

18.8.4.7 *Ex Situ* Thermal Destruction

Incineration

Incineration can effectively eliminate gasoline from soils by complete oxidation. Rotary kilns, fluidized beds, and other systems, either fixed or mobile types, may achieve 99.99% removal. One of the limitations of *ex situ* thermal destruction is associated with soil excavation. Mobile units may be further limited by the permitting process. Costs for incineration vary significantly depending on the particular characteristics of the soil and waste material. Soil containing higher gasoline waste is more economical to treat than a soil with lower gasoline waste, especially when compared with other treatment methods.

Infrared thermal destruction

Infrared thermal destruction technology is a thermal processing system that uses electrically powered silicon carbide rods to heat organic wastes to combustible temperatures. Any remaining combustibles are incinerated in an afterburner. One configuration made by ECOVA Corporation consists of four components[65]:

1. An electric-powered infrared primary chamber
2. A gas-fired secondary combustion chamber
3. An emissions control system
4. A control center

Waste is fed into the primary chamber and exposed to infrared radiant heat up to 1010°C (1850°F) provided by silicon carbide rods above the belt. A blower delivers air to selected locations along the belt to control the oxidation rate of the waste feed. The ash material in the primary chamber is quenched by using the scrubber water effluent. The ash is then conveyed to an ash hopper, where it is removed to a holding area and analyzed for organic contaminants, such as PCB content. Volatile gases from the primary chamber flow into a secondary chamber, which uses higher temperatures, greater residence time, turbulence, and supplemental energy (if required) to destroy these gases. Gases from the secondary chamber are passed through the emissions control system.

This technology is suitable for soils or sediments with organic contaminants. The optimal waste characteristics are as follows:

1. Particle size, 5 μm to 50 mm
2. Moisture content, up to 50% by weight
3. Density, 481 to 2083 kg/m^3 (30 to 130 lb/ft^3)
4. Heating value, up to 5556 kg-cal/kg, or 5556 cal-g/g (10,000 Btu/lb)
5. Chlorine content, up to 5% by weight

6. Sulfur content, up to 5% by weight
7. Phosphorus, 0 to 300 mg/L
8. pH, 5 to 9
9. Alkali metals, up to 1% by weight

Plasma arc vitrification

Plasma arc vitrification, developed by Retech, uses a plasma centrifugal furnace, where heat from transferred arc plasma creates a molten bath that detoxifies the feed material. Organic contaminants vaporize and react at temperatures between 2000 and 2500°F to form innocuous products. Solids are melted and vitrified in the molten bath at 2800 to 3000°F. When metals are cooled, they are rendered to a nonleachable, glassy residue that meets the toxicity characteristic leachate procedure (TCLP) criteria.

This technique can treat soils contaminated with organic compounds and is also suitable for treating liquids and solids containing organic compounds and metals.

18.9 PHENOMENA RELATED TO THE RELEASE OF DNAPLs AND OTHER HAZARDOUS SUBSTANCES

Besides petroleum products, other hazardous substances (see Tables 18.7–18.9) are also stored in USTs. Among them, a common and important group is the dense nonaqueous phase liquids (DNAPLs). This group has some different physical properties from petroleum (especially gasoline) that make them behave differently in the way they move underground. This section presents the important factors associated with the cleanup of DNAPLs.

The relative vapor density (RVD) values in Table 18.9 have been calculated as the density of dry air saturated with the compound of interest at 20°C. This represents the weighted mean molecular weight of the compound-saturated air relative to the mean molecular weight of dry air, which is 29 g/mol. The RVD value may be calculated from Equation 18.23:

$$\mathrm{RVD} = \frac{P_o(\mathrm{MW}) + (760 - P_o)(29)}{(760)(29)} \tag{18.23}$$

where RVD = relative vapor density (dimensionless), MW = molecular weight of the compound of interest, and P_o = vapor pressure (torr or mmHg).

18.9.1 CHEMICAL AND PHYSICAL PROPERTIES OF DNAPLs

DNAPLs are mainly liquid hydrocarbons such as chlorinated solvents, wood preservatives, coal tar wastes, and pesticides. Table 18.7 lists some common such chemicals.[81]

DNAPLs have higher densities than water, most between 1 and 2 g/mL, some are near 3 g/mL, for example, bromoform, which has a density of 2.89 g/mL. They have limited water solubilities, and are usually found as the free-phase immiscible with water or as residuals trapped by soil. Most DNAPLs are volatile or semivolatile; Pankow[82] has listed information on their physical and chemical properties, such as molecular weight, density, boiling points, solubility in water, vapor pressure, sediment/water partition coefficient, viscosity, Henry's law constant, and so on (see Tables 18.8 and 18.9).

18.9.2 FATE OF DNAPL RELEASE UNDERGROUND

Similar to gasoline, the properties of DNAPLs such as immiscibility with water, volatility, and solubility of some of its components cause the presence of multiphase (pure product, solute, gas, and adsorbate) products and movement that is typical of the phenomena associated with DNAPL release. The theory associated with the interaction of gasoline with soil is applicable to DNAPLs. However,

TABLE 18.7
DNAPL-Related Chemicals

Halogenated Volatiles	Nonhalogenated Semivolatiles
Chlorobenzene	2-Methyl naphthalene
1,2-Dichloropropane	o-Cresol
1,1-Dichloroethane	p-Cresol
1,1 Dichloroethylene	2,4-Dimethylphenol
1,2-Dichloroethane	m-Cresol
Trans-1,2-dichloroethylene	Phenol
Cis-1,2-dichloroethylene	Naphthalene
1,1,1-Trichloroethane	Benzo(a) anthracene
Methylene chloride	Fluorene
1,1,2-Trichloroethane	Acenaphthene
Trichloroethylene	Anthracene
Chloroform	Dibenzo (a,h) anthracene
Carbon tetrachloride	Fluoranthene
1,1,2,2-Tetrachloroethane	Pyrene
Tetrachloroethylene	Chrysene
Ethylene dibromide	2,4-Dinitrophenol
Halogenated Semivolatiles	**Miscellaneous**
1,4-Dichlorobenzene	Coal tar
1,2-Dichlorobenzene	Creosote
Aroclor 1242, 1254, 1260	
Dieldrin	
2,3,4,6-Tetrachlorophenol	
Pentachlorophenol	

Source: U.S. EPA, Estimating Potential for Occurrence of DNAPL at Superfund Sites, EPA Publication: 9355.4-O7FS, U.S. EPA, Washington, January 1992.

Many of these chemicals are found mixed with other chemicals or carrier oils.

the gas phase may not be detected as significantly as in the case of gasoline, because the main part of the DNAPL plume sinks below the water table. Therefore the vapor phase does not exist in equilibrium with the free DNAPL phase. Figure 18.20 illustrates such a phenomenon.

The property of DNAPLs that most contrasts to that of gasoline is density, which is higher than water. Thus, the DNAPL plume tends to sink to the bottom of the groundwater body and penetrate down through rock openings instead of floating above the water table. Therefore, DNAPLs are more difficult than gasoline to access and clean up. However, most DNAPLs have higher viscosities than gasoline, and thus may be less transportable with groundwater flow. Moreover, because DNAPLs do not float on the surface of the water table, their capillary movement (though they are important residuals in the vadose zone) has less impact than gasoline release.

18.9.3 SITE REMEDIATION

The remedial technologies[83–85,90–93] described in previous sections for gasoline release are applicable, for the most part, for remediation of DNAPLs. For example, the pumping or trench method for free products, vacuum extraction, biodegradation, pumping and treatment, soil flushing, and soil excavation and treatment are suitable for cleanup of various phases of DNAPLs. Again, because of

TABLE 18.8
Physical and Chemical Properties of Dense Solvent Compounds

Compound	MW (g)	S (mg/L)	P_o (torr)	K_{oc} (mL/g)	d (g/cm^3)	BP (°C)
Nonaromatics						
Dichloromethane (DCM)	84.9	20,000	349	8.8	1.33	40
Chloroform	119.4	8,200	151	44	1.49	62
Bromodichloromethane	163.8	4,500	50	61	1.97	90
Dibromochloromethane	208.3	4,000	76	84	2.38	119
Bromoform	252.8	3,010	5	116	2.89	150
Trichlorofluoromethane	137.4	1,100	667	159	1.49	24
Carbon tetrachloride	153.8	785	90	439	1.59	77
1,1-Dichloroethane	99.0	5,500	180	30	1.17	57
1,2-Dichloroethane	99.0	8,690	61	14	1.26	83
1,1,1-Trichloroethane (1,1,1-TCA)	133.4	720[a]	100	152	1.35	74
1,1,2-Trichloroethane	133.4	4,500	19	56	1.44	114
1,1,2,2-Tetrachloroethane	167.9	2,900	5	118	1.60	146
1,1-Dichloroethylene	97.0	400	590	65	1.22	32
1,2-Dibromoethane (EDB)	187.9	4	11[a]	—	2.18	132
1,2-*Cis*-dichloroethylene	97.0	800[a]	200[a]	—	1.28	60
1,2-*Trans*-dichloroethylene	97.0	600	326	59	1.26	48
Trichloroethylene (TCE)	131.5	1,100	58	126	1.46	87
Tetrachloroethylene (PER)	165.8	200	14	364	1.63	121
1,2-Dichloropropane	113.0	2,700	42	51	1.16	97
Trans-1,3-dichloropropylene	110.0	1,000	25	48	1.22	112
Ethers						
Bis(chloromethyl) ether	115.0	22,000	30[a]	1.2	1.32	104
Bis(2-chloroethyl) ether	143.0	10,200	0.7	14	1.22	178
Bis(2-chloroisopropyl) ether	171.1	1,700	0.9	61	1.11	187
2-Chloroethyl vinyl ether	106.6	15,000	27	6.6	1.05	108
Monocyclic Aromatics						
Chlorobenzene	112.6	488[a]	12	330	1.11	132
o-Dichlorobenzene	147.0	100	1.0	1700	1.31	180
m-Dichlorobenzene	147.0	123[a]	2.3[a]	1700	1.29	172

Source: Pankow, J.F., *Dense Chlorinated Solvents in Porous and Fractured Media*, Lewis Publisher, Freidrich Schwille, 1988, p. 146. With permission.

Temperature of measurement is 20°C unless otherwise noted.

MW = molecular weight (g); S = solubility in water (mg/L or ppm); P_o = Vapor pressure (torr or mmHg);

K_{oc} = sediment/water partition coefficient (mL/g); d = density (g/cm^3); BP = boiling point at 760 torr pressure (°C).

[a] Value measured at 25°C.

the higher density of DNAPLs, some remedial processes may have to be arranged differently, such as in the pumping systems for free product and bioremediation.

18.9.3.1 Pumping Systems for Free Product Recovery

Similar to pumping systems for gasoline remediation, single or dual arrangements can be used. The difference is that the product screen is located below the groundwater in the aquifer. Furthermore, in the dual-pumping systems, an additional screen interval is used in the groundwater zone, located vertically upward from the DNAPL screen intake. Groundwater is withdrawn from the upper screen, resulting in an upwelling of DNAPLs (see Figure 18.21), improving the rate of recovery and result-

TABLE 18.9
More Physical and Chemical Properties of Dense Solvent Compounds

Compound	μ Absolute Viscosity (cp)	ν Kinematic Viscosity (cs)	H (atm-m^3/mol)	Relative Vapor Density^a
Nonaromatics				
Dichloromethane (DCM)	0.44	0.32	0.0017	1.89
Chloroform	0.56	0.38	0.0028	1.62
Bromodichloromethane	1.71	0.87	0.0024	1.31
Dibromochloromethane	—	—	0.00099	1.62
Bromoform	2.07	0.72	0.00056	1.05
Trichlorofluoromethane	—	—	0.11	4.28
Carbon tetrachloride	0.97	0.61	0.023	1.51
1,1-Dichloroethane	0.50	0.43	0.0043	1.57
1,2-Dichloroethane	0.84	0.67	0.00091	1.19
1,1,1-Trichloroethane (1,1,1-TCA)	0.84	0.62	0.013	1.47
1,1,2-Trichloroethane	—	—	0.00074	1.09
1,1,2,2-Tetrachloroethane	1.76	1.12	0.00038	1.03
1,1-Dichloroethylene	0.36	0.30	0.021	2.54
1,2-*Cis*-dichloroethylene	0.48	0.38	0.0029	1.62
1,2-*Trans*-dichloroethylene	0.40	0.32	0.072	2.01
Trichloroethylene (TCE)	0.57	0.39	0.0071	1.27
Tetrachloroethylene (PER)	0.90	0.54	0.0131	1.09
1,2-Dichloropropane	—	—	0.0023	1.16
Trans-1,3-dichororpropylene	—	—	0.0013	1.09
Ethers				
Bis(chloromethyl) ether	—	—	0.00021	1.12
Bis(2-chloroethyl) ether	2.41	1.98	0.000013	1.004
Bis(2-chloroisopropyl) ether	—	—	0.00011	1.005
2-Chloroethyl vinyl ether	—	—	0.00025	1.10
Monocyclic Aromatics				
Chlorobenzene	0.80	0.72	0.0036	1.05
o-Dichlorobenzene	1.41	1.28	0.0019	1.005
m-Dichlorobenzene	1.08	0.84	0.0036	1.01

Source: Pankow, J.F., *Dense Chlorinated Solvents in Porous and Fractured Media*, Lewis Publisher, Freidrich Schwille, 1988, p. 146. With permission.

μ = absolute viscosity (cP); ν = kinematic viscosity (cSt); H = Henry's Law constant for partitioning between air and water (atm-m^3/mol); and RVD = vapor density relative to dry air (dimensionless).

ing in a more efficient operation. The groundwater withdrawal rate must be carefully determined; too much will result in DNAPLs rising excessively and mixing with water or being suppressed by the higher water velocity; too low will not cause the required upwelling.

Other enhanced DNAPL recovery techniques have been implemented utilizing both water flooding and well bore vacuum. Essentially, this minimizes drawdown, allowing a maximum pumping rate of the DNAPL/water mixture.

18.9.3.2 Biodegradation

As stated previously in Section 18.8, one of the advantages of biodegradation is that it imposes a permanent solution, especially if the release is trapped in cracks or is highly adsorbed. Because

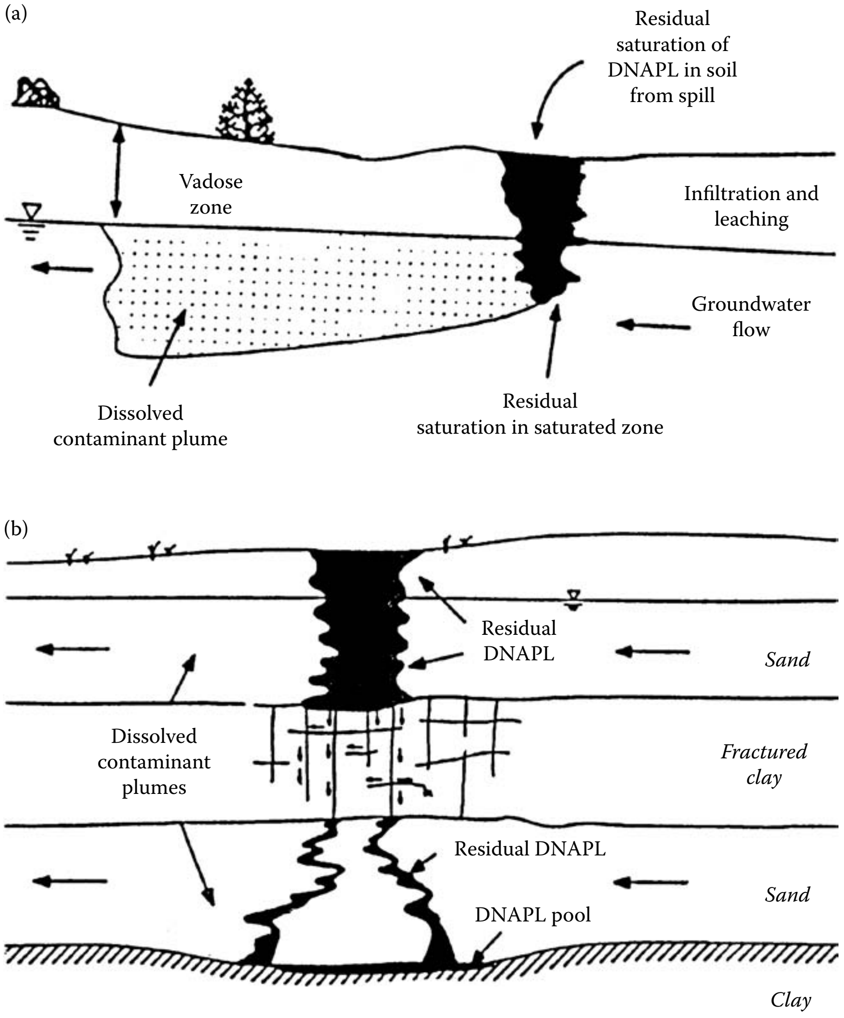


FIGURE 18.20 Groundwater contamination by DNAPL.

DNAPL release has a higher tendency to sink deep down, entering cracks, biodegradation may be more significant for DNAPL release than for gasoline.

The reader may have noticed that Section 18.8 relates biodegradation only to the contaminated groundwater and soil, but not to the free products. In fact in most cases, biodegradation is not suitable for free products. The pure phase, either DNAPLs or gasoline, creates a highly hostile environment for the survival of most microorganisms. Thus, the bioremediation technique is more applicable to groundwater or residuals than to pure free product, and biodegradation is used after the main DNAPL product is recovered. When toxicity has been reduced by product recovery, biodegradation or bioremediation can then be used to further reduce the contaminants at the site.[90–93]

18.9.3.3 U.S. EPA Corrective Action Measures through 2006

Figure 18.22 provides an illustration of historical cleanup backlog trends in the U.S. from 1989 to 2006.[86] Since the beginning of the program, U.S. EPA has cleaned up almost 75% of all releases, and reduced the cleanup backlog to 113,914 cases, a 33% decrease from a peak backlog of 170,000 cases for the 5-year period 1995 to 2000 (see Figure 18.22).

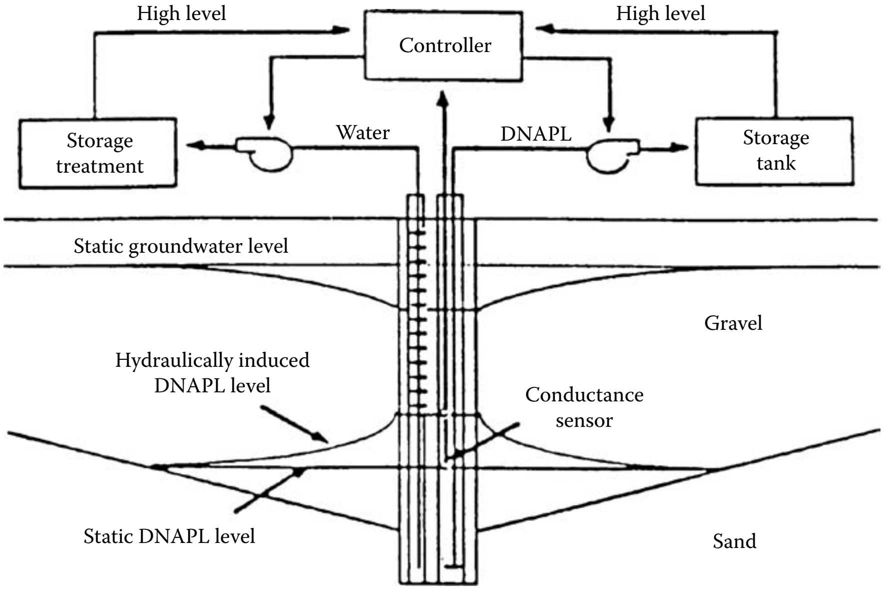


FIGURE 18.21 A DNAPL recovery system where deliberate upwelling of the static coal-tar surface is used to increase the flow of product into the recovery wells.

18.9.4 PRACTICAL EXAMPLES

18.9.4.1 Conversion between Kinetic Viscosity and Absolute Viscosity for Air

Kinematic viscosity of air at 1 bar and 40°C is 16.97 cSt (16.97×10^{-6} m^2/s) (cSt = centistokes). Determine the air's dynamic viscosity or absolute viscosity.

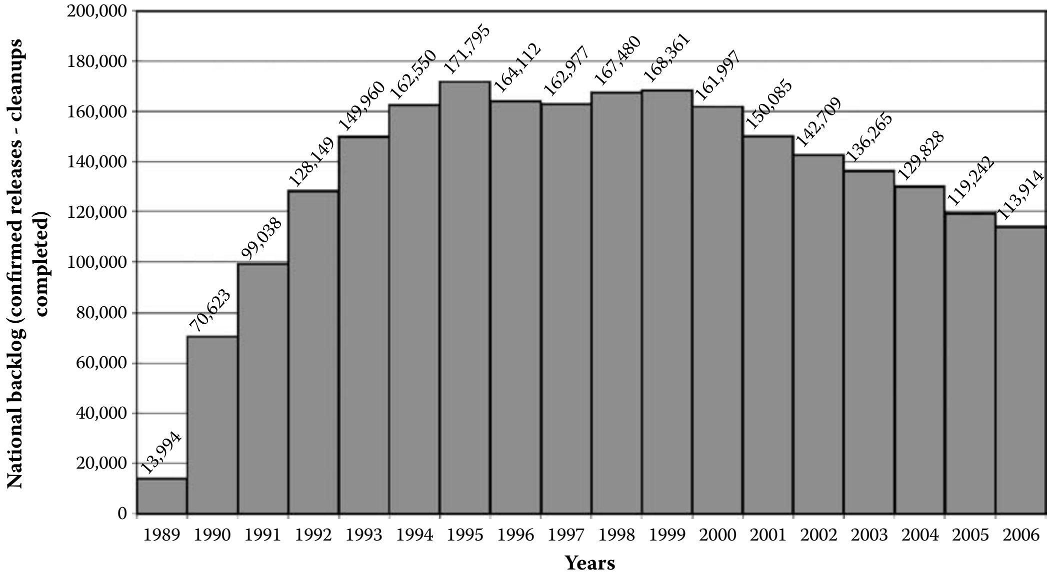


FIGURE 18.22 UST national backlog: 1989 through 2006. (Taken from U.S. EPA, Underground Storage Tanks Corrective Action Measures Archives, FY 2006 End-of-Year Activity Report, U.S. EPA, Washington, 2007. Available at http://www.epa.gov/OUST/cat/camarchv.htm.)

Solution

The density of air may be estimated by the Ideal Gas Law:

$$P = \frac{10^5}{(287)(313)} = 1.11\,\text{kg/m}^3$$

The absolute viscosity can then be calculated using Equation 18.2:

$$\begin{aligned}
\mu &= (v)(p)\\
&= (1.11\ \text{kg/m}^3)\ (16.97 \times 10^{-6}\ \text{m}^2\text{/s})\\
&= 1.88 \times 10^{-5}\ \text{kg/m-s}\\
&= 1.88 \times 10^{-5}\ \text{N-s/m}^2\\
&= 1.88 \times 10^{-5}\ \text{Pa-s}\\
&= 1.88 \times 10^{-4}\ \text{poise}\\
&= 1.88 \times 10^{-4}\ \text{dyne-s/cm}^2\\
&= 1.88 \times 10^{-4}\ \text{g/cm-s}\\
&= 1.88 \times 10^{-2}\ \text{cP}
\end{aligned}$$

18.9.4.2 Conversion between Kinetic Viscosity and Absolute Viscosity for Water

Viscosity is a measure of a fluid's resistance to flow. The knowledge of viscosity is needed for proper design of required temperatures for storage, pumping, or injection of hazardous fluids. Define the viscosity terminologies, and provide technical data of typical liquid pollutants for illustration.

Solution

The viscosity of a fluid is an important property in the analysis of liquid behavior and fluid motion near solid boundaries. Viscosity is the fluid resistance to shear or flow and is a measure of the adhesive/cohesive or frictional fluid property. The resistance is caused by intermolecular friction exerted when layers of fluids attempt to slide by one another.

The dynamic (absolute) viscosity is the tangential force per unit area required to move one horizontal plane with respect to the other at a unit velocity when maintained at a unit distance apart by the fluid. The readers are referred to Equations 18.1 and 18.2 for the dynamic viscosity.

Kinematic viscosity is the ratio of absolute or dynamic viscosity to density—a quantity in which no force is involved. Kinematic viscosity can be obtained by dividing the absolute viscosity of a fluid by its mass density, as shown in Equation 18.3.

Commonly used units for viscosity include the following:

1. CentiPoises (cP) = centistokes (cSt) × density
2. Saybolt Universal Seconds (SUS) = centistokes (cSt) × 4.55
3. Degree Engler × 7.45 = centistokes (cSt)
4. Seconds Redwood × 0.2469 = centistokes (cSt)

Saybolt Universal Seconds (SUS) are used to measure viscosity. The efflux time is the SUS required for 60 mL of a petroleum product to flow through the calibrated orifice of a Saybolt Universal viscometer, under carefully controlled temperature and as prescribed by test method ASTM D 88. This method has largely been replaced by the kinematic viscosity method. SUS is also called the SSU number (Seconds Saybolt Universal) or SSF number (Saybolt Seconds Furol).

TABLE 18.10
Viscosity and Specific Gravity of Liquid Pollutants

CentiPoise (cP)	CentiStoke (cSt)	Saybolt Universal Seconds (SUS)	Liquid Pollutant	Specific Gravity
1	1	31	Water	1.0
3.2	4	40	Milk	—
12.6	15.7	80	No. 4 fuel oil	0.82–0.95
16.5	20.6	100	Cream	—
34.6	43.2	200	Vegetable oil	0.91–0.95
88	110	500	SAE 10 oil	0.88–0.94
176	220	1000	Tomato juice	—
352	440	2000	SAE 30 oil	0.88–0.94
820	650	5000	Glycerine	1.26
1561	1735	8000	SAE 50 oil	0.88–0.94
1760	2200	10,000	Honey	—
5000	6250	28,000	Mayonnaise	—
15,200	19,000	86,000	Sour cream	—
17,640	19,600	90,000	SAE 70 oil	0.88–0.94

Source: The Engineering Toolbox, Dynamic, Absolute and Kinematic Viscosity, 2007. Available at http://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d_412.html. With permission.

Degree Engler is used in Great Britain as a scale to measure kinematic viscosity. Unlike the Saybolt and Redwood scales, the Engler scale is based on comparing a flow of the substance being tested to the flow of another substance—water. Viscosity in Engler degrees is the ratio of the time of a flow of 200 cm^3 of the fluid whose viscosity is being measured to the time of flow of 200 cm^3 of water at the same temperature (usually 20°C but sometimes 50°C or 100°C) in a standardized Engler viscosity meter.[89]

Saybolt Universal Seconds (SUS), Degree Engler, and Seconds Redwood are applicable to fluids with centistokes greater than 50.

The viscosity of a fluid is highly temperature dependent and, for either dynamic or kinematic viscosity to be meaningful, the reference temperature must be quoted. In ISO 8217 the reference temperature for a residual fluid is 100°C. For a distillate fluid the reference temperature is 40°C.

The physical and chemical properties of hazardous dense solvent compounds are given in Tables 18.8 and 18.9, in which the absolute viscosity and kinematic viscosity are expressed in centipoises and centistokes, respectively.

For the purpose of illustration, the viscosity and specific gravity of some typical liquids (including hazardous No. 4 fuel oil, vegetable oil, SAE-10 oil, glycerine, SAE-50 oil, SAE-70 oil) are listed in Table 18.10 for reference.[89]

NOMENCLATURE

B	Carbon bed (M), (lb)
B_h	Carbon bed depth (L), (ft)
B_{hm}	Carbon bed depth (L), (m)
B_m	Carbon bed (M), (kg)
BP	Boiling point at 760 torr pressure (°C)
C	Unabsorbed concentration of contaminant left in solution (M/L^3)
C_c	Actual carbon dosage (M/L^3), (lb/1000 gal)

C_{cm}	Actual carbon dosage (M/L^3), (kg/m^3)
d	Density (M/L^3), (lb/ft^3), (g/cm^3)
d_{m}	Carbon density (kg/m^3)
$\mathrm{d}V_{\mathrm{s}}/\mathrm{d}y$	Velocity gradient across the surfaces
D_{c}	Carbon column diameter (in.)
D_{cm}	Carbon column diameter (cm)
D_{p}	Mean carbon particle diameter (mm)
f	Removal efficiency of a stripper
g	Gravitational acceleration (L/T^2)
G	Volumetric rate of air (L^3/T)
h_{A}	Head added to the fluid with a mechanical device such as a pump (L)
h_{L}	Head losses from the system due to friction (L)
h_{R}	Head removed from the fluid with a mechanical device such as fluid motor (L)
h_1	Groundwater elevation at beginning of the aerated zone, L
h_2	Groundwater elevation at end of aerated zone, L
H	Henry's law constant for partitioning between air and water (atm-m^3/mol)
k	Constant
K	Hydraulic conductivity, L/T
K_{c}	Carbon adsorption coefficient
K_{oc}	Sediment/water partition coefficient (L^3/M), (mL/g)
L	Volumetric rate of contaminated groundwater (L^3/T)
L_{a}	Length of aerated zone, L
M_{c}	Weight of contaminant (mol)
M_{w}	Weight of water (mol)
MW	Molecular weight of the compound of interest (g)
n	Constant
$1/n$	Slope of the straight-line isotherm
ρ	Density of liquid (M/L^3)
P_1	Pressure at point 1 (M/L^2)
P_2	Pressure at point 2 (M/L^2)
P_{a}	Particle vapor pressure of VOC (atm)
P_{atm}	Pressure (atm)
P_{d}	Pressure drop (in.Hg)
P_{dm}	Pressure drop (mmHg)
P_{o}	Vapor pressure (torr or mmHg)
P_1/γ	Pressure head at point 1 (L)
P_2/γ	Pressure head at point 2 (L)
Q	Flow rate (gal/min)
Q_{m}	Influent rate (m^3/min)
R	Stripping factor
RVD	Relative vapor density (dimensionless)
S	Solubility in water (M/L^3) (mg/L)
Sg	Specific gravity (dimensionless)
S_{s}	Shearing stress (M/LT^2)
t	Contact time (min)
t_{r}	Residence time, T
T	On-stream cycle time (d)
$v_1^2/2g$	Velocity head at point 1 (L)
$v_2^2/2g$	Velocity head at point 2 (L)
V	Volume (m^3)
V_{s}	Velocity along the surfaces (L/T)

W	Weight of activated carbon (M)
X	Amount of contaminant adsorbed (M)
X_a	Mole fraction of VOC in water (mol/mol)
X_{in}	Influent contaminant concentration in water (M/L^3)
X_{out}	Effluent contaminant concentration in water (M/L^3)
y	Distance (L) between the moving and fixed surfaces
Y_{in}	Influent contaminant concentration in air (M/L^3)
Y_{out}	Effluent contaminant concentration in air (M/L^3)
Z_1	Elevation of point 1 (L)
Z_2	Elevation of point 2 (L)
γ	Density of liquid (M/L^3)
μ	Proportionality constant = dynamic viscosity or absolute viscosity of the fluid (M/LT)
ν	Kinematic viscosity (centiStoke)

ACRONYMS

ABF	Automatic backwash filtration
API	American Petroleum Institute
bgs	Below ground surface
BOD	Biochemical oxygen demand
BTEX	Benzene, toluene, ethylbenzene, and xylenes (collectively)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act—Superfund
CWA	Clean Water Act
DAF	Dissolved air flotation
DCE	1,2-Dichloroethane
DIPE	Disopropyl ether
DNAPL	Dense nonaqueous phase liquid
DO	Dissolved oxygen
EDB	Ethylenedibromide
F/M	Food/microorganisms ratio
GAC	Granular activated carbon
IAF	Induced (dispersed or froth) air flotation
MTBE	Methyl tertiary-butyl ether
NAPL	Nonaqueous phase liquids
OSHA	Occupational Safety and Health Administration
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCP	Pentachlorophenol
RCRA	Resource Conservation and Recovery Act
SVE	Soil vapor extraction
TCLP	Toxicity characteristic leachate procedure
TDS	Total dissolved solids
TESVE	Thermal-enhanced soil vapor extraction
TOC	Total organic carbon
TSS	Total suspended solids
TTHM	Total trihalomethane
U.S. EPA	United States Environmental Protection Agency
USTs	Underground storage tanks
UV	Ultraviolet
VOCs	Volatile organic compounds

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19 Biological Treatment Processes for Urea and Formaldehyde Containing Wastewater

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CONTENTS

19.1 GENERATION OF WASTEWATER

19.1.1 PRODUCTION PROCESS

Approximately one million metric tons of urea-formaldehyde resin are produced annually all over the world. More than 70% of this urea-formaldehyde resin is consumed by the forest products industry. The resin is used in the production of an adhesive for bonding particleboard (61% of the urea-formaldehyde used in the industry), medium-density fiberboard (27%), hardwood plywood (5%), and as a laminating adhesive (7%) for bonding furniture case goods, overlays to panels, and interior flush doors, for example.

Urea-formaldehyde resins are the most prominent examples of the thermosetting resins usually referred to as amino resins, comprising ca. 80% of the amino resins produced worldwide. Melamine-formaldehyde resins constitute most of the remainder of this class of resins, with other minor amounts of resins being produced from the other aldehydes or amino compounds (especially aniline), or both.

Amino resins are often used to modify the properties of others materials. These resins are added during the processing of diverse products such as textiles (to impart permanent press characteristics), automobile tires (to improve the bonding of the rubber to the tire cord), paper (to improve its strength, especially when wet), and alkyds and acrylics (to improve their cure). Amino resins are also used for molding products, such as electrical devices, jar caps, buttons, dinnerware, and in the production of countertops.

Urea-formaldehyde resins are used as the main adhesive in the forest product industry because they have a number of advantages, including low cost, ease of use under a wide variety of curing conditions, low cure temperatures, water solubility, resistance to microorganisms and to abrasion, hardness, excellent thermal properties, and a lack of color, especially in the cured resin.

The major disadvantage associated with urea-formaldehyde adhesives as compared with the other thermosetting wood adhesives, such as phenol-formaldehyde and polymeric diisocyanates, is their lack of resistance to moist conditions, especially in combination with heat. These conditions lead to a reversal of the bond-forming reactions and the release of formaldehyde, so these resins are usually used for the manufacture of products intended for interior use only. However, even when used for interior purposes, the slow release of formaldehyde (a suspected carcinogen) from products bonded with urea-formaldehyde adhesives is observed.

19.1.1.1 Chemistry of Urea-Formaldehyde Resin Formation

The synthesis of urea-formaldehyde resin takes place in two stages. In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups of urea (Figure 19.1). This reaction is in reality a series of reactions that lead to the formation of mono-, di-, and trimethylolureas. Tetramethylolurea does not appear to be produced, at least not in a detectable quantity. The addition of formaldehyde to urea takes place over the entire pH range, but the reaction rate is dependent on the pH.

The second stage of urea-formaldehyde synthesis consists of the condensation of methylolureas to low-molecular-weight polymers. The rate at which these condensation reactions occur is very dependent on pH (Figure 19.2) and, for all practical purposes, occurs only at acidic pHs. The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of the following:

1. Methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules (Figure 19.3a)
2. Methylene ether linkages by the reaction of two methylol groups (Figure 19.3b)
3. Methylene linkages from methylene ether linkages by the splitting out of formaldehyde (Figure 19.3c)

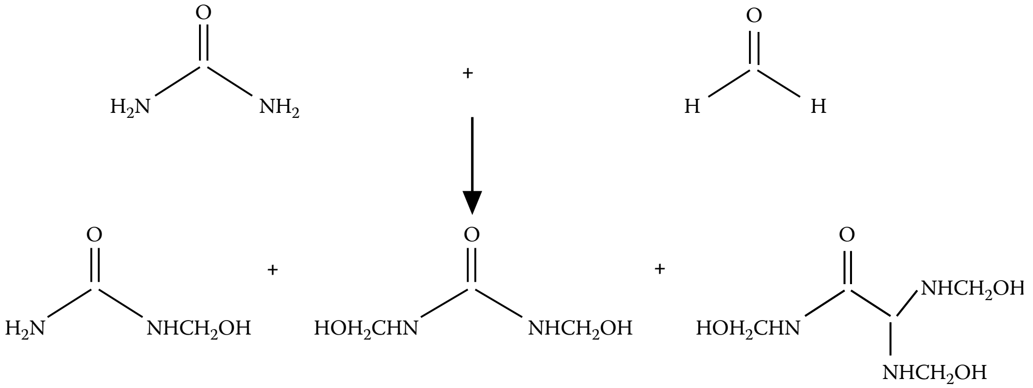

FIGURE 19.1 Formation of mono-, di-, and trimethylolurea by addition of formaldehyde to urea.

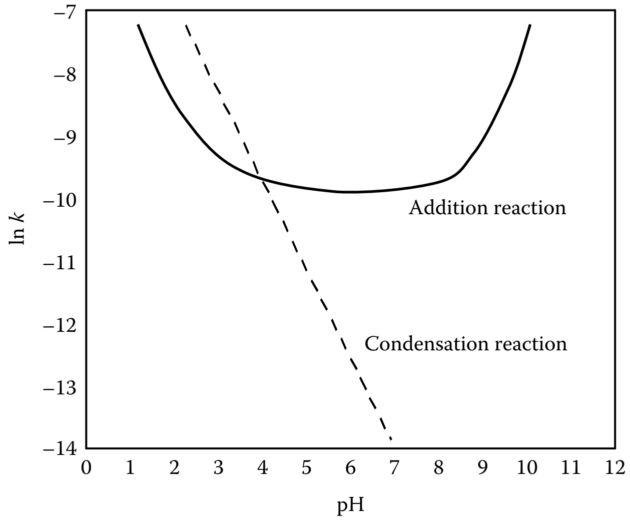

FIGURE 19.2 Influence of pH on the rate constant *k* of addition (solid line) and condensation (dashed line) reactions of urea and formaldehyde.

4. Methylene linkages by the reaction of methylol groups splitting out water and formaldehyde (Figure 19.3d)

The difference between the pH profiles of the two stages of urea-formaldehyde resin synthesis is taken advantage of in the production of these resins (Figure 19.2). In general, the commercial production of urea-formaldehyde adhesive resins is carried out in two major steps. The first step consists of the formation of methylolureas under basic conditions (pH 8 to 9), to allow the methylolation reactions to proceed in the absence of reactions involving the condensation of the methylolureas.

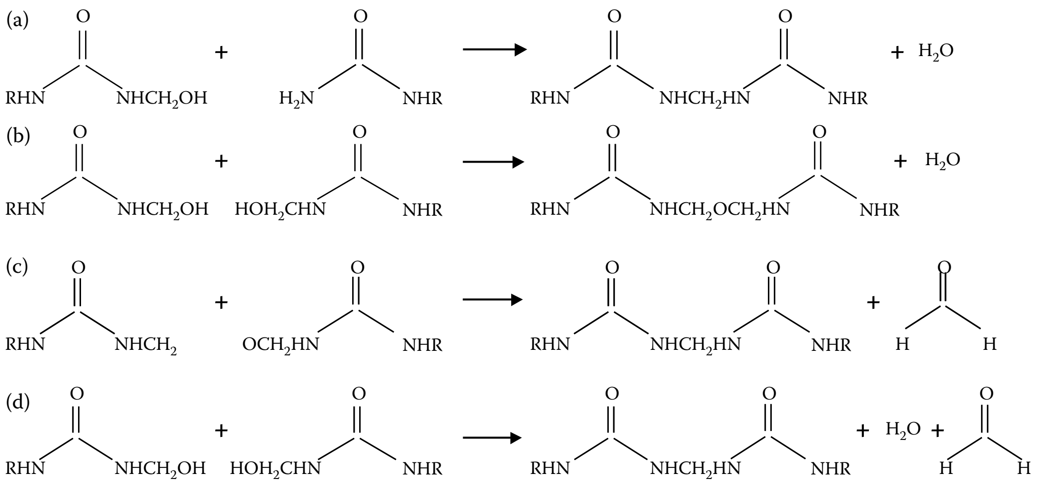

FIGURE 19.3 Condensation reactions of methylolureas to form (a) methylene bridges between amido nitrogens, (b) methylene ether linkages, and (c) and (d) methylene linkages. Reactions of these types produce higher molecular weight oligomers and polymers.

In the second step, the reaction mixture is brought to acid conditions, at ca. pH 5, and the condensation reactions are carried out until the desired viscosity is reached. The reaction mixture is then cooled and neutralized.

An acidic-cure catalyst is added to the urea-formaldehyde resin before it is used as an adhesive. Ammonium chloride and ammonium sulfate are the most widely used catalysts for resins in the forest products industry. A variety of other chemicals can be used as a catalyst, including formic acid, boric acid, phosphoric acid, oxalic acid, and acid salts of hexamethylenetetramine.

Resin cure is normally conducted at a temperature of 120°C and $pH < 5$. The reactions that occur during the final cure of the resin are thought to be similar to those that occur during the acid condensation of the methylolureas. These reactions lead to the formation of the crosslinked polymeric network characteristic of the hardened, cured resin.

19.1.2 CHARACTERIZATION OF THE EFFLUENT

The effluent generated during the production of the resins arises from different operations within the factory. The effluent of the production processes comes mainly from cleaning operations of reactors, storage tanks, filters from the towers of formaldehyde production, and the filters from the reactors. Another source for disposal comprises the spills occurring during the transfer of the resins from the reactors to the storage tanks and from these to the truck used to distribute them to other factories.

Because of the processes carried out in the plant, the expected compounds in wastewater are formaldehyde, urea, and polymers of these compounds. The global effluent of this kind of factory is characterized by a high chemical oxygen demand (COD) (due mainly to formaldehyde), relatively high values of nitrogen (arising from urea and copolymers) and a low content of phosphorus and inorganic carbon. The main characteristics of the effluent of a resin factory are showed in Table 19.1.

19.2 BIOLOGICAL TREATMENT

19.2.1 BIOLOGICAL PROCESSES AND STRATEGIES

The wastewaters generated by the adhesive industries contain high concentrations of both carbon and nitrogen compounds. The process chosen to treat these wastewaters will depend on their COD/N ratio. When the COD/N ratio is high, an anaerobic treatment is the best option as it will save costs

TABLE 19.1
Characteristics of the Effluent from a Resin Factory

	Vidal et al.[1]	Garrido et al.[2]	Garrido et al.[3]	Eiroa et al.[4]
COD (g/L)	0.46–3.9	1.1–4.1	0.46–4.0	0.12–6.85
Formaldehyde (g/L)	0.22–4.0	0.20–2.8	0.22–4.0	0.007–2.7
TKN (g/L)	0.12–0.81	0.13–0.70	0.11–0.80	0.056–1.46
$N\text{-}NH_4^+$ (g/L)	0.003–0.018	—	—	0.006–0.36
TSS (mg/L)	19–150	—	—	12–664
VSS (mg/L)	16–140	—	—	—
pH	—	—	7.1–11.2	6.5–9.6
TOC (g/L)	—	0.30–2.08	—	—
Alkalinity (mg $CaCO_3$/L)	—	—	—	167–2000
$P\text{-}PO_4^{3-}$ (mg/L)	—	—	—	0.1–31

COD, chemical oxygen demand; TKN, total Kjeldahl nitrogen; TSS, total suspended solids; VSS, volatile suspended solids; TOC, total organic carbon.

(less energy, less sludge production). In this process, formaldehyde is degraded to methane and carbon dioxide and urea is hydrolyzed to ammonium:

Anaerobic degradation of formaldehyde

$$2\ CH_2O \longrightarrow CH_4 + CO_2 \qquad (19.1)$$

Urea hydrolysis

$$H_2N\text{-}CO\text{-}NH_2 + 2\ H_2O \longrightarrow 2\ NH_4^+ + CO_2 + 2\ OH^- \qquad (19.2)$$

Generally, the sole use of an anaerobic stage is not enough to reduce COD sufficiently to reach the required concentration for disposal, and the concentration of nitrogen compounds remains practically constant. Therefore, to remove the nitrogen compounds and the remaining COD, a posttreatment based on the nitrification–denitrification process is necessary. This process can be used in a post-denitrifying or predenitrifying configuration (Figure 19.4).

19.2.1.1 Postdenitrifying Configuration

In this case, the wastewater is fed to the aerobic reactor where the remaining formaldehyde is oxidized to CO_2 (Equation 19.3) and urea is hydrolyzed to ammonia. This ammonia is then oxidized to nitrate (Equation 19.4). Nitrate goes to the denitrifying unit where it is reduced to dinitrogen gas in the presence of an electron donor, which is generally provided by organic matter (Equation 19.5). Because formaldehyde is oxidized in the first unit, methanol is commonly added to carry out this process, which produces an increase in operational costs.

Aerobic degradation of formaldehyde

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O \qquad (19.3)$$

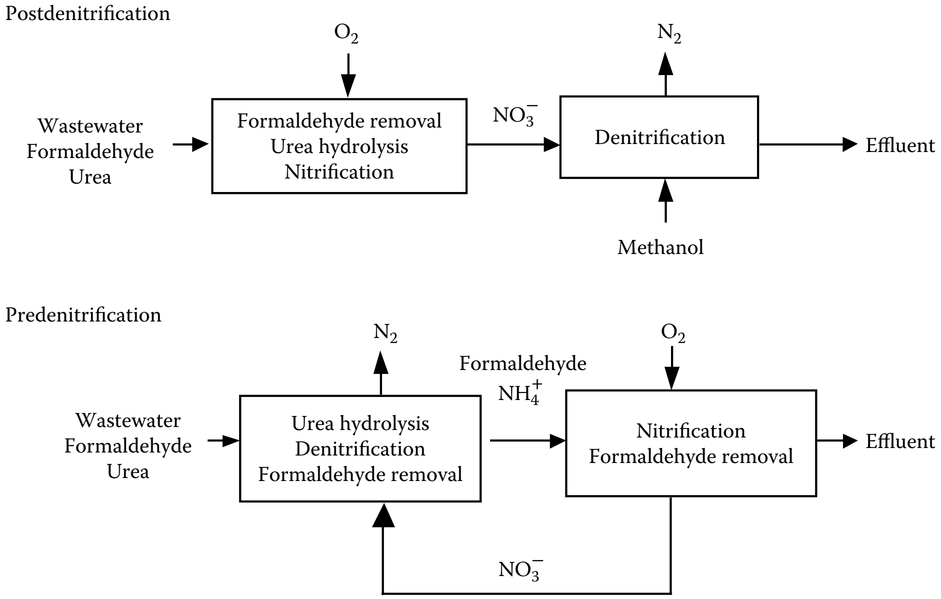

FIGURE 19.4 Postdenitrification and predenitrification configurations for the treatment of wastewaters containing formaldehyde and urea.

Nitrification

$$NH_4^+ + 2\,O_2 \longrightarrow NO_3^- + H_2O + 2\,H^+ \tag{19.4}$$

Denitrification

$$4\,NO_3^- + 5\,CH_2O \longrightarrow 2\,N_2 + 5\,CO_2 + 3\,H_2O + 4\,OH^- \tag{19.5}$$

19.2.1.2 Predenitrifying Configuration

Wastewater is supplied to the anoxic unit, where the nitrate recycled from the nitrifying unit is denitrified using the formaldehyde as the electron donor. When the COD/N ratio of the wastewater is high, the anaerobic degradation of formaldehyde and denitrification can occur in the same unit, this last process having preference for thermodynamic reasons.[3] The hydrolysis of urea is also carried out in the anoxic reactor. The wastewater containing ammonia and a low concentration of formaldehyde is fed to the aerobic tank, where ammonia is nitrified to nitrate and the remaining formaldehyde is oxidized. The disadvantage of this configuration is the dependence of the percentage of nitrogen removal on the recycling ratio between the aerobic and anoxic units:

$$\eta = \frac{R}{R+1} \times 100 \tag{19.6}$$

where η is the percentage of nitrogen removal and R is the recycling ratio between the aerobic and anoxic units.

If the COD/N ratio of the wastewater is low, a better option is the use of a nitrification–denitrification stage without a previous anaerobic digestion in order to preserve organic matter for denitrification.

19.2.2 INTERACTIONS BETWEEN BIOLOGICAL PROCESSES AND COMPOUNDS

Maintaining the stability of a biological treatment of wastewaters containing formaldehyde and urea is complicated because some compounds exert a toxic effect on the processes involved. Figure 19.5 shows the possible toxic interactions between the different compounds and processes.

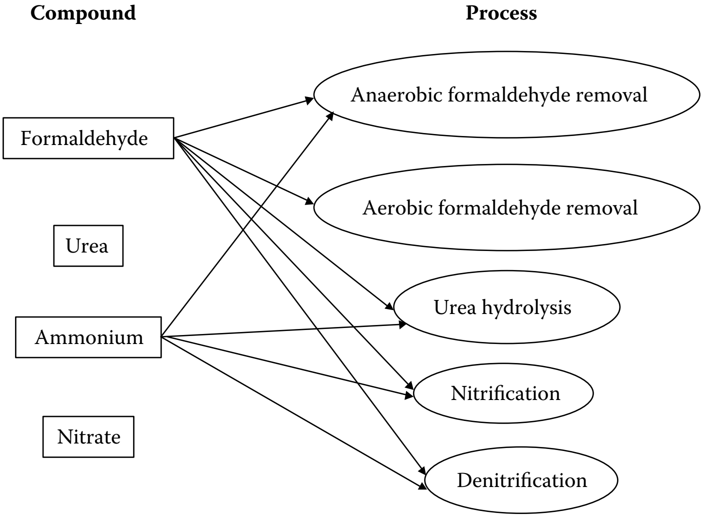

FIGURE 19.5 Compounds and intermediates of wastewater treatment, with arrows indicating the inhibitory effects of them on the different processes.

19.2.2.1 Anaerobic Formaldehyde Removal

Biodegradation pathway

Different pathways have been proposed to explain the anaerobic biodegradation of formaldehyde according to the intermediate products observed.[5–7]

González-Gil and colleagues[5] carried out anaerobic activity tests using formaldehyde as the only carbon source and found that part of this compound was readily transformed into methanol. These authors could recover all substrate COD as methane when assayed for initial formaldehyde doses of 200 and 600 mg/L COD, but no methane production was observed for an initial dose of 1400 mg/L COD due to the toxic effect of the formaldehyde on the reaction. Nevertheless, the conversion of formaldehyde into methanol was not inhibited. During formaldehyde conversion, a peak of hydrogen was observed, this peak being related to the initial amount of formaldehyde dosed. It is likely that formaldehyde was first oxidized to formate and then reduced to methanol. Considering that all formaldehyde is converted into methanol and formate, the following reactions are proposed:

Oxidation

$$HCHO + H_2O \longrightarrow HCOOH + H_2 \tag{19.7}$$

Reduction

$$HCHO + H_2 \longrightarrow CH_3OH \tag{19.8}$$

Total

$$2\,HCHO + H_2O \longrightarrow CH_3OH + HCOOH \tag{19.9}$$

Omil and colleagues[6] also carried out anaerobic activity tests to study the biodegradation of formaldehyde in the presence and absence of cosubstrate. In the absence of cosubstrate, these authors suggest that the hydrogen generated during formaldehyde removal was consumed both for direct methane conversion and for methanol generation. In Table 19.2, two possible formaldehyde degradation reactions are shown (reactions *i* and *ii*). Both are dependent on hydrogen concentration. Although degradation via methanol is thermodynamically favored in standard conditions, this pathway would imply, for the complete mineralization of formaldehyde, the synergistic action of methylotroph methanogenic bacteria (reaction *iii*) which suggests a situation of certain competition between reaction *iii* and the consecutive reactions *iv* and *vi*. In this way, when autotrophic methanogenic bacteria become inhibited and hydrogen concentration begins to accumulate in the medium, methanol generation becomes more favorable.

In the presence of a cosubstrate, formaldehyde removal was highly enhanced especially by acetate (*vii*) but not by propionate (*viii*) and butyrate (*ix*). The effect that acetate degradation exerts on formaldehyde removal may be related to the inorganic carbon generated, which allows autotrophic bacteria to convert hydrogen into methane (reaction *vi*) under more favorable conditions. When low concentrations of volatile fatty acids (VFA) and methanol are present, the direct conversion into methane by methylotrophic methanogenic bacteria should be the most favorable pathway for methanol degradation (in competition with the acetogenic bacteria (*v*)), and autotrophic methane generation would not be favorable; therefore, both direct conversion into methane and the acetogenic pathway should be considered for methanol consumption. Neither are hydrogen dependent.

Oliveira and colleagues[7] found intermediate compounds with 2 to 5 carbons during the degradation of formaldehyde (with 12% methanol) as the sole carbon source and attribute this to a chemical reaction as formaldehyde can form polymers in aqueous solution. The reactions are rapid in the absence of methanol, which is added to formaldehyde solutions to prevent such polymerization. In aqueous solution, when methanol is consumed, formaldehyde is almost completely hydrated to

TABLE 19.2
Estimated Free Energy Changes of Selected Biological Reactions Involved in the Anaerobic Degradation of Formaldehyde and Methanol

Reactions	ΔG^0 (kJ)
Formaldehyde	
(i) $HCOH + H_2O \rightarrow 2\ H_2 + CO_2$	−21.8
(ii) $HCOH + H_2 \rightarrow CH_3OH$	−44.0
Methanol	
Methanogenesis	
(iii) $4\ CH_3OH \rightarrow 3\ CH_4 + HCO_3^- + H^+ + H_2O$	−314.6
Hydrogen generation	
(iv) $CH_3OH + 2\ H_2O \rightarrow 3\ H_2 + HCO_3^- + H^+$	23.0
Acetogenesis	
(v) $4\ CH_3OH + 2\ HCO_3^- \rightarrow 3\ CH_3COO^- + H^+ + 4\ H_2O$	−221.6
Hydrogen and VFA	
(vi) $4\ H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\ H_2O$	−135.6
(vii) $CH_3COO^- + 2\ H_2O \rightarrow CH_4 + HCO_3^-$	−31.0
(viii) $CH_3CH_2COO^- + 3\ H_2O \rightarrow CH_3COO^- + HCO_3^- + H_2 + H^+$	+76.0
(ix) $CH_3CH_2CH_2COO^- + 2\ H_2O \rightarrow 2\ CH_3COO^- + 2\ H_2 + H^+$	+48.1

VFA, volatile fatty acids.

methylene glycol, which may polymerize to form a series of polyoxymethylene glycols. These authors suggested that the intermediate compounds come from the anaerobic degradation of the formed polymers. Another possibility is an aldo condensation, which occurs in the presence of weak bases, forming glycolic aldehyde and carbohydrates.

Toxic effects

The toxicity of formaldehyde during anaerobic treatment has been reported by several authors.[5,8] Its toxicity depends of several different parameters:

1. Nature of the cosubstrates
2. Operational mode (batch or continuous)
3. Type of reactor (suspended or attached growth systems)
4. Formaldehyde/microorganisms ratio
5. COD/formaldehyde ratio

The importance of the nature of the cosubstrate was shown by Todini and Hulshoff Pol,[9] who determined the specific activity of formaldehyde-degrading microorganisms with different cosubstrates such as hydrogen, sodium butyrate, and sucrose. They obtained the highest degradation rates with sucrose. Vidal and colleagues[1] treated wastewater containing formaldehyde in an upflow anaerobic sludge blanket (UASB) reactor using glucose as the cosubstrate, as this compound enhances the reduction of aldehyde to methanol, which is less toxic for the bacteria. Values of 80 mg/L of formaldehyde were reported when acetate was used,[10] whereas Todini and Hulshoff Pol[9] reported a 50% inhibition at 238 mg/L of formaldehyde when sucrose was fed as the main cosubstrate.

Bhattacharya and Parkin[11] studied the influence of the operational mode on formaldehyde degradation. They showed that higher formaldehyde concentrations were tolerated when they were added continuously to acetate and propionate enriched systems rather than when slug doses were used, thus indicating that continuous operation is more favorable for bacterial acclimation.

Sharma and colleagues[12] evaluated the anaerobic biodegradation of petrochemical wastewater containing 4.5 g/L of formaldehyde, and found a higher resistance to microorganisms when biomass concentration was increased by immobilization using biomass-supporting particles. Formaldehyde was observed to exert toxicity at 375 mg/L in the reactor working with these supporting particles, whereas only 125 mg/L was tolerated in the control reactor with suspended biomass.

The formaldehyde/biomass ratio is also reported to be a key factor, as demonstrated by de Bekker and colleagues,[13] who determined that 0.89 g formaldehyde/g VSS in batch operation exerted a complete inhibition of anaerobic bacteria. They also reported that anaerobic treatment of wastewaters containing formaldehyde is possible only when the COD/formaldehyde ratio is higher than 1000.[13] However, other authors such as Parkin and colleagues[14] achieved a stable operation with lower COD/formaldehyde ratios (about 6), using acetate as the main substrate and a continuous addition of 400 mg/L formaldehyde to an anaerobic filter. They found that formaldehyde exhibits reversible inhibition, recovery being accelerated by removing the toxicant from the liquid phase. These results agree with those of Gonzalez-Gil and colleagues,[15] who found that the inhibition exerted by formaldehyde on the methane production rate is partially reversible when formaldehyde concentrations in the reactor are lower than 22 mg/L C-formaldehyde.

There is no information about the mechanisms of formaldehyde toxicity, and the information available in the literature about formaldehyde toxicity in batch and continuous systems is difficult to extrapolate for design purposes (Tables 19.3 and 19.4).

The hydrolysis of urea releases ammonia to the liquid bulk, which can cause inhibition of the methanogenic sludge.[21] Nevertheless, these authors found a toxic effect at 1300 mg/L N-NH_3, this value being higher than the nitrogen concentration of these wastewaters and no inhibitory effects could be expected.

19.2.2.2 Aerobic Degradation of Formaldehyde

Biodegradation pathway

The aerobic degradation of formaldehyde in wastewater has been studied by different authors in both continuous[22] and batch experiments.[23–25] The degradation can occur by two possible paths (see Equations 19.10 and 19.11):

1. Initiated by a dismutation reaction, yielding formic acid and methanol as products, if the microorganism has a formaldehyde dismutase enzyme
2. Via formic acid if the microorganism has the enzymes formaldehyde and formate dehydrogenase[24]

The biodegradation of the metabolites starts after exhaustion of formaldehyde in the medium.

$$2\,\mathrm{HCHO} \xrightarrow[\text{dismutase}]{\text{Formaldehyde}} \mathrm{CH_3OH} + \mathrm{HCOOH} \tag{19.10}$$

$$\mathrm{HCHO} \xrightarrow[\text{dehydrogenase}]{\text{Formaldehyde}} \mathrm{HCOOH} \xrightarrow[\text{dehydrogenase}]{\text{Formate}} \mathrm{CO_2} \tag{19.11}$$

Toxic effects

Zagornaya and colleagues[22] reported the complete biodegradation of 2300 mg/L of formaldehyde in wastewater treated in an activated sludge plant, whereas Gerike and Gode[26] observed that 30 mg/L

TABLE 19.3
Formaldehyde Studies in Batch Systems at 35°C

Biomass	Main Substrate	Tested HCHO (mg/L)	IC_{50} (mg/L)	Reference
Anaerobic digested sludge	—	10–100	—	[16]
Domestic wastewater	—	1–10,000	200	[17]
Sludge treating water from seafood processes	VFA	50–200	125	[1]
Granular sludge from a UASB	Sucrose	—	254	[9]
Activated sludge from a plant treating wood-processing-industry wastewater	Glucose	2–400	300	[18]

IC_{50}, 50% inhibition concentration; VFA, volatile fatty acids.

formaldehyde inhibited oxygen consumption in activated sludge. Eiroa and colleagues[25] studied the inhibitory effect of formaldehyde in batch tests; they found no inhibition and also that high concentrations of formaldehyde up to 3890 mg/L could be removed using it as the single carbon source. When the same formaldehyde concentrations in the presence of methanol as cosubstrate were tested, higher formaldehyde biodegradation rates were obtained. This possibility of formaldehyde biodegradation despite the presence of an alternative readily metabolizable carbon source is a characteristic of significant practical interest when formaldehyde needs to be removed in environments containing other carbon sources, as in the case of wastewaters from synthetic resin-producing factories. Glancer-Soljan and colleagues[24] also found no inhibitory effects of formaldehyde biodegradation in batch assays with an initial concentration of 1000 mg/L using a mixed culture containing two bacterial strains.

19.2.2.3 Urea Hydrolysis

A wide variety of aerobic and anaerobic microorganisms are able to express the enzyme urease (urea amidohydrolase), which catalyses the hydrolysis of urea to ammonia and carbon dioxide.[27] So far,

TABLE 19.4
Some Results from Literature Obtained in Continuous Systems Treating Formaldehyde-Containing Wastewater

Reactor	Tested HCHO (mg/L)	Limiting Dose (mg HCHO/L)	Formaldehyde Removal Efficiency (%)	Reference
Anaerobic filter	100–400	400	—	[14]
CST	—	125	85–88	[12]
CST immobilized biomass	—	375	88–95	[12]
Chemostat	100–1110	1110	99.9	[19]
EGSB	333	—	>93	[20]
EGSB	200/400/600	—	High	[5]
UASB	50–2000	100	98	[1]
UASB	95–950	380	95	[1]
HAIB	26–1158	Not observed	>95	[7]

CST, continuous stirred tank; EGSB, expanded granular sludge blanket; HAIB, horizontal-flow anaerobic immobilized biomass.

most authors have preferred anaerobic conditions for the biological treatment of high-strength urea wastewaters with urea concentrations of up to 2g/L.[1,28] Also, wastewaters containing high loads of urea together with ammonia and formaldehyde have been treated under anoxic conditions,[3] and an aerobic urea hydrolysis has been described by Gupta and Sharma[29] and Hamoda.[30] Rittstieg and colleagues,[31] treating an industrial wastewater containing high concentrations of urea and sulfate, proposed the use of the aerobic process to avoid the production of sulfide if an anaerobic stage were used.

There are no clear results as to which microorganism causes hydrolysis in aerobic conditions. Prosser[32] reported that *Nitrosomonas* or *Nitrospira* were not ureolytic, which agrees with the conclusion of Campos and colleagues,[33] who observed no degradation of urea when this compound was fed to a nitrification reactor. However, Koops and Chritian[34] pointed out that the five genera of ammonia-oxidizing bacteria might use urea as an ammonia source. Gupta and Sharma[29] and Hamoda[30] observed hydrolysis of urea and high nitrification percentages when they treated effluents from fertilizer industries aerobically. Recently, Sliekers and colleagues[35] have observed that anaerobic ammonium oxidation (anammox) bacteria did not hydrolyze urea by themselves.

Toxic effects

Different effects of formaldehyde on the hydrolysis of urea are reported. On the one hand, Garrido and colleagues,[3] applying anoxic conditions, observed that an inhibitory effect started at 50 mg/L formaldehyde and the levels of inhibition were 50% and 90% for concentrations of formaldehyde of 100 mg/L and 300 mg/L, respectively. Similar effects were found by Campos and colleagues,[33] working with an anoxic USB, who observed that formaldehyde concentrations in the reactor of 250 to 300 mg/L caused an inhibition of around 53%. This inhibition on the ureolytic activity was also reported by Walker.[36] On the other hand, Eiroa and colleagues[37] carried out batch assays at different initial urea concentrations from 90 to 370 mg/L N-urea in the presence of 430 mg/L formaldehyde. They observed that a complete hydrolysis was achieved and initial urea hydrolysis rates remained constant.

Eiroa and colleagues[37] operated a denitrifying granular sludge blanket with inlet urea concentrations between 100 and 800 mg/L N-urea, and always maintained the efficiency of the hydrolysis in spite of the presence of concentrations of ammonia up to 730 mg/L N (110 mg/L N-NH_3). The ammonia levels in the effluent corresponded to ca. 77.5% of the amount of urea fed, the unaccounted portion being attributed to microbial assimilation. However, Garrido and colleagues,[3] when increasing the urea loading rate in a multifed upflow filter (MUF) by increasing the inlet concentration, observed that fully hydrolytic efficiency was maintained for a short period of time but later decreased to 55%. These authors attribute the loss of ureolytic activity of the sludge to the higher ammonia concentrations.

19.2.2.4 Nitrification

Nitrification is a two-step process where ammonia is first oxidized to nitrite by ammonia-oxidizing bacteria (*Nitrosomonas*, *Nitrosococcus*, *Nitrosospira*, and so on) and the produced nitrite is finally oxidized to nitrate by nitrite-oxidizing bacteria (*Nitrobacter*, *Nitrospina*, *Nitrospira*, etc.) (Equation 19.12 and Equation 19.13). Both ammonia- and nitrite-oxidizing bacteria are autotrophic microorganisms, which supposes a low growth rate, nitrification being the limiting process during nitrogen removal.

$$NH_4^+ + 3/2\,O_2 \longrightarrow NO_2^- + H_2O + 2\,H^+ \tag{19.12}$$

$$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^- \tag{19.13}$$

Generally, ammonia oxidation is slower than nitrite oxidation and, therefore, no nitrite production is observed. However, when the amount of carbon source available in the effluent is not high enough to complete the denitrification process (low COD/N ratio), the addition of external organic matter is necessary, which produces an increase in treatment costs. In this case the partial nitrification of ammonia to nitrite reduces not only the oxygen requirements for the oxidation, but also the amount of added organic matter required for denitrification.[3]

Toxic effects

Osislo and Lewandowski[38] studied the effects of several organic compounds on nitrification (acetone, methanol, formaldehyde, and glucose) and found that formaldehyde was the most inhibitory. This inhibition was not due to heterotrophic growth, but to a toxic effect. Campos and colleagues[33] shocked a nitrifying system with different concentrations of formaldehyde (100, 200, and 300 mg/L formaldehyde) over 3h. These shocks caused ammonia to appear in the effluent for a short time, but nitrite was never detected. These authors observed a linear tendency between formaldehyde concentration in the reactor and the decrease in the nitrification rate. They also found that most of this compound was consumed in the reactor. Eiroa and colleagues[25] studied the effect of formaldehyde on nitrification in batch assays. These authors found that initial concentrations of formaldehyde above 350 mg/L start to decrease the nitrification rate, with complete inhibition at an initial concentration of 1500 mg/L. An increase in the lag phase before nitrification started was also observed. When the authors repeated the experiments in presence of methanol, they found that the inhibitory effect was greater at lower formaldehyde concentrations. In the presence of methanol, at initial formaldehyde concentrations of 175 mg/L, nitrification started to decrease and was completely inhibited at 500 mg/L. The authors explained the differences by the fact that the COD/total Kjeldahl nitrogen (TKN) ratio was higher in the assays with formaldehyde and methanol as carbon sources than in assays without methanol. Therefore, the competition between heterotrophic bacteria and nitrifiers for oxygen and ammonium was higher. However, Eiroa and colleagues[39] observed that the simultaneous removal of formaldehyde and ammonium may be carried out in an activated sludge unit, maintaining a nitrification efficiency of 99.9%.

Anthonisen and colleagues[40] found that free ammonia (NH_3) is an inhibitory compound for both steps of nitrification, nitrite oxidation being more sensitive. Concentrations of this compound depend on dissolved NH_4^+ and pH; therefore, for a certain concentration of NH_4^+, pH can be a suitable parameter to control inhibition by the substrate. Gupta and colleagues,[41] treating wastewaters containing both ammonia and urea, found nitrite in the effluent due to the inhibition of nitrite oxidation. Eiroa and colleagues,[25] during batch assays with wastewaters containing ammonia and formaldehyde, observed the transitory accumulation of nitrite, probably as a result of the high initial free ammonium (3.9 mg/L $N\text{-}NH_3$).

19.2.2.5 Denitrification

The denitrification process is carried out by heterotrophic bacteria such as *Pseudomonas*, *Acinetobacter*, *Paracoccus*, *Alcaligenes*, and *Thiobacillus*. The route of nitrogen reduction is showed in Equation 19.14. Generally, dinitrogen gas is the final product, but nitrous oxide may be the final product of denitrification if the denitrifying microorganisms lack N_2O reductase,[42] at low pH values,[42] or in the presence of toxic compounds.[43] The presence of low dissolved oxygen concentrations during denitrification also causes the accumulation of N_2O[44]:

$$NO_3^- \xrightarrow{r_1} NO_2^- \xrightarrow{r_2} NO \xrightarrow{r_3} N_2O \xrightarrow{r_4} N_2 \tag{19.14}$$

Garrido and colleagues,[43] treating wastewaters containing formaldehyde and urea, observed a relation between the formaldehyde concentration in the reactor and the percentage of nitrous oxide produced in the gas phase, which indicates that, probably, the reduction of nitrous oxide to nitrogen is inhibited by the presence of formaldehyde. Therefore, nitrous oxide measurement might serve to check for the presence of formaldehyde or other toxic or inhibitory compounds in denitrifying reactors and consequently to advise the plant supervisor about a possible failure in the system.

As trace gases concentration in biological processes changes rapidly with operating conditions, nitrous oxide could serve to monitor denitrifying systems as well as it was proposed for hydrogen or carbon monoxide for monitoring methanogenic systems.

Because wastewater may contains a low COD/N ratio, the oxidation of ammonia to nitrite during nitrification contributes to decrease the amount of organic matter needed during denitrification:

$$4\,NO_2^- + 3\,CH_2O \longrightarrow 2\,N_2 + 3\,CO_2 + H_2O + 4\,OH^- \qquad (19.15)$$

The theoretical formaldehyde requirements for denitrifying nitrite or nitrate, if biomass production is not considered, are 0.64 and 1.07 kg C/kg N-NO_x^-, respectively. Garrido and colleagues[3] found C/N ratios of 0.8 and 1.3 kg C/kg N-NO_x^- for denitrification of nitrite and nitrate, respectively, these values being 20% higher than the theoretical ones.

Toxic effects

A negative effect of formaldehyde on the denitrification process has been observed by several authors.[3,33] Campos and colleagues[33] found a decrease of 85% in nitrate consumption when formaldehyde accumulated in a denitrifying USB reactor (up to 300 mg/L formaldehyde) with an increase of the formaldehyde loading rate. The efficiency of denitrification was totally restored after the formaldehyde accumulation was eliminated by decreasing the loading rate, showing a reversible inhibitory effect. However, Garrido and colleagues[3] found only a slight decrease in the denitrification efficiency, from 90 to 80% at concentrations of 700 mg/L of formaldehyde, during the operation of a MUF. Nevertheless, these authors detected nitrous oxide in the off-gas at concentrations higher than 100 mg/L of formaldehyde, this probably being related to a partial inhibition by this compound in the last step of denitrification.

Eiroa and colleagues[37] carried out batch denitrifying assays with an initial concentration of 430 mg/L of formaldehyde. They found that formaldehyde was completely biodegraded in less than 30 h, but the denitrification process lasted several days. Therefore, formaldehyde was transformed into other organic compounds (methanol and formic acid), which were then used as carbon sources for denitrification. These authors operated a denitrifying granular sludge blanket reactor at different COD/N-NO_3^- ratios and at formaldehyde inlet concentrations up to 5000 mg/L, and obtained a mean denitrification efficiency of 98.4%. This high efficiency can be related to the low formaldehyde concentration in the reactor (below 10.3 mg/L), even when the formaldehyde inlet concentrations were increased. Meanwhile, Zoh and Stenstrom[45] carried out batch tests to determine the denitrifying kinetics of nitrite using different carbon sources. These authors found that acetate and formaldehyde showed similar rates.

Denitrification can be affected by free ammonia, but this inhibition does not appear up to 300 to 400 mg/L NH_3.[46] This high concentration can justify that no inhibition of the denitrification process has been reported for this kind of wastewater.[3,4] Eiroa and colleagues[37] observed that nitrate was eliminated much faster at higher initial urea concentrations. However, they also found an increase of nitrite accumulation, which was later removed, due to high urea concentrations.

19.3 TECHNOLOGIES FOR WASTEWATER TREATMENT

Different kinds of bioreactors and configurations have been used to treat wastewater containing formaldehyde and urea, and three different kinds of treatments can be applied: anaerobic treatment, aerobic treatment, and combined nitrification and denitrification treatments.

19.3.1 ANAEROBIC TREATMENT

Anaerobic treatment is recommended for highly concentrated COD wastewater, as the amount of methane generated can compensate for the energy cost in maintaining the temperature of the reactor.

Moreover, this process produces less sludge compared to aerobic treatment. During the anaerobic process, formaldehyde is converted to CO_2 and CH_4 and urea is hydrolyzed to ammonia; therefore, this process only removes organic matter and a small amount of nitrogen due to ammonia assimilation by anaerobic microorganisms. Most of the time, in order to fulfill disposal targets, a posttreatment to remove nitrogen and the remaining organic matter is necessary.

Different kinds of reactors have been used at the laboratory scale to anaerobically treat wastewater containing formaldehyde. Qu and Bhattacharya,[19] using a chemostate, treated a synthetic influent with formaldehyde concentrations up to 1100 mg/L. These authors obtained efficiencies for formaldehyde removal of 99% at volumetric loading rates up to 0.38 $kg/m^3 \cdot d$ CH_2O. Vidal and colleagues[1] and Garrido and colleagues[3] used a UASB reactor and a MUF to treat synthetic influents with formaldehyde and urea. Vidal and colleagues,[1] using glucose as cosubstrate, managed to treat up to 3 $kg/m^3 \cdot d$ of formaldehyde, while Garrido and colleagues[3] removed 0.5 $kg/m^3 \cdot d$ of formaldehyde. The discrepancies between the values might be due to the presence of the cosubstrate, which favors the reduction of the aldehyde to methanol, which is less toxic to the biomass. Nevertheless, the volumetric hydrolytic rates of urea achieved in both systems were similar (0.46 kg /$m^3 \cdot d$ N-urea[3] and 0.58 $kg/m^3 \cdot d$ N-urea[1]), being lower than the value of 1.5 $kg/m^3 \cdot d$ obtained by Latkar and Chakrabarti[47] in a UASB.

At an industrial scale, Zoutberg and de Been[20] treated wastewaters from a chemical factory containing up to 10 g/L of formaldehyde and 40 g/L of COD. These authors used a Biobed® EGSB (expanded granular sludge blanket) of 275 m^3 with a hydraulic retention time (HRT) of 1.25 d, achieving efficiencies up to 98% (Figure 19.6). To avoid the inhibitory effect of high concentrations of formaldehyde, they operated at a recycle ratio of 30, that is, a superficial upflow liquid velocity of 9.4 m/h, which is rather higher than the 1 m/h used in conventional UASBs. The effluent of the Biobed EGSB was posttreated in a low loaded carrousel to meet the strict demands (overall COD efficiency higher than 99.8%).

19.3.2 AEROBIC TREATMENT

During aerobic treatment formaldehyde is oxidized to CO_2 and urea is hydrolyzed, the generated ammonia being oxidized to nitrate if the operational conditions are suitable for nitrification. During this treatment organic matter can be removed, but only a small amount of nitrogen is removed by assimilation; therefore, this treatment is not good enough to fulfill disposal requirements with regard to nitrogen compounds.

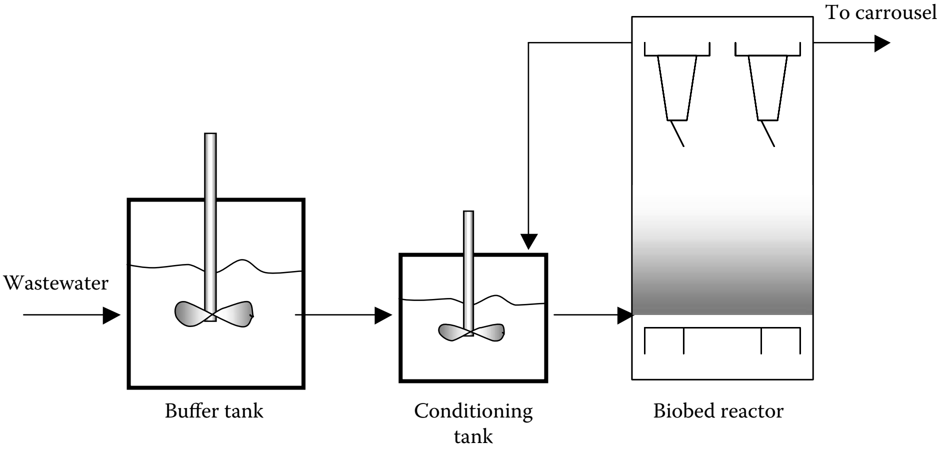

FIGURE 19.6 Schematic of a plant to treat wastewater containing formaldehyde.

Canals[48] managed to treat wastewater from a petrochemical factory at concentrations of up to 2000 mg/L of formaldehyde using an activated sludge reactor, and Zagornaya and colleagues[22] obtained a good removal of this compound when treating resin wastewater in an aerobic reactor.

Garrido and colleagues[2] treated wastewaters from a formaldehyde-urea factory using three activated sludge units operating with solids retention times of 10, 17 and 25 d. These authors applied an organic loading rate (OLR) between 0.2 and 1.2 kg/m^3·d COD and obtained removal efficiencies of 80 to 95% and 99.4% for COD and formaldehyde, respectively. Their system achieved a nitrification rate (0.1 kg N-NO_x^-/m^3 · d), the percentage of TKN removal being 45 to 65% due to the biomass growth.

19.3.3 TREATMENT COMBINING NITRIFICATION AND DENITRIFICATION UNITS

In order to fulfill disposal requirements the best option to treat wastewaters containing formaldehyde and urea is the combination of nitrification and denitrification units in a predenitrifying configuration. In the denitrifying tank, nitrate recycled from the nitrifying unit is denitrified using formaldehyde as the electron donor and urea is hydrolyzed to ammonia. In the nitrification unit, ammonia and the remaining formaldehyde are oxidized to nitrate and CO_2, respectively. The nitrogen removal percentage will depend on the recycling ratio between both units.

Garrido and colleagues[3] operated a MUF under anaerobic and anoxic conditions and achieved, under anoxic conditions, the treatment of up to 2 kg/m^3·d of formaldehyde and a hydrolysis rate of up to 0.37 kg/m^3 · d N-urea. These authors observed that formaldehyde biodegradation is more stable under anoxic conditions than under anaerobic conditions, but only 80% of urea was hydrolyzed in an anoxic environment while a complete conversion occurred under anaerobic conditions. Eiroa and colleagues[49] obtained similar values operating a denitrifying granular sludge blanket reactor with synthetic wastewaters containing formaldehyde and urea. They applied up to 2.8 kg/m^3·d of formaldehyde and 0.44 kg/m^3 · d N-urea, obtaining efficiencies of 99.5 and 77.5% for formaldehyde removal and urea hydrolysis, respectively. Campos and colleagues,[33] using an anoxic USB, achieved a loading rate of hydrolyzed urea of 0.94 kg/ · m^3 · d N-urea and a loading rate of 2.35 kg/m^3 · d for formaldehyde.

In systems treating formaldehyde, the loading rates of removed nitrate ranged from 0.44 kg/m^3·d to 0.94 kg/m^3 · d N-NO_3^-.[33,49] These values are in the range of denitrifying loading rates obtained for other kinds of wastewaters (1.1 kg/m^3 · d or 1.5 kg/m^3 · d N-NO_3^-),[50,51] which means formaldehyde can be used efficiently as an electron donor for denitrification.

Garrido and colleagues[2] used an activated sludge nitrification–denitrification system to treat wastewater from a formaldehyde-urea adhesive factory (Figure 19.7). The treated wastewater contained 590 to 1545 mg/L COD, 197 to 953 mg/L formaldehyde and 129 to 491 mg/L TKN and was also characterized by the presence of polymers with a molecular weight higher than 8000 g/mol, which are not biodegradable. The system was capable of achieving removal efficiencies of 99, 70 to 85, and 30 to 50% for formaldehyde, COD, and TKN, respectively. The COD removal percentage was

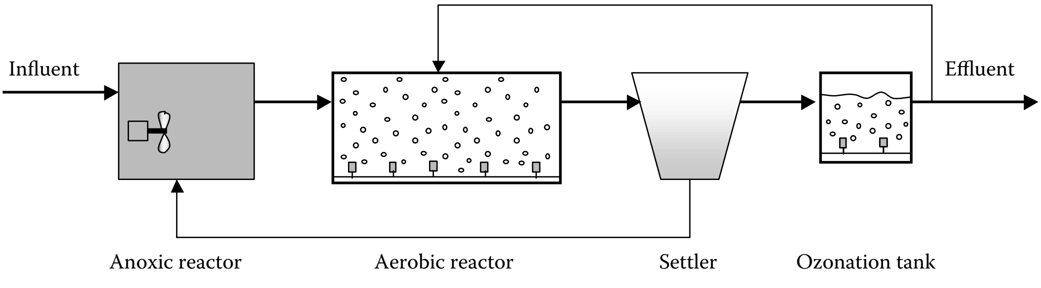

FIGURE 19.7 Schematic representation of a nitrification–denitrification activated sludge plant.

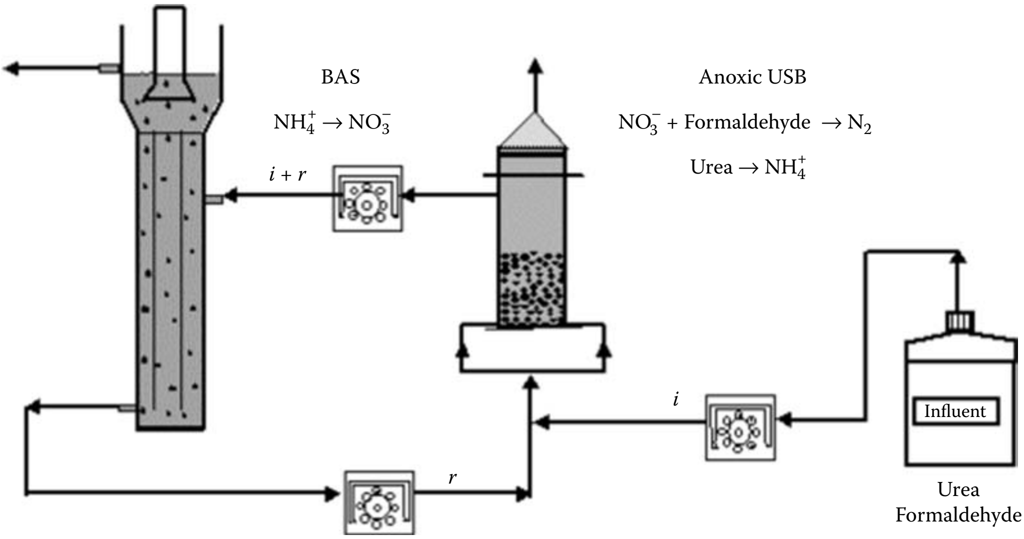

FIGURE 19.8 Plant for the integral treatment of wastewaters containing formaldehyde and urea.

not related to the operational conditions but to the percentage of COD from the formaldehyde. COD removal essentially took place in the anoxic stage, as was the case for formaldehyde, and only nitrification was carried out in an aerobic reactor.

To remove urea and formaldehyde from synthetic wastewater, Campos and colleagues[33] operated a coupled system consisting of a biofilm airlift suspension (BAS) reactor to carry out nitrification and an anoxic USB reactor to carry out the denitrification and urea hydrolysis (Figure 19.8).

These authors studied the effect of the recycling ratio (calculated as the ratio *r*/*i* of the flows) for different fed C/N ratios (0.58, 1.0, and 1.5 g C-formaldehyde/g $N\text{-}NH_4^+$), always using a constant urea inlet concentration of 400 g/L N-urea. The nitrogen removal percentages achieved are shown in Table 19.5. The maximum nitrogen removal percentages were achieved at a C/N ratio of 1.0 g C-formaldehyde/g $N\text{-}NH_4^+$ for both recycling ratios. When this ratio is lower (0.58) not enough organic matter is present to remove nitrate in the anoxic stage, whereas a fed C/N ratio of 1.5 caused a decrease in the efficiency of the system with respect to nitrogen removal, due to the presence of formaldehyde in the BAS reactor, which decreased the nitrification.

When the system was operated at a high inlet C/N ratio, part of the formaldehyde was not removed in the anoxic reactor and entered the nitrification reactor. This led to a heterotrophic layer

TABLE 19.5
Percentages of Nitrogen Removal

r/*i*	C/N	Nitrogen Removal (%)
3	0.58	43.5 ± 10.2
3	1.00	66.2 ± 7.3
3	1.50	8.4 ± 1.8
9	0.58	51.2 ± 3.1
9	1.00	82.4 ± 3.8
9	1.50	68.6 ± 7.4

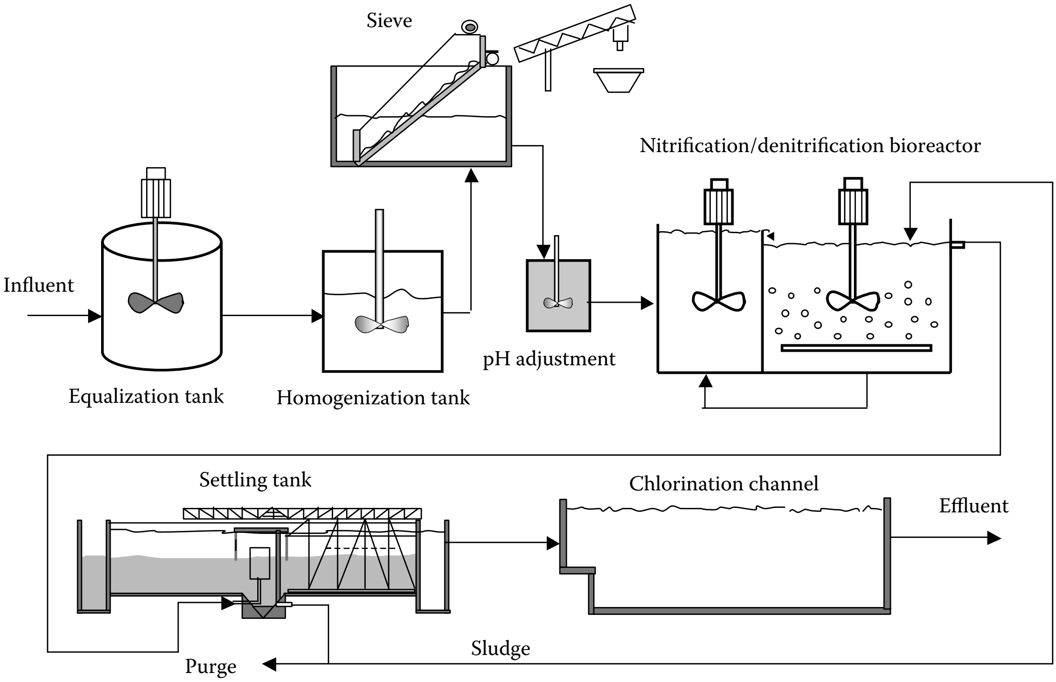

FIGURE 19.9 Industrial plant for the integral treatment of wastewaters from an adhesive factory.

being formed around the nitrifying biofilm, which consumed formaldehyde, and depleted the oxygen for the nitrifiers. The loss of nitrification capacity caused a snowball effect, as no nitrate was available for denitrification, which caused the presence of higher concentrations of formaldehyde in the anoxic system and, then, instability of the denitrification and urea hydrolysis processes. These negative effects of formaldehyde can be reduced by operating at higher recycling ratios, because the increase of the recycling ratio causes a dilution effect in the streams, the formaldehyde concentration in the reactors being lower.

Cantó and colleagues[52] operated an integrated anoxic–aerobic treatment of wastewaters from a synthetic resin producing factory (Figure 19.9). These authors managed to treat up to 2.01 kg/m^3·d COD and up to 0.93 kg/m^3·d TKN with removal efficiencies of 80 to 95% and 58 to 93% for COD and TKN, respectively.

As wastewater from resin-producing factories contains recalcitrant compounds, the removal efficiencies achieved by means of the nitrification–denitrification systems could not reach the required disposal values and a posttreatment, such as ozonation, would be necessary to enhance the biodegradability of those compounds.[2,53]

19.4 GUIDELINES FOR THE DESIGN OF A WASTEWATER TREATMENT PLANT FOR WASTEWATER CONTAINING FORMALDEHYDE AND UREA

19.4.1 Decision Tree Structure

The technology chosen to treat wastewater containing formaldehyde and urea will basically depend on the COD concentration and COD/N ratio. The following decision tree structure can be used in the choice of an approach for wastewater treatment (Figure 19.10).

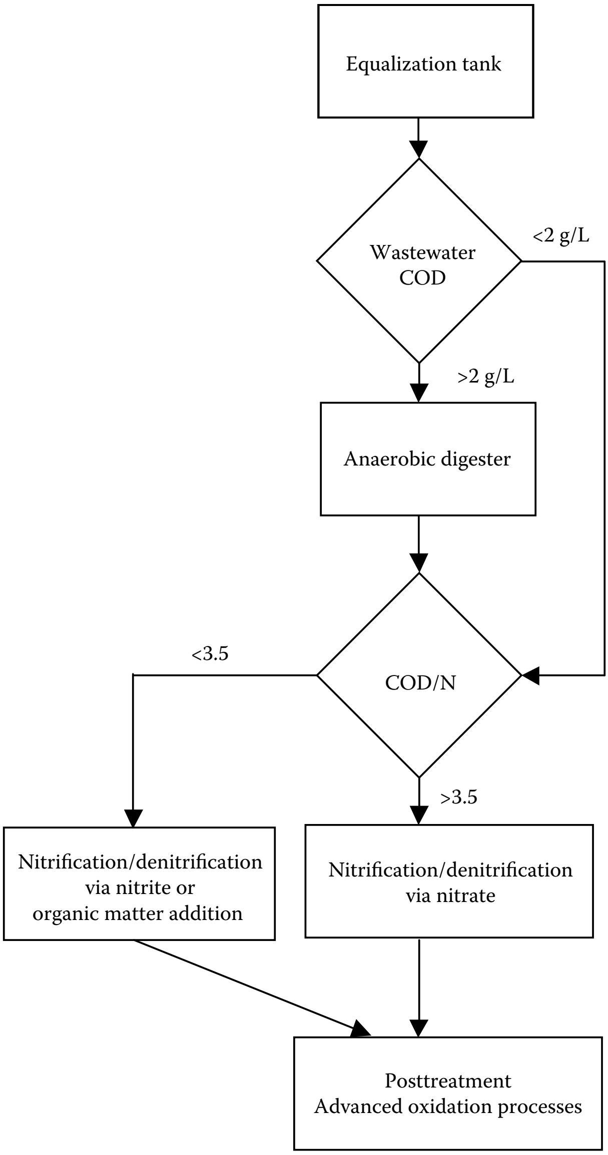

FIGURE 19.10 Decision tree structure.

19.4.2 RECOMMENDATIONS

Because formaldehyde is the most toxic compound present in this kind of wastewater, to control its concentration in reactors is important in order to maintain the stability of the wastewater treatment plant. For this reason the following are recommended:

1. To use an equalization tank to minimize the possible inlet of a peak of formaldehyde.
2. To use anaerobic digesters with high internal recycling ratios to maintain a low concentration of formaldehyde inside the system.
3. To maintain high recycling ratios between the nitrification and denitrification units. This recommendation is also useful to increase the efficiency of nitrogen removal.

When denitrification via nitrate is not possible (COD/N ratios lower than 3.5) there are two possible options to remove nitrogen:

1. To control the dissolved oxygen in the nitrification unit to obtain a partial oxidation of ammonia to nitrite
2. To add an external carbon source

As the adhesive factory will consume a large amount of methanol in its processes, the addition of this compound to carry out nitrogen removal would have a low cost, and is one of the most feasible options.

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20 Hazardous Waste Deep-Well Injection

Nazih K. Shammas and Lawrence K. Wang

CONTENTS

20.1 INTRODUCTION

The technology of deep-well injection has been around for more than 70 years. "Most Americans would be surprised to know that there is a waste management system already in operation in the U.S. that has no emissions into the air, no discharges to surface water, and no off-site transfers, and exposes people and the environment to virtually no hazards."[1] The U.S. Environmental Protection Agency (U.S. EPA) has stated that Class 1 wells are safer than virtually all other waste disposal practices for many chemical industry wastes.

A typical injection well consists of concentric pipes that extend several thousand feet down from the surface level into highly saline, permeable injection zones that are confined vertically by impermeable strata. The outermost pipe or surface casing extends below the base of any underground sources of drinking water (USDW) and is cemented back to the surface to prevent contamination of the USDW. Directly inside the surface casing is a long string casing that extends to and sometimes into the injection zone. This casing is filled with cement all the way to the surface in order to seal off the injected waste from the formations above the injection zone back to the surface. The casing provides a seal between the wastes in the injection zone and the upper formations. The waste is injected through the injection tubing inside the long string casing either through perforations in the long string or in the open hole below the bottom of the long string. The space between the string casing and the injection tube, called the annulus, is filled with an inert, pressurized fluid, and is sealed at the bottom by a removable packer preventing injected wastewater from backing up into the annulus.[2]

The geochemical fate of deep-well-injected wastes must be thoroughly understood to help avoid problems when incompatibility between the injected wastes and the injection-zone formation is a possibility. An understanding of geochemical fate will also be useful when a geochemical no-migration demonstration must be made. This chapter was written to address both of these needs by presenting state-of-the-art information on the geochemical fate of hazardous deep-well-injected wastes. Furthermore, operators of any new industrial-waste injection well who must consider the possibility of incompatibility will find this chapter helpful in identifying geochemical reactions of potential concern and methods for testing incompatibility.

U.S. EPA regulations (53 *Federal Register* 28118–28157, July 26, 1988) stipulate that deep-well injection of hazardous wastes is allowed only if either of the following two no-migration standards is met[3]:

1. Fluid movement conditions are such that the injected fluids will not migrate within 10,000 years vertically upward out of the injection zone; or laterally within the injection zone to a point of discharge or interface with an Underground Source of Drinking Water (USDW).
2. Before the injected fluids migrate out of the injection zone or to a point of discharge or interface with USDW, the fluid will no longer be hazardous because of attenuation, transformation, or immobilization of hazardous constituents within the injection zone by hydrolysis, chemical interactions, or other means.

According to the Federal Remediation Technology Roundtable (FRTR) the factors that may limit the applicability and effectiveness of this technology include the following[2]:

1. Injection will not be used for hazardous waste disposal in any areas where seismic activity could potentially occur.
2. Injected wastes must be compatible with the mechanical components of the injection well system and the natural formation water. The waste generator may be required to perform physical, chemical, biological, or thermal treatment for removal of various contaminants or constituents from the waste to modify the physical and chemical character of the waste to assure compatibility.

3. High concentrations of suspended solids (typically >2 mg/L) can lead to plugging of the injection interval.
4. Corrosive media may react with the injection well components, with injection zone formation, or with confining strata with very undesirable results. Wastes should be neutralized.
5. High iron concentrations may result in fouling when conditions alter the valence state and convert soluble species to insoluble species.
6. Organic carbon may serve as an energy source for indigenous or injected bacteria, resulting in rapid population growth and subsequent fouling.
7. Wastestreams containing organic contaminants above their solubility limits may require pretreatment before injection into a well.
8. Site assessment and aquifer characterization are required to determine the suitability of a site for wastewater injection.
9. Extensive assessments must be completed prior to receiving approval from regulatory authority.

State-of-the-art fluid-transport modeling is considerably more advanced than that of geochemical-fate and transport modeling. Consequently, geochemical-fate modeling is most likely to be used if a fluid-flow no-migration standard cannot be met. Geochemical-fate transport modeling of deep-well-injected hazardous wastes is in the early stages of development, and its use in meeting current U.S. EPA Underground Injection Control regulations is unbroken ground. However, where the no-migration standard must be considered, there is a U.S. EPA guide[3] that can help determine whether geochemical-fate/transport modeling of a specific waste is even feasible, and what approaches might be taken.

20.2 CHARACTERISTICS OF INJECTED HAZARDOUS WASTES

This section discusses the characteristics of hazardous wastes typically injected into Class I injection wells. It includes the following:

1. The properties that define a waste as hazardous
2. The sources, amounts, and composition of existing deep-well-injected hazardous wastes
3. Trends and distribution of industrial and hazardous waste injection
4. The design and construction of deep-injection wells

20.2.1 IDENTIFYING HAZARDOUS WASTES

Wastes are defined as hazardous for the purposes of regulatory control in 40 CFR Part 261.[4] In this regulation, wastes are classified as hazardous either by being listed in tables within the regulation or by meeting certain specified characteristics. Thus, under 40 CFR Part 261 hazardous wastes are known either as “listed” or “characteristic” wastes. Some listed wastestreams, such as spent halogenated solvents, come from many industries and processes. Other listed wastestreams, such as American Petroleum Institute (API) separator sludges from the petroleum-refining industry, come from one particular industry and one process. A characteristic waste is not listed, but is classified as hazardous because it exhibits one or more of the following characteristics[4,5]:

1. Toxicity to living organisms
2. Reactivity
3. Corrosivity
4. Ignitability

Listed wastes also exhibit one or more of these characteristics. The significance of each of the characteristics listed above is discussed below and is summarized in Table 20.1.[3] Deep-well-injected

TABLE 20.1
Hazardous and Physicochemical Properties of Injected Wastes

Characteristic	Comment
Hazardous Characteristics	
Toxicity	Has toxic properties that result in classification as a hazardous waste, but specific properties may vary greatly
Reactivity	Reactivity usually reduced by dilution; actual concentration may affect toxicity and mobility
Corrosivity	May be a significant consideration in well design and geochemical fate
Ignitability	Not a significant consideration under injection conditions
Physical/Chemical Properties	
Normal physical state	Liquids or dissolved solids
Molecular weight	May affect structure–activity relationships
Density/specific gravity	Must be miscible in water
Solubility	Must be soluble or miscible in water
Boiling point	Greater than ambient temperatures
Melting point	Less than ambient temperatures
Vapor pressure/density	Water-soluble volatile compounds may be involved, but vapor pressure and vapor density are not significant considerations in deep-well injection
Flash point/autoignition point	Greater than ambient temperatures.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

wastes commonly contain several components that classify the waste as hazardous, along with other nonhazardous components.

20.2.1.1 Toxicity

A waste is toxic under 40 CFR Part 261 if the extract from a sample of the waste exceeds specified limits for any one of eight elements and five pesticides (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, methoxychlor, toxaphene, 2,4-D and 2,4,5-TP Silvex using extraction procedure (EP) toxicity test methods. Note that this narrow definition of toxicity relates to whether a waste is defined as hazardous for regulatory purposes; in the context of this chapter, toxicity has a broader meaning because most deep-well-injected wastes have properties that can be toxic to living organisms.

20.2.1.2 Reactivity

Reactivity describes a waste's tendency to interact chemically with other substances. Many wastes are reactive, but it is the degree of reactivity that defines a waste as hazardous. Hazardous reactive wastes are those that are normally unstable and readily undergo violent change without detonating, react violently with water, form potentially explosive mixtures with water, generate toxic gases or fumes when combined with water, contain sulfide or cyanide and are exposed to extreme pH conditions, or are explosive. Because deep-well-injected wastestreams are usually dilute (typically less than 1% waste in water), hazardous reactivity is not a significant consideration in deep-well injection, although individual compounds may exhibit this property at higher concentrations than those that exist in the wastestream. Nonhazardous reactivity is, however, an important property in deep-well injection, because when a reactive waste is injected, precipitation reactions that can lead to well plugging may occur.

20.2.1.3 Corrosivity

Corrosive wastes are defined as those wastes with a pH ≤ 2 or pH ≥ 12.5 (i.e., the waste is very acidic or very basic). Beyond its importance in defining a waste as hazardous, the corrosivity of wastes is also a property of concern to deep-well injection systems and operations. Corrosive wastes may damage the injection system, typically by electrochemical or microbiological means. Corrosion of injection-well pumps, tubing, and other equipment can lead to hazardous waste leaking into strata not intended for injection. For information on various types of electrochemical corrosion relevant to the injection-well system, the reader is referred to Warner and Lehr.[6] Other recommended sources include references 7 to 10. These sources discuss saturation and stability indexes for predicting the potential for corrosion or scaling (accumulation of carbonate and sulfate precipitates) in injection wells. The Stiff and Davis index[10] is recommended by Warner and Lehr[6] as most applicable to deep-well injection of hazardous wastes, because it is intended for use with highly saline groundwaters. Additionally, Ostroff[11] provides examples of how to use the index, Watkins[12] describes procedures that test for corrosion, and Davis[13] thoroughly discusses microbiological corrosion of metals.

20.2.1.4 Ignitability

As noted, deep-well-injected wastes are relatively dilute. Therefore, ignitability is not a significant consideration in deep-well injection, although in a concentrated form, individual compounds may exhibit this property. Ignitability has no further implications for the fate of deep-well-injected waste.

20.2.2 Sources, Amounts, and Composition of Deep-Well-Injected Wastes

The sources, amounts, and composition of injected hazardous wastes are a matter of record, because the Resource Conservation and Recovery Act (RCRA)[5,14] requires hazardous waste to be manifested (i.e., a record noting the generator of the waste, its composition or characteristics, and its volume must follow the waste load from its source to its ultimate disposal site). The sources and amounts of injected hazardous waste can be determined, therefore, based on these records. Table 20.2 shows the estimated volume of deep-well-injected wastes by industrial category.[3] More than 11 billion gallons of hazardous waste were injected in 1983. Organic chemicals (51%) and petroleum-refining and petrochemical products (25%) accounted for three-quarters of the volume of injected wastes that

TABLE 20.2
Estimated Volume of Deep-Well Injected Wastes by Industrial Category

Industrial Category	Volume (MG/yr)	Percent of Total
Organic chemical	5868	51
Petroleum refining and petrochemical products	2888	25
Miscellaneous chemical products	687	6
Agricultural chemical products	525	4.5
Inorganic chemical products	254	2.2
Commercial disposal	475	4
Metals and minerals	672	5.8
Aerospace and related industry	169	1.5
Total	11,538	100.0

Source: U.S. EPA, Report to Congress on Injection of Hazardous Wastes, EPA 570/9-85-003, NTIS PB86-203056, U.S. EPA, Washington, 1985.

year. The remaining 24% was divided among six other industrial categories: miscellaneous chemical products, agricultural chemical products, inorganic chemical products, commercial disposal, metals and minerals, and aerospace and related industry.

Although the general composition of each shipment of wastes to an injection well may be known, a number of factors makes it difficult to characterize fully the overall composition of industrial wastewaters at any one well. These factors include the following[15]:

1. Variations in flow, in concentrations, and in the nature of organic constituents over time
2. Biological activity that may transform constituents over time
3. Physical inhomogeneity (soluble and insoluble compounds)
4. Chemical complexity; an example of the complexity of organic wastes is illustrated in the work of Roy and colleagues,[16] which presents an analysis of an alkaline pesticide-manufacturing waste—this waste contained more than 50 organic compounds, two-fifths of which could not be precisely identified

Although no systematic database exists on the exact composition of deep-well-injected wastes, in a survey of 209 operating waste-injection wells, Reeder[17] found that 53% injected one or more chemicals identified in that study as hazardous. The U.S. EPA gathered data for 108 wells (55% of total active wells) that were under operation.[3] A little more than half of the undiluted waste volume was composed of nonhazardous inorganics (52%). Acids were the most important constituent by volume (20%), followed by organics (17%). Heavy metals and other hazardous inorganics made up less than 1% of the total volume in the 108 wells. About a third of the wells injected acidic wastes and about two-thirds injected organic wastes. Although the percentage of heavy metals by volume was low, almost one-fifth of the wells injected wastes containing heavy metals. An injected wastestream is composed of the waste material and a large volume of water. It is reported that typical ratios in the total volume of injected fluids are 96% water and 4% waste.

The U.S. EPA gathered data also showed that the average concentration of all the acidic wastes exceeded 40,000 mg/L. Concentrations of metals ranged from 1.4 mg/L (chromium) to 5500 mg/L (unspecified metals, probably containing multiple species). Five of the 18 organic constituents exceeded 10,000 mg/L (total organic carbon, organic acids, formaldehyde, chlorinated organics, and formic acid); four others exceeded 1000 mg/L (oil, isopropyl alcohol, urea nitrogen, and organic peroxides).

20.2.3 GEOGRAPHIC DISTRIBUTION OF HAZARDOUS WASTE INJECTION WELLS

The use of wells for disposal of industrial wastes dates back to the 1930s, but this method was not used extensively until the 1960s, when it was implemented primarily in response to more stringent water pollution control regulations.

The number of industrial-waste injection wells more than doubled between 1967 and 1986.[3] In 1986, Class I injection wells were concentrated in two states, Texas (112 wells) and Louisiana (70 wells), which between them had a total of 69% of all wells (263 wells). Growth from 1984 to 1986 was concentrated in Texas, with a 38% increase from 81 to 112 wells. The only other states to show a significant increase from 1984 to 1986 were Indiana (13 proposed wells) and California (7 proposed wells). Nine states had had industrial-waste injection wells in the past but did not have any permitted Class I wells in 1986 (Alabama, Colorado, Iowa, Mississippi, Nevada, North Carolina, Pennsylvania, Tennessee, and Wyoming). One state (Washington) had a Class I well in 1986, but no record of industrial wastewater injection before that year. The total number of industrial-waste injection wells increased to 300 at the end of the 1990s and beginning of this century, approximately 100 Class I hazardous waste injection wells and about 200 Class I wells that hold nonhazardous waste.[1,18]

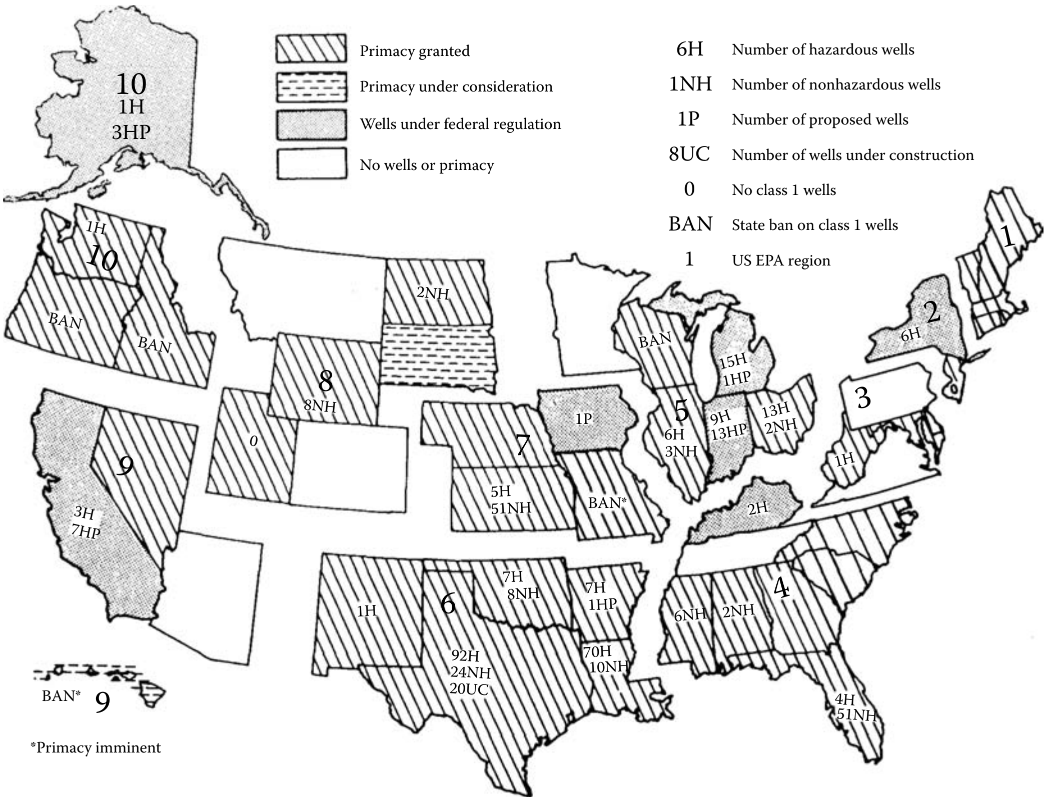


FIGURE 20.1 Regulatory status and number of Class I wells in the U.S. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

Figure 20.1 shows the number of Class I wells in the 1986 survey by state, divided into U.S. EPA regions, and also indicates the regulatory status of such wells in each state as of 1989. The map shows the heavy concentration of hazardous waste injection wells in three geologic basins: Gulf Coast, Illinois Basin, and the Michigan Basin.[3]

20.2.4 DESIGN AND CONSTRUCTION OF DEEP-INJECTION WELLS

The following subsections give a description of the design and construction of deep-injection wells.[19–23]

20.2.4.1 Surface Equipment Used in Waste Disposal

Figure 20.2 shows the surface equipment used in a typical subsurface waste-disposal system. Detailed discussion of surface treatment methods can be found in Warner and Lehr.[6] The individual elements are listed in the following:

1. *Sump tank*. A sump tank or an open 113,550 to 189,250 L (30,000 to 50,000 gal) steel tank is commonly used to collect and mix wastestreams. An oil layer or, in a closed tank, an inert gas blanket is often used to prevent air contact with the waste. Alternatively, large, shallow, open ponds may provide sufficient detention time to permit sedimentation of particulate matter. Such ponds are often equipped with cascade, spray, or forced-draft

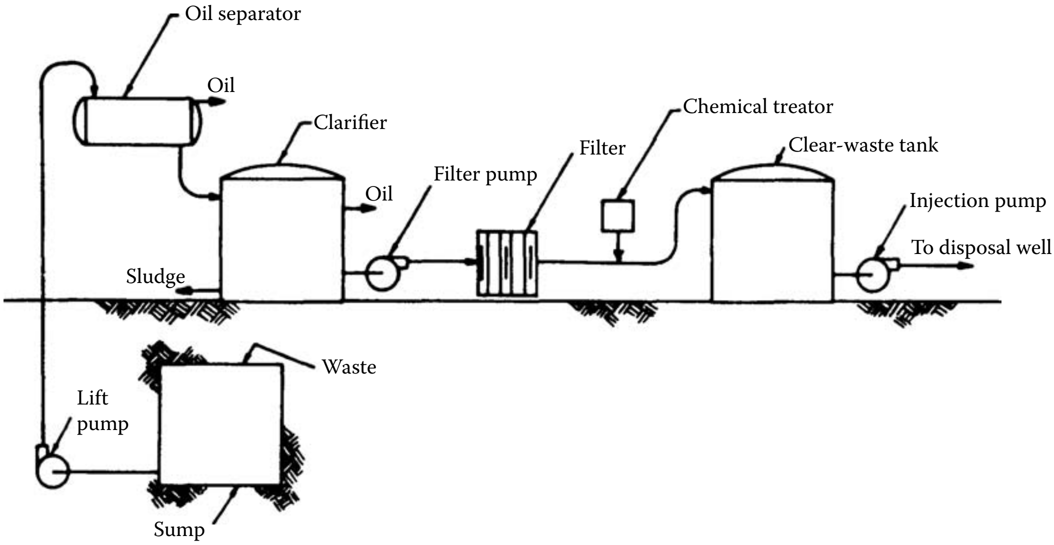


FIGURE 20.2 Above-ground components of a subsurface waste disposal system. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

aerators to oxidize iron and manganese salts to insoluble forms that precipitate in the aeration ponds.

2. *Oil separator.* An oil separator is used when the waste contains oil, because oil tends to plug the disposal formation. The waste is passed through a settling tank equipped with internal baffles to separate the oil from the waste.[24]
3. *Clarifier.* A clarifier removes such particulate matter as polymeric flocs, dirt, oil, and grease. It is often a tank or a pond in which the detention time is long enough to allow suspended particles to settle gradually.[25] The process may also be accelerated by adding a flocculating agent such as aluminum sulfate, ferric sulfate, or sodium aluminate.[26] Tank clarifiers are often equipped with a mechanical stirrer, sludge rake, and surface skimmer that continuously remove sludge and oil.
4. *Filter.* A filter is used in some cases when coagulation and sedimentation do not completely separate the solids from the liquid waste in areas where sand and sandstone formations are susceptible to plugging. Filters with a series of metal screens coated with diatomaceous earth or cartridge filters are typically used.[27] Where limestone formations with high solution porosity are used for injection, filtration is usually not required.
5. *Chemical treater.* A chemical treater is used to inject a bactericide if microorganisms could cause fouling of injection equipment and plugging of the injection reservoir.
6. *Clear-waste tank.* An unlined steel clear-waste tank is typically used to hold clarified waste before injection. The tank is equipped with a float switch designed to start and stop the injection pump at predetermined levels.
7. *Injection pump.* An injection pump is used to force the waste into the injection zone, although in very porous formations, such as cavernous limestone, the hydrostatic pressure of the waste column in the well is sufficient. The type of pump is determined primarily by the well-head pressures required, the volume of liquid to be injected, and the corrosiveness of the waste. Single-stage centrifugal pumps are used in systems that require well-head pressures up to about 10.5 kg/cm^2 (150 psi), and multiplex piston pumps are used to achieve higher injection pressures.

20.2.4.2 Injection-Well Construction

Most injection wells are drilled using the rotary method, although, depending on the availability of equipment and other site-specific factors, reverse-rotary or cable-tool drilling may be used. The construction of an injection well incorporates several important elements[28]:

1. Bottom-hole and injection-interval completion
2. Casing and tubing
3. Packing and cementing
4. Corrosion control
5. Mechanical integrity testing.

A detailed discussion of the technical aspects of industrial-waste injection-well construction can be found in Warner and Lehr.[6] U.S. EPA[20] also presents a survey of well construction methods and materials used for 229 hazardous waste injection wells. Two types of injection well completions are used with hazardous waste injection wells:

1. *Open hole.* Open hole completion is typically used in competent formations such as limestone, dolomite, and consolidated sandstone that will stand unsupported in a borehole. In 1985, 27% of Class I wells were of this type, with most located in the Illinois Basin.
2. *Gravel pack.* Gravel pack and perforated completions are used where unconsolidated sands in the injection zone must be supported. In gravel-pack completions the cavity in the injection zone is filled with gravel or, more typically, a screen or liner is placed in the injection-zone cavity before the cavity is filled with gravel. In perforated completions, the casing and cement extend into the injection zone and are then perforated in the most permeable sections. In 1985, 53% of Class I wells were perforated and 17% were screened.[20]

Casing and tubing are used to prevent the hole from caving in and to prevent aquifer contamination by confining wastes within the well until they reach the injection zone. Lengths of casing of the same diameter are connected together to form casing strings. Usually, two- or three-casing strings are used. The outer casing seals the near-surface portion of the well (preferably to below the point where aquifers containing less than 10,000 mg/L total dissolved solids, potential underground sources of drinking water, are located). The inner casing extends to the injection zone. Tubing is placed inside the inner casing to serve as the conduit for injected wastes, and the space between the tubing and casing is usually filled with kerosene or diesel oil after packing and cementing are completed.

Packers are used at or near the end of the injection tubing to plug the space, called the annulus, between the injection tubing and the inner casing. Cement is applied to the space between the outer walls of the casing and the borehole or other casing. Portland cement is used most commonly for this purpose, although when acidic wastes are injected, special acid-resistant cements are sometimes used in the portion of the well that passes through the confining layers.

Corrosion control can be handled several ways:

1. By using corrosion-resistant material in constructing the well
2. By treating the wastestream through neutralization or other measures
3. By cathodic protection

Mechanical integrity testing is required by U.S. EPA regulations (40 CFR 146.08) to ensure that an injection well has been constructed or is operating without significant leakage from the casing, tubing, or packer or upward movement of fluid through vertical channels adjacent to the well bore. A detailed discussion of mechanical integrity can be found in Reference 28.

20.3 PROCESSES AFFECTING THE GEOCHEMICAL FATE OF DEEP-WELL-INJECTED WASTES

This section examines the major processes that affect the fate of deep-well-injected hazardous wastes. The focus is on processes that (1) are known to occur in the deep-well environment or (2) have not been directly observed but are theoretically possible.

20.3.1 Overview of Fate-Influencing Processes in Chemical Systems

20.3.1.1 Key Characteristics of Chemical Systems

A chemical system is a mixture of individual components. Chemical systems can be described by interactions that occur within the system and by the effect these processes have on the chemical composition and phases of the system. Interactions that change the chemical structure of system components are called chemical reactions. (Other interactions, such as processes that alter the solubility of system components, change the system without altering chemical structures.) Whether one reaction or a set of reactions occurs and how quickly the reaction proceeds are determined by the thermodynamics and kinetics of the system.

A substance may exist in one of three phases—solid, liquid, or gas. The mobility of a substance in the subsurface is influenced by which of several forms or species it may take. Species in deep-well-injection formations fall into six main categories[3]:

1. Free ions are surrounded only by water molecules and are very mobile in groundwater. Acid–base and dissolution reactions create free ions.
2. Species with low solubility in water may exist in solid form (e.g., Ag_2S, $BaSO_4$) or liquid form (e.g., chlorinated solvents). Precipitation reactions and immiscible-phase separation are important processes affecting this type of speciation.
3. Metal/ligand complexes (such as $Al[OH]^{2+}$, Cu–humate) and organic/ligand complexes tend to be mobile in groundwater.
4. Physically adsorbed species are immobile in groundwater but may be remobilized if replaced by other species with a stronger affinity to the solid surface.
5. Species held on a surface by ion exchange (such as calcium ions on clay) are also immobile in groundwater. As with physically adsorbed species, they may be replaced by ions with a greater affinity to the solid surface.
6. Species may differ by oxidation state: for example, manganese(II) and (IV); iron(II) and (III); and chromium(III) and (VI). Oxidation state is influenced by the redox potential. Mobility is affected because oxidation state influences precipitation–dissolution reactions and also toxicity in the case of heavy metals.

Dissolved species may be ionic or nonionic. In ionic species, an excess or shortage of electrons in the chemical structure creates a net positive or negative charge. In nonionic species, all negative and positive charges cancel each other out to form a neutral molecule. Cations are positively charged ions (Na^+, Ca^{2+}) and anions are negatively charged (SO_4^{2-}). The ability of a neutral substance to dissociate into ionic species is more common with inorganic substances than with organic substances. Acid–base reactions determine the distribution between ionic and nonionic species.

Neutral species may be nonpolar or polar. In nonpolar species, positively charged protons and negatively charged electrons are arranged in the molecular structure so as to create a uniform neutral charge on the molecule's surface. In polar species, the molecular structure creates chained poles on the molecule, even though the net charge is zero. Water (H_2O) is a polar molecule, with the positive pole on the side of the hydrogen atom and the negative pole on the side of the oxygen atoms. Nonpolar molecules tend to be hydrophobic (water-avoiding).

The thermodynamics of a system relate to the stability of substances within the system, that is, whether a reaction can occur. Kinetics relates to reaction mechanisms and rate, that is, how fast reactions can occur. Bedient and colleagues[29] reviewed the basic empirical equations defining zero-order, first-order, and second-order kinetic rate laws. An equilibrated state implies that as long as there are no significant changes in environmental factors affecting the system, the chemical composition and phases of the system will not change. Equilibrium does not necessarily imply that chemical processes cease. However, it does mean that for every reaction in one direction, a compensating reaction occurs in the opposite direction.

In nonequilibrium systems, chemical processes spontaneously alter the composition or phase of the system until equilibrium is attained. Simple systems, such as a mixture of sodium chloride and water, attain equilibrium quickly, whereas complex systems may reach equilibrium only after decades or eons.

The term "steady state" is sometimes used to describe chemical systems where thermodynamically unstable species exist but the rate of conversion to stable species is so slow that a quasi-equilibrated state exists. Because deep-well-injected wastes may be very complex chemical systems, the attainment of true equilibrium is uncertain.

Chemical reactions may result from interactions among and between the three phases of matter: solid, liquid, and gas. The major interactions that occur in the deep-well environment are those between different liquids (injected waste with reservoir fluids) and those between liquids and solids (injected wastes and reservoir fluids with reservoir rock). Although gases may exist, they are usually dissolved in liquid at normal deep-well pressures.

Two chemical properties important in predicting fate in the deep-well environment are homogeneity and reversibility. Chemical processes can be broadly classified as either homogeneous or heterogeneous and either reversible or irreversible.

Homogeneous reactions in the deep-well environment take place in only one phase (aqueous). These reactions generally occur uniformly throughout the phase and are easier to study and predict than heterogeneous reactions. Heterogeneous reactions (for example, adsorption) tend to occur at the interface between phases. Some reactions (such as precipitation) may result in phase changes. Heterogeneous reactions also tend to occur more actively at some locations in the chemical system than at others. Bacterial decomposition of wastes is a heterogeneous process that will be more active in locations with conditions favorable to organisms and less active elsewhere.

The reversibility of reactions is another important characteristic in assessing the fate of deep-well-injected wastes. Depending on environmental conditions, reversible reactions readily proceed in either or both directions. Most acid–base reactions exemplify reversible processes. In aqueous solutions, relatively minor changes in such factors as pH or concentration can change the direction of these reactions. Irreversible reactions, typified by hydrolysis, have a strong tendency to go in one direction only.

Table 20.3 lists the reversible and irreversible processes that may be significant in the deep-well environment.[3] The characteristics of the specific wastes and the environmental factors present in a well strongly influence which processes will occur and whether they will be irreversible. Irreversible reactions are particularly important. Waste rendered nontoxic through irreversible reactions may be considered permanently transformed into a nonhazardous state. A systematic discussion of mathematical modeling of groundwater chemical transport by reaction type is provided by Rubin.[30]

20.3.1.2 Fate-Influencing Processes in the Deep-Well Environment

At the simplest level, the processes that most influence geochemical fate can be divided into three groups: partition, transformation, and transport:

1. *Partition processes* affect the form or state of a specific chemical substance at a given time or under specific environmental conditions, but not its chemical structure or toxicity.

TABLE 20.3
Characteristics of Chemical Processes That May Be Significant in the Deep-Well Environment

Characteristic	Types of Reactions
Homogeneous	Acid–base, hydrolysis, hydration, neutralization, oxidation–reduction, polymerization, thermal degradation
Heterogeneous	Adsorption–desorption, precipitation-dissolution, immiscible-phase separation, biodegradation, complexation
Reversible	Acid–base, neutralization, oxidation–reduction (most inorganic and some biologically mediated), adsorption–desorption, precipitation-dissolution, complexation
Irreversible	Hydrolysis, oxidation–reduction (biodegradation of anthropogenic inorganics), immiscible-phase separation

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

Thus, a substance may be in a solid form or in solution (described by the precipitation–dissolution process), but its toxicity remains unaltered regardless of form. The form or state of a substance, however, influences the transformation and transport processes that can occur. For this reason, partition processes are important to define in a fate assessment.

2. *Transformation processes* alter the chemical structure of a substance. In the deep-well environment, the transformation processes that may occur are largely determined by the conditions created by partition processes and the prevalent environmental factors. Transport processes do not need to be considered if transformation processes irreversibly change a hazardous waste to a nontoxic form.
3. *Transport processes* carry wastes through the subsurface environment and must be considered in a fate assessment if the interaction of partition and transformation processes does not immobilize or alter the hazardous waste. Waste migration can take place either in solution or in solid form (particle migration).

Table 20.4 presents the partition and transformation processes known to occur in the near-surface environment along with the special factors that should be considered when evaluating data in the context of the deep-well environment. Geochemical processes affecting hazardous wastes in deep-well environments have been studied much less than those occurring in near-surface environments (such as soils and shallow aquifers). Consequently, laboratory data and field studies for a particular substance may be available for near-surface conditions, but not for deep-well conditions.

As Table 20.4 shows, several processes can occur in both the near-surface and deep-well environments. For example, neutralization of acidic or alkaline wastes is a straightforward process, and although temperature differences between the two environments may need to be considered, no other factors make the deep-well setting distinctly different. The same holds true for oxidation–reduction (redox) processes.

The remaining processes, although they occur under near-surface and deep-well conditions, are less applicable to the latter. Distinct differences between the two environments, however, can lead to significant differences in how the processes affect a specific hazardous substance. Compared with the near-surface environment, the deep-well environment is characterized by higher temperatures, pressures, and salinity, and lower organic matter content and Eh (oxidation–reduction potential).

Table 20.5 lists the partition and transformation processes applicable in the deep-well environment and indicates whether they significantly affect the toxicity or mobility of hazardous wastes. None of the partition processes results in detoxification (decomposition to harmless inorganic constituents), but all affect mobility in some way. All transformation processes except complexation can result in detoxification; however, because transformation processes can create new toxic substances, the mobility of the waste can be critical in all processes except neutralization.

TABLE 20.4
Near-Surface Geochemical Processes and Their Relevance to the Deep-Well Environment

Process	Surface Data Applicability to Deep-Well Environment	Comments
Partition Processes		
Acid–base equilibria	Partly	Near-surface studies tend to investigate fresh or moderately saline water, which creates quite different conditions for acid–base equilibria. Studies of ocean geochemistry come closest to approximating deep-well conditions.
Adsorption–desorption	Partly	Mechanisms for adsorption on similar materials will be similar. Soil adsorption data generally do not reflect the saturated conditions of the deep-well environment. Organic-matter content is a major factor affecting adsorption in the near-surface; its significance in the deep-well environment is less clear. Fate studies involving artificial recharge are probably useful, but differences between fresh waters and deep brines may reduce relevance.
Precipitation–dissolution	Partly	Higher temperatures, pressures, and salinity of the deep-well environment may result in significant differences between reactions in the two environments.
Immiscible-phase separation	No	Fluids (such as gasoline) that are immiscible in water are a significant consideration in near-surface contamination. Deep-well injection is limited to wastestreams that are soluble in water. Well blowout from gaseous carbon dioxide formation is an example of this process that is distinct to the deep-well environment.
Transformation Processes		
Volatilization	No	No atmosphere.
Photolysis	No	No sunlight.
Biodegradation	Partly	Some near-surface bacteria appear capable of entering and surviving in the deep-well environment. However, in general, temperature and pressure conditions in the deep-well environment are unfavorable for microbiota that are adapted to near-surface conditions. Biological transformations are primarily anaerobic.
Complexation	Partly	Humic substances are very significant factors in near-surface complexation processes, probably less so in the deep-well environment. Data on complexation in saline waters are probably most relevant.
Hydrolysis	Partly	Basic processes will be the same. Higher salinity of deep-well environment may affect rate constants.
Neutralization	Partly	Basic process is the same, but some adjustments may be required for pressure/temperature effects.
Oxidation–reduction	Partly	The deep-well environment tends to be more reducing than the near-reduction surface environment, but equally reducing conditions occur in the near-surface. Some adjustments may be required for pressure/temperature effects.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

TABLE 20.5
Significance of Chemical Processes in the Deep-Well Environment

Process	Detoxification	Mobility	Biotic/Abiotic
Partitioning			
Acid–base equilibrium	No	Yes	Both
Adsorption–desorption	No	Yes	Abiotic
Precipitation–dissolution	No	Yes	Abiotic
Immiscible-phase separation	No	Yes	Both
Transformation			
Biodegradation	Yes	Yes	Biotic
Complexation	No	Yes	Abiotic
Hydrolysis	Yes	Yes	Both
Neutralization	Yes	No	Abiotic
Oxidation–reduction	Yes	Yes	Both

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

Table 20.5 also indicates whether a process is biotic (mediated or initiated by organisms in the environment), abiotic (not involving biological mediation), or both. Biotic processes are limited to environmental conditions that favor growth of mediating organisms. Abiotic processes occur under a wide range of conditions. Adsorption, precipitation, complexation, and neutralization are abiotic; all other processes in Table 20.5 may be either.

20.3.2 PARTITION PROCESSES

Partition processes determine how a substance is distributed among the liquid, solid, and gas phases and determine the chemical form or species of a substance. Partitioning usually does not affect the toxic properties of the substance. Partitioning can, however, affect the mobility of the waste, its compatibility with the injection zone, or other factors that influence fate in the deep-well environment. The major partition processes are as follows:

1. Acid–base reactions
2. Adsorption–desorption
3. Precipitation–dissolution
4. Immiscible-phase separation

20.3.2.1 Acid–Base Reactions

Acid–base reactions affect pH (the concentration of hydrogen ions in solution), which is a controlling factor in the type and rate of many other chemical reactions.

Acids dissociate in solution yielding hydrogen ions and anions according to the general reaction

$$\text{HA (neutral)} \longleftrightarrow \text{H}^+ \text{ (cation)} + \text{A}^- \text{ (anion)} \quad (20.1)$$

The ionization is reversible. The anion (acting as a weak base) can recombine with the hydrogen ion to reform neutral HA. Both reactions occur continuously in solution, with the extent of ionization dependent on the strength of the acid. Strong acids, such as HCl, ionize completely in dilute aqueous solution. Thus a 0.01 molar (10^{-2} molar) solution has a pH of 2. Weak acids, such as acetic and other organic acids, ionize only slightly in solution and form solutions with pH from 4 to 6.

In the above example, the anion (A^-) functions as a base when it combines with a hydrogen ion. (By definition, any substance that combines with hydrogen ions is a base. Like strong acids, strong bases ionize completely in a dilute aqueous solution.) Thus NaOH dissolves in water to form hydroxide ions, which in turn function as a base when they combine with hydrogen ions to form water, as shown by the general equations

$$\mathrm{MOH} \longleftrightarrow \mathrm{M}^+ + \mathrm{OH}^- \tag{20.2a}$$

$$\mathrm{OH}^- + \mathrm{H}^+ \longleftrightarrow \mathrm{H_2O} \tag{20.2b}$$

Strong acids (those that ionize completely in solution) are more likely to dissolve solids because charged particles such as hydrogen ions will interact more strongly with solids than will neutral particles. Weak acids do not readily donate hydrogen ions and consequently remain mostly in the neutral form. As a result, weak acids do not dissolve solids as readily as strong acids.

Strong bases (those that most readily extract hydrogen ions from solution) are also found predominantly in ionic forms and are similarly more reactive with solids than weak bases, which remain mostly in neutral form. The extent to which any base will extract hydrogen ions from solution depends on pH and the strength of the base.Acid–base reactions occur quickly. When the pH of a solution changes, acids and bases readily attain a new equilibrium between neutral and ionic forms. Because toxic organics almost always exist in very low concentrations and tend to be weak acids or weak bases, they have little, if any, influence on the pH of water. Acid–base equilibrium reactions involving hazardous organic compounds do not affect the toxicity of the waste and, as noted above, do not strongly influence pH.

When weak acids and bases ionize in wastestreams, pH is affected very little, but when strong acids and bases ionize in wastestreams, pH is affected dramatically. By definition, wastestreams having a $\mathrm{pH} \leq 2$ (highly acidic) or a $\mathrm{pH} \geq 12.5$ (strongly basic) are highly corrosive and are regulated as hazardous. Acid–base reactions can neutralize acidic or basic hazardous waste by raising or lowering its pH.

20.3.2.2 Adsorption and Desorption

Adsorption is a physicochemical process whereby ionic and nonionic solutes become concentrated from solution at solid–liquid interfaces.[31,32] Adsorption and desorption are caused by interactions between and among molecules in solution and those in the structure of solid surfaces. Adsorption is a major mechanism affecting the mobility of heavy metals and toxic organic substances and is thus a major consideration when assessing transport. Because adsorption is usually fully or partly reversible (desorption), only rarely can it be considered a detoxification process for fate-assessment purposes. Although adsorption does not directly affect the toxicity of a substance, the substance may be rendered nontoxic by concurrent transformation processes such as hydrolysis and biodegradation. Many chemical and physical properties of both aqueous and solid phases affect adsorption, and the physical chemistry of the process itself is complex. For example, adsorption of one ion may result in desorption of another ion (known as ion exchange).

Adsorption is typically exothermic (i.e., releases energy in the process of bonding), but can be endothermic, and can be classified into two groups, based on the energies involved: chemical adsorption and physical adsorption. Chemical adsorption is more significant for heavy metals, either in the form of ion exchange or interactions involving metal complexes.

In chemical adsorption (also called chemisorption), chemical bonds are formed between the adsorbate molecule and the adsorbent. These bonds typically involve energies on the order of 7 kcal/mol or greater.[33] These energies distinguish them from physical bonds, which typically involve energies less than 7 kcal/mol. Ion exchange, ligand exchange, protonation, and hydrogen bonds typically fall in the category of chemical bonds. Depending on the classification scheme used, numerous distinct types of chemical bonds have been identified in the laboratory under controlled conditions. Determining bonding mechanisms in the natural environment is much more difficult because of the diversity and complexity of adsorption surfaces.

20.3.2.3 Precipitation and Dissolution

Precipitation is a phase-partitioning process whereby solids separate from a solution.[34] Dissolution involves movement from the solid or gaseous phase to the aqueous phase. Solids dissolve into ions, whereas gases retain their original chemical structure when dissolved. The solubility of a compound (its tendency to dissolve in water or other solutions) is the main property affecting the precipitation–dissolution process.

The concentration of a compound in water is controlled by its equilibrium solubility or solubility constant (the maximum amount of a compound that will dissolve in a solution at a specified temperature and pressure). Equilibrium solubility will change with environmental parameters such as temperature, pressure, and pH; for example, the solubility of most organic compounds triples when temperature rises from 0°C to 30°C. Each type of waste has a specific equilibrium solubility at a given temperature and pressure. The solubility of toxic organic compounds is generally much lower than that of inorganic salts. This characteristic is particularly true of nonpolar compounds because of their hydrophobic character.

Precipitation usually occurs when the concentration of a compound in solution exceeds the equilibrium solubility, although slow reaction kinetics may result in "supersaturated" solutions. For organic wastes in the deep-well environment, precipitation is not generally a significant partitioning process; in certain circumstances, however, it may need to be considered. For example, pentachlorophenol precipitates out of solution when the solution has a pH of <5,[35,36] and polychlorophenols form insoluble precipitates in water high in Mg^{2+} and Ca^{2+} ions.[37] Also, organic anions react with such elements as Ca^{2+}, Fe^{2+}, and Al^{3+} to form slowly soluble to nearly insoluble compounds.

Precipitation may be significant for heavy metals and other inorganic constituents in injected wastes. For example, sulfide ions have a strong affinity for metal ions, precipitating as metal sulfides. The dissolved constituents in injected wastes and reservoir fluids would not be in equilibrium with the *in situ* brines because of the fluids' different temperature, pH, and Eh. When the fluids are mixed, precipitation reactions can lead to injection-well plugging.

Coprecipitation is a partitioning process whereby toxic heavy metals precipitate from the aqueous phase even if the equilibrium solubility has not been exceeded. This process occurs when heavy metals are incorporated into the structure of silicon, aluminum, and iron oxides when these latter compounds precipitate out of solution. Iron hydroxide collects more toxic heavy metals (chromium, nickel, arsenic, selenium, cadmium, and thorium) during precipitation than aluminum hydroxide.[38] Coprecipitation is considered to effectively remove trace amounts of lead and chromium from solution in injected wastes at New Johnsonville, Tennessee.[39] Coprecipitation with carbonate minerals may be an important mechanism for dealing with cobalt, lead, zinc, and cadmium.

Dissolution of carbonates (acidic wastes), sand (alkaline wastes), and clays (both acidic and alkaline wastes) can neutralize deep-well-injected wastes.[39] Because precipitation–dissolution reactions are highly dependent on environmental factors such as pH and Eh, changes in one or more factors as a result of changes in injected-waste characteristics, or varying percentages of injected waste and reservoir fluids concentrations, may result in re-solution or reprecipitation of earlier reaction products. This sensitivity to environmental factors increases the complexity of predicting precipitation–dissolution reactions, because different equilibrium solubilities of a compound may exist in different parts of the injection zone depending on the proportions of waste and reservoir fluid. Similarly, a sequence of precipitation and dissolution reactions may take place at a given location of the injection zone as the concentration of injected wastes increases.

20.3.2.4 Immiscible-Phase Separation

An insoluble liquid or gas will separate from water, resulting in immiscible-phase separation. The behavior of nonaqueous-phase liquids (NAPLs) that may be lighter (LNAPLs) or denser (DNAPLs) than water is important in near-surface groundwater contamination studies.[40] However, aqueous-phase separation is generally not an issue in the deep-well environment because injected hazardous wastes are usually dilute. Failure to remove immiscible oily fluids from injected wastes potentially may cause plugging in the injection zone. Density and viscosity differences between injected and reservoir fluids, however, may need to be considered in transport modeling. Generally, pressures are high enough in the deep-well environment to keep gases such as carbon dioxide, generated as products of waste–reservoir interactions, in solution. Under certain conditions of high temperature and high waste concentrations, however, injected hydrochloric acid can cause carbon dioxide to separate from the liquid and produce a well blowout.

20.3.3 TRANSFORMATION PROCESSES

Transformation processes change the chemical structure of a compound. Because not all transformation processes convert hazardous wastes to nonhazardous compounds, geochemical fate assessment must consider both the full range of transformation processes that may occur and the toxicity and mobility of the resulting products. For deep-well-injected wastes, transformation processes and subsequent reactions may lead to one or more of the following:

1. Detoxification
2. Transtoxification
3. Toxification

Detoxification is an irreversible change in a substance from toxic to nontoxic form. For example, when an organic substance breaks down into its inorganic constituents, detoxification has taken place. Transtoxification occurs when one toxic compound is converted into another toxic compound. Toxification is the conversion of a nontoxic compound to a toxic substance. Table 20.6 lists some examples of each.

Transformation processes that may be significant in deep-well-injection fate assessments are as follows:

1. Neutralization
2. Complexation
3. Hydrolysis
4. Oxidation–reduction
5. Catalysis
6. Polymerization
7. Thermal degradation
8. Biodegradation

Two other processes that may transform hazardous wastes are photolysis and volatilization, but they are not considered here because they do not occur in the deep-well environment.

20.3.3.1 Neutralization

Acidic wastes with a pH of ≤2.0 and alkaline wastes with a pH of ≥12.5 are defined as hazardous (40 CFR Part 261). To meet the regulatory definition of nonhazardous, acidic wastes must be neutralized to a pH of >2.0 by reducing the hydrogen ion concentration, and alkaline wastes must be neutralized to a pH of ≤12.5 by increasing the hydrogen ion concentration.

Carbonates (limestone and dolomite) will dissolve in and neutralize acidic wastes with the following process:

$$CaCO_3 \longrightarrow Ca^{2+} + CO_3^{2-} \text{ (dissolution)} \tag{20.3}$$

$$CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O \text{ (neutralization)} \tag{20.4}$$

TABLE 20.6
Examples of the Effects of Transformation Processes on the Toxicity of Substances

Examples	
Type of Transformation	**Process**
Detoxification	
Cyanide → amide → acids + ammonia	Hydrolysis
Cyanide → sulfate + carbon + nitrogen	Biooxidation
Nitrile → amide → acids + ammonia	Hydrolysis
Alkyl halide → alcohol + halide ion	Hydrolysis
Chlorobenzene → $CO_2 + Cl^- + H_2O$	Biooxidation
1,3-Dichlorobenzene → $CO_2 + Cl^- + H_2O$	Biooxidation
1,4-Dichlorobenzene → $CO_2 + Cl^- + H_2O$	Biooxidation
Vinyl chloride → $CO_2 + Cl^- + H_2O$	Bioreduction
Transtoxification	
2,4-D ester → 2,4-D acid (increased)	Hydrolysis
Phenol + formaldehyde → phenolic resins	Polymerization
Aldrin → dieldrin	Oxidation
DDT → DDD	Reduction
o-Xylene → o-toluic acid	Cometabolism
Benzene → phenol	Biooxidation
Carbon tetrachloride → chloroform → methylene chloride	Bioreduction
Ethylbenzene → phenylacetic acid	Cometabolism
1,1,1 -Trichloroethane → 1,1-dichloroethane → chloroethane	Bioreduction
Tetrachloroethylene → trichloroethylene → various dichloroethenes → vinyl chloride	Bioreduction
1,2-Dichloroethane → vinyl chloride	Hydrolysis
Inorganic mercury → methyl mercury	Bioreduction
Nitrilotriacetate → nitrosamines	Bioreduction
Toxification	
Amines → nitrosamines	Biooxidation

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

When calcium carbonate goes into solution, it releases basic carbonate ions (CO_3^{2-}), which react with hydrogen ions to form carbon dioxide (which will normally remain in solution at deep-well-injection pressures) and water. Removal of hydrogen ions raises the pH of the solution. However, aqueous carbon dioxide serves to buffer the solution (i.e., re-forms carbonic acid in reaction with water to add H^+ ions to solution). Consequently, the buffering capacity of the solution must be exceeded before complete neutralization will take place. Nitric acid can react with certain alcohols and ketones under increased pressure to increase the pH of the solution, and this reaction was proposed by Goolsby[41] to explain the lower-than-expected level of calcium ions in backflowed waste at the Monsanto waste injection facility in Florida.

Quartz (SiO_2) and other silicates are generally stable in acidic solutions but will dissolve in highly alkaline waste solutions, decreasing the pH of the waste. The process by which this reaction occurs is complicated because it creates complex mixtures of nonionic and ionic species of silica. Scrivner and colleagues[39] discuss these reactions in some detail. They observe that the silicates in solution buffer the liquid. Also, laboratory experiments in which alkaline wastes have been mixed with sandstone have shown relatively small reductions in pH. At near-surface temperature and pressure conditions, an alkaline waste remains hazardous, but at simulated subsurface temperatures and pressures, the waste is rendered nonhazardous, ranging in pH from 11.5 to 12.4 in the experiments performed by Roy and colleagues.[33] However, the pH of the sandstone–waste mixture remained above 12.5 in other investigations, possibly because a higher solid/liquid ratio (less sandstone per volume of liquid) was used.

Reactions with clay minerals can neutralize both low-pH and high-pH solutions. Neutralization of acids occurs when hydrogen ions replace Al, Mg, and Fe. In alkaline solutions, neutralization is more complex and may involve cation exchange, clay dissolution, and reaction of cations with hydroxide ions to form new minerals called zeolites.[39]

20.3.3.2 Complexation

A complex ion is one that contains more than one ion. Because of its effect on mobility, complexation, the process by which complex ions form in solution, is very important for heavy metals and may be significant for organic wastes. Heavy metals are particularly prone to complexation because their atomic structure (specifically the presence of unfilled d-orbitals) favors the formation of strong bonds with polar molecules, such as water and ammonia (NH_3), and anions, such as chloride (Cl^-) and cyanide (CN^-). Depending on the chemistry of an injected waste and existing conditions, complexation can increase or decrease the waste's mobility.

Complexation is more likely in solutions with high ionic strength (which is typical of fluids found in the deep-well-injection environment). This is true because the large number of ions present in solution increases the number of chemical species that can form.[42] Many variables affect the stability of a complex ion relative to ions and metals that can serve as potential ligands to the central metal, the most important of which is the valence (charge) of the central cation and its radius. As a rule, the stability of complexes formed with a given ligand increases with cation charge and decreases with cation radius.[43]

The solubility of most metals is much higher when they exist as organometallic complexes.[44,45] Naturally occurring chemicals that can partially complex with metal compounds and increase the solubility of the metal include aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols. Several complexation processes, including chelation and hydration, can occur in the deep-well environment.

20.3.3.3 Hydrolysis

Hydrolysis occurs when a compound reacts chemically with water (i.e., new chemical species are formed by the reaction), and can be a significant transformation process for certain hazardous wastes in the deep-well environment (see Table 20.7). Hydrolysis reactions fall into two major categories: replacement and addition. The rates at which these reactions occur are also significant in a fate assessment because some take so long to occur that they will not take place during the analytical time frame (10,000 years).

20.3.3.4 Oxidation–Reduction

Oxidation–reduction (redox) reactions involve the loss of electrons and increase in oxidation number (oxidation) by one substance or system, with an associated gain of electrons and decrease in oxidation number (reduction) by another substance or system. Thus for every oxidation reaction there must be a reduction reaction. The oxidation number of an atom represents the hypothetical charge an atom would have if the ion or molecule were to dissociate.[46,47]

Because redox reactions involve the transfer of electrons, the intensity of redox reactions is measured by electrical potential differences, termed Eh. Highly oxidizing conditions will have an Eh of about 0.8 V; highly reducing conditions will have an Eh of about –0.4 V. Eh is difficult to

TABLE 20.7
Listed Hazardous Organic Wastes for Which Hydrolysis May Be a Significant Transformation Process in the Deep-Well Environment

Group/Compound	Half-Life (d)
Pesticides	
DDT	81–4400
Dieldrin	3800
Endosulfan/endosulfan sulfate	21
Heptachlor	1
Halogenated aliphatic hydrocarbons	
Chloroethane (ethyl chloride)	38
1,2-Dichloropropane	180–700
1,3-Dichloropropene	60
Hexachlorocyclopentadiene	14
Bromomethane (methyl bromide)	20
Bromodichloromethane	5000
Halogenated ethers	
bis(Chloromethyl) ether	<1
2-Chloroethyl vinyl ether	1800
Monocyclic aromatics	
Pentachlorophenol	200
Phthalate esters	
Dimethyl phthalate	1200
Diethyl phthalate	3700
Di-*n*-butyl phthalate	7600
Di-*n*-octyl phthalate	4900

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

measure accurately, and groundwater systems are often not in equilibrium with respect to redox reactions. Consequently, the Eh of a chemical system indicates the types of redox reactions that may occur rather than predicting the specific reactions that are occurring. In inorganic chemical systems, redox reactions tend to be reversible, whereas microbiologically mediated redox reactions involving hydrocarbons tend to be irreversible. Therefore, inorganic oxidation–reduction equilibria are somewhat analogous to acid–base equilibria. Examples of redox reactions are given in Table 20.8 and the relative oxidation states of organic groups are shown in Table 20.9.

20.3.3.5 Catalysis

The rate of many reactions increase in the presence of a catalyst, which itself remains unchanged in quantity and composition afterward. Although the catalyst itself is not transformed, the catalyst speeds up reactions that would occur naturally or promotes reactions that would not occur otherwise. For example, metal ions catalyze the hydrolysis and oxidation reactions in biochemical systems.[47] Phenol and phenol derivatives are normally resistant to oxidation in wastewaters, but the reaction can be accomplished by metal-ion catalysis when Fe^{2+}, Mn^{2+}, Cu^{2+}, and Co^{2+} are combined with chelating agents.[48,49] The reactions involved in destroying the aromatic ring in these compounds are complex and more likely to occur during waste pretreatment than as a result of processes in the deep-well environment. Certain metals in the presence of clays can also catalyze the polymerization of phenols and benzenes. Organic reactions that are catalyzed by clay minerals have been reviewed by Laszlo.[50]

TABLE 20.8
Redox Reactions in a Closed Groundwater System

Reaction	Equation
Aerobic respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
Denitrification	$5\ CH_2O$ + nitrate ($4\ NO_3^-$) + $4\ H^+ \rightarrow$ nitrogen ($2\ N_2$) + $5\ CO_2 + 7\ H_2O$
Mn(IV) reduction	$CH_2O + 2\ MnO_2 + 4\ H^+ \rightarrow 2\ Mn^{2+} + CO_2 + 3\ H_2O$
Fe(III) reduction	$CH_2O + 8\ H^+ + 4\ Fe(OH)_3 \rightarrow 4\ Fe^{2+} + CO_2 + 11\ H_2O$
Sulfate reduction	$2\ CH_2O$ + sulfate (SO_4^{2-}) + $H^+ \rightarrow HS^- + 2\ CO_2 + 2\ H_2O$
Methane fermentation	$2\ CH_2O + CO_2 \rightarrow$ methane (CH_4) + $2\ CO_2$
Nitrogen fixation	$3\ CH_2O + 3\ H_2O + 2\ N_2 + 4\ H^+ \rightarrow$ ammonia ($4\ NH_4^+$) + $3\ CO_2$

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

20.3.3.6 Polymerization

Polymerization is the formation of large molecules (polymers) by the bonding together of many smaller molecules. For example, styrene polymerizes to form polystyrene. Polymerization can enhance the tendency of a substance to be adsorbed on mineral surfaces by increasing the molecular weight, but is not likely to result in detoxification of hazardous wastes.

Polar organic compounds such as amino acids normally do not polymerize in water because of dipole–dipole interactions. However, polymerization of amino acids to peptides may occur on clay surfaces. For example, Degens and Metheja[51] found kaolinite to serve as a catalyst for the polymerization of amino acids to peptides. In natural systems, Cu^{2+} is not very likely to exist in significant concentrations. However, Fe^{3+} may be present in the deep-well environment in sufficient amounts to enhance the adsorption of phenol, benzene, and related aromatics. Wastes from resin-manufacturing facilities, food-processing plants, pharmaceutical plants, and other types of chemical plants occasionally contain resin-like materials that may polymerize to form solids at deep-well-injection pressures and temperatures.

20.3.3.7 Thermal Degradation

Thermal degradation occurs when heat causes compounds to undergo structural changes, leading to the formation of simpler species. For example, many organophosphorus esters isomerize when heated

TABLE 20.9
Relative Oxidation States of Organic Functional Groups

Functional Group Oxidation State				
–4	–2	0	+2	+4
Least Oxidized			Most Oxidized	
RH	ROH	RC(O)R	RCOOH	CO_2
	RCl	$(R)_2CCl_2$	$RC(O)NH_2$	CCl_4
RNH_2			$RCCl_3$	
	C=C	—C≡C—		

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

and break down into component molecules. Temperatures and pressures common in the deep-well environment are normally too low to initiate high-temperature reactions, but if the right chemicals (not necessarily hazardous) are present, thermal degradation might be initiated. For example, thermal decarboxylation is probably the mechanism of acetate degradation in oilfield waters[52] where temperatures exceed 200°C; however, injection zones usually do not reach this temperature. At depths of 900 m (approximately 3000 ft), temperatures range from 50°C to 100°C.[33]

Smith and Raptis[53] have suggested using the deep-well environment as a wet-oxidation reactor for liquid organic wastes. This process, however, does not involve deep-well injection of wastes but rather uses temperatures and pressures in the subsurface to increase the oxidation rate of organic wastes, which are then returned to the surface.

20.3.3.8 Biodegradation

Biotransformation is the alteration of a compound as a result of the influence of organisms. It is one of the most prevalent processes causing the breakdown of organic compounds in the near-surface environment. Biodegradation is a more specific term used to describe the biologically mediated change of a chemical into simpler products. The term includes, and sometimes obscures, a series of distinctive processes of toxicological significance in natural ecosystems. Biodegradation is probably more significant in the decomposition of the nonhazardous components of deep-well-injected organic wastes, although a few hazardous compounds, such as acrylonitrile and some monocyclic aromatic hydrocarbons and halogenated aliphatics, may be subject to biodegradation in the deep-well environment.

Microorganisms are by far the most significant group of organisms involved in biodegradation. They can mineralize (convert to CO_2 and H_2O) many complex organic molecules that higher organisms, such as vertebrates, cannot metabolize. They are often the first agents in biodegradation, converting compounds into the simpler forms required by higher organisms. Most biodegradation in near-surface environments is carried out by heterotrophic bacteria (microorganisms that require organic matter for energy and oxygen).[54]

Biodegradation in deep-well environments is performed predominantly by anaerobic microorganisms, which do not consume oxygen and are either obligate (oxygen is toxic to the organism) or facultative (the organism can live with or without oxygen or prefers a reducing environment). The two main types of anaerobic bacteria, methanogenic (methane-producing) and sulfate-reducing do not degrade the same compounds. The byproducts of sulfate reduction are hydrogen sulfide, carbon dioxide, and water. Methanogenic bacteria produce methane and carbon dioxide (see Table 20.9). The extent to which either type proliferates is strongly influenced by pH. As a group, anaerobic organisms are more sensitive and susceptible to inhibition than aerobic bacteria. Typically, aerobic degradation is also more efficient than anaerobic degradation, and high temperatures are not as limiting for aerobes as for anaerobes.[54]

Alexander[55] identifies six major kinds of biodegradation: mineralization, cometabolism, detoxification, transtoxification, activation, and defusing. Table 20.10 describes each of these processes and gives examples.

For several reasons, mineralization (decomposition to inorganic constituents) is generally a more effective form of biodegradation than cometabolism (conversion to another compound without using the original compound for energy or growth). First, detoxification is more likely to occur during mineralization. Second, mineralizing populations will increase until the compound is completely degraded, because they use the compound as a source of energy. In contrast, cometabolized compounds tend to change slowly, and the original compound and its reaction products tend to remain in the environment because the cometabolized compounds are not used for energy.

Almost all the specific chemical reactions in biodegradation can be classified as oxidation–reduction, hydrolysis, or conjugation. Hydrolysis and oxidation–reduction have been discussed before. Conjugation involves the addition of functional groups or a hydrocarbon moiety to an organic

TABLE 20.10
Descriptions of the Major Types of Biological Transformation Processes

Process	Description
Mineralization	The complete conversion of an organic compound to inorganic constituents (water, carbon dioxide). Generally results in complete detoxification unless one of the products is of environmental concern, such as nitrates and sulfides under certain conditions.
Cometabolism	Conversion of an organic compound to another organic compound without the microorganism using the compound as a nutrient. Resulting compounds may be as toxic (DDT to DDE or DDD) or less toxic (xylenes to toluic acid).
Detoxification	Conversion of a toxic organic compound to a nontoxic organic compound. The pesticide 2,4-D can be detoxified microbially to 2,4-dichlorophenol.
Transtoxification	Conversion of a toxic compound to another toxic compound with similar, increased, or reduced toxicity.
Activation	Conversion of a nontoxic molecule to one that is toxic, or a molecule with low potency to one that is more potent. Examples include the formation of the phenoxy herbicide 2,4-D from the corresponding butyrate, formation of nitrosamines, and methylation of arsenicals to trimethylarsine.
Defusing	Conversion of a compound capable of becoming hazardous to another nonhazardous compound by circumventing the hazardous intermediate. This has been observed in the laboratory, but not identified in the environment. An example is the direct formation of 2,4-dichlorophenol from the corresponding butyrate of 2,4-D.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

molecule or inorganic species. For example, conjugation occurs when microbial processes transform inorganic mercury into dimethyl mercury.

At least 26 oxidative, 7 reductive, and 14 hydrolytic transformations of pesticides had been identified. Detailed identification and discussion of specific reactions can be found in the works of Alexander[56] and Scow.[57]

20.3.4 TRANSPORT PROCESSES

Many factors and processes must be considered when evaluating the movement of deep-well-injected hazardous wastes. Four factors are relevant to geochemical characteristics:

1. Hydrodynamic dispersion
2. Osmotic potential
3. Particle migration
4. Density and viscosity

20.3.4.1 Hydrodynamic Dispersion

Hydrodynamic dispersion refers to the net effect of a variety of microscopic, macroscopic, and regional conditions that affect the spread of a solute front through an aquifer.[58] Quantifying the dispersion is important to fate assessment because contaminants can move more rapidly through an aquifer by this process than would be predicted by simple plugflow (i.e., uniform movement of water through an aquifer with a vertical front). In other words, physical conditions (such as more-permeable zones, where water can move more quickly) and chemical processes (e.g., movement of dissolved species at greater velocities than the water moves by molecular diffusion) result in more rapid movement of contaminants than would be predicted by groundwater equations for physical flow, which must assume average values for permeability. Dispersion on the microscopic scale is caused by the following:

1. Velocity variations resulting from variations in pore geometry and the fact that water velocity is higher in the center of a pore space than that for water moving near the pore wall
2. Molecular diffusion along concentration gradients
3. Variations in fluid properties such as density and viscosity

Dispersion on the macroscopic scale is caused by variations in hydraulic conductivity and porosity, which create irregularities in the seepage velocity with consequent mixing of the solute. Finally, over large distances, regional variations in hydrogeologic units can affect the amount of dispersion. In hydrogeologic modeling, the hydrodynamic dispersion coefficient D is often expressed as the sum of a mechanical dispersion coefficient D_m and molecular (Fickian) diffusion D^*.

In most instances, hydrodynamic dispersion is not great enough to require detailed consideration in hydrogeologic modeling for fate assessment of deep-well-injected wastes. However, regional variations (such as the presence of an USDW in the same aquifer as the injection zone, as is the case in parts of Florida) should be evaluated before a decision is made to exclude it.

20.3.4.2 Osmotic Potential

Osmotic potential refers to the energy required to pull water away from ions in solution that are attracted to the polar water molecules. In the presence of a semipermeable membrane between two solutions, water molecules will move through the membrane to the side with the higher concentration. This property may be important to fate assessment because in the deep-well environment, shales that serve as confining layers can act as semipermeable membranes if the injected waste significantly changes the solute concentrations.[59] In laboratory experiments, Kharaka[60] found that retardation sequences across geologic membranes varied with the material, but that monovalent and divalent cations generally followed identical sequences: $Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$.

If osmotic effects are possible, several other effects would need to be considered in a geochemical-fate assessment, depending on whether the solute concentration is increased or decreased. If solute concentrations are increased, pressures associated with injection would increase beyond those predicted without osmotic effects. Also, the movement of ions to the injection zone from the aquifer with lower salinity (above the clay confining layer) would increase the salinity above those levels predicted by simple mixing of the reservoir fluid and the injected wastes. This action could affect the results of any geochemical modeling.

If solute concentrations are decreased, the remote possibility exists that wastes would migrate through the confining layer. For this to occur, solute concentrations above the confining layer would have to be higher than those in the injection zone, and movement, in any event, would be very slow. As USDWs have salinities less than 10,000 mg/L, compared with typical salinities in injection zones of 20,000 to 70,000 mg/L, even if this process were to occur it would cause migration only to overlying aquifers that are not USDWs.

20.3.4.3 Particle Migration

Particle migration can occur when the mixing of incompatible fluids mobilizes clays or very fine particles precipitate out of solution. This process is most likely to occur when solutions with low concentrations of salts are mixed with reservoir fluids containing high concentrations, or when highly alkaline solutions dissolve silica and release fines. This type of reaction is of concern primarily when it occurs near the injection zone, because particle migration can clog pores and drastically reduce permeability. McDowell-Boyer and colleagues[61] provide a good review of the literature on subsurface particle migration.

TABLE 20.11
Physical Parameters Affecting Particle Migration in Porous-Media Flow

Parameter	Significance
Matrix	
Porosity	Indicates voids; space available for retention of clogging material.
Particle size for which 10% of the matrix is smaller than that size	Termed the effective size for filter sands.
Particle size for which 60% of the matrix is smaller than that size	The ratio of the 60% size to the 10% size is an indicator of the uniformity.
Bulk density	For a given material, indicates the closeness of packing and propensity for material movement under stress.
Specific surface area	Relates to surface-active phenomena and adsorption rate.
Grain shapes	Affects shape of pores and thus fluid-flow patterns.
Surface roughness of grains	Affects retention of suspension on the particle surface.
Pore-diameter size and size distribution	Propensity for entrapment or filtration of suspension.
Surface charge of grains	Negatively charged surface grains will attract a suspended particle with a positive charge.
Fluid	
Viscosity	Shear forces and fluid resistance to flow.
Density	Mixing effects when different densities are involved; may affect direction and rate of flow.
Velocity of flow	Hydrodynamic forces on the medium and suspension.
Pressure	Driving force moving the liquid and suspension into and through the medium.
Suspended Particles	
Concentration (inflow, within medium, outflow)	Material available for inflow, retention, and through-flow.
Size	Ability to pass through pore openings.
Shape	Effect on retention or through-flow due to orientation.
Electric charge	Attraction or repulsion to medium or intermediate materials.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

It is possible for complex metals ions that are adsorbed onto very small particles of clay to migrate as metal-clay particles. Laboratory experiments found that radioisotope-clay particles at a low salinity were retained in a sand core, but passed through it at a high salinity.[44] Clay-metal particles would not be expected to travel long distances in deep-well reservoir rocks because the pores would be too small.

Injection of highly acid or alkaline wastes has the potential to dissolve some reservoir rock to create channels that would allow more distant transport of small particles. Table 20.11 summarizes the various physical parameters that affect particle migration in porous-media flow.

20.3.4.4 Density/Viscosity Differences

Wastes having different densities or viscosities (tendency to resist internal flow) than the injection zone fluids will tend to concentrate in the upper (lower density/viscosity) or lower (higher density/viscosity) portions of the injection zone. Frind[62] and Larkin and Clark[63] examined the basic requirements for the mathematical simulation of density-dependent transport in groundwater. Miller and colleagues[64] described a density-driven flow model designed specifically for evaluating the potential for upward migration of deep-well-injected wastes.

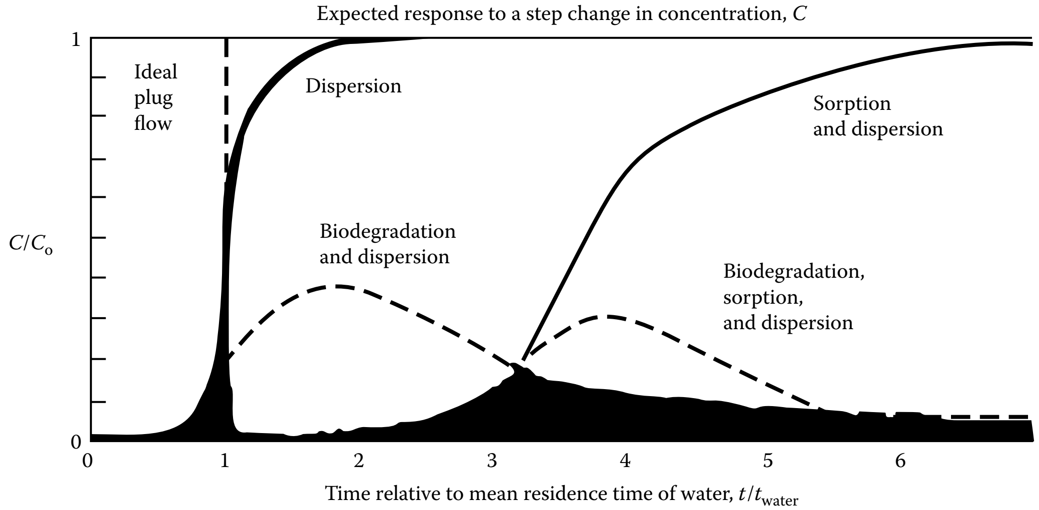


FIGURE 20.3 Effects of dispersion, adsorption, and biodegradation on the time change in concentration of an organic compound in an aquifer observation well. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

20.3.5 INTERACTION OF PARTITION, TRANSFORMATION, AND TRANSPORT PROCESSES

The actual movement of a specific deep-well-injected hazardous substance depends on the types of processes that act on the waste and on the ways in which different processes interact. Figure 20.3 shows the expected change in concentration over time of a deep-well-injected organic compound in an observation well at an unspecified distance from the original point of injection.

With only dispersion operating, low concentrations are observed before the arrival of a fluid exhibiting ideal plug flow, but dispersion also serves to delay the time it takes for 100% of the initial concentration to be observed. Adsorption combined with dispersion delays the arrival of the compound, and eventually the contaminant will reach full concentration when adsorption capacity is reached. When biodegradation occurs, initial concentrations might well be governed by dispersion alone, until sufficient time has passed for an acclimated bacterial population to establish itself and become large enough to change the organic concentration significantly. If this occurs, the concentration would decrease and level out at some minimum value. When adsorption acts with biodegradation, the arrival of the contaminant is delayed, as with adsorption alone; then the concentration of the contaminant rises to a maximum level below that of the original concentration and declines as biodegradation becomes active.

20.4 ENVIRONMENTAL FACTORS AFFECTING DEEP-WELL-INJECTION GEOCHEMICAL PROCESSES

Environmental conditions determine in large part the chemical reactions that will occur when waste is injected. For example, precipitation–dissolution reactions are strongly controlled by pH. Thus, iron oxides, which may be dissolved in acidic wastes, may precipitate when injection-zone mixing increases the pH of the waste. Similarly, redox potential (Eh) exerts a strong control on the type of microbiological degradation of wastes.

The most variable and site-specific factor is the reservoir rock matrix. Geologic formations vary greatly in chemical and physical properties depending on the conditions under which they formed and the geologic processes to which they have been subjected.

20.4.1 MAJOR ENVIRONMENTAL FACTORS INFLUENCING GEOCHEMICAL-FATE PROCESSES

The previous chapter examined the geochemical processes that can occur in the deep-well environment. The type and outcome of reactions that will actually occur when a waste is injected, however, depend on its chemical characteristics and on injection-zone conditions. This chapter examines six major environmental factors that must be taken into consideration.

20.4.1.1 pH

The pH of a system greatly influences what chemical processes will occur in the deep-well environment. Directly or indirectly, pH also affects most of the other environmental factors. Table 20.12 summarizes the significance and some major effects of changes in pH on chemical processes and environmental factors in the deep-well environment.

TABLE 20.12
Effects of pH on Deep-Well Geochemical Processes and Other Environmental Factors

Process/Factor	Significance of pH
Partition Processes	
Acid–base	Measures acid–base reactions. Strong acids (bases) will tend to change pH; weak acids (bases) will buffer solutions to minimize pH changes.
Adsorption–desorption	Strongly influences adsorption, because hydrogen ions play an active role in both chemical and physical bonding processes. Mobility of heavy metals is strongly influenced by pH. Adsorption of some organics is also pH-dependent.
Precipitation–dissolution	Strongly influences precipitation–dissolution reactions. Mixing of solutions with different pH often results in precipitation reactions. See also reservoir matrix below.
Transformation Processes	
Complexation	Strongly influences positions of equilibria involving complex ions and metal-chelate formation.
Hydrolysis	Strongly influences rates of hydrolysis. Hydrolysis of aliphatic and alkylic halides optimum at neutral to basic conditions.[43] Other hydrolysis reactions tend to be faster at either high or low pH.[186]
Oxidation–reduction	Redox systems generally become more reducing with increasing pH.[74]
Environmental Factors	
Biodegradation	In combination with Eh, pH strongly influences the types of bacteria that will be present. High- to medium-pH, low-Eh environments will generally restrict bacterial populations to sulfate reducers and heterotrophic anaerobes.[187] In reducing conditions, pH strongly affects whether methanogenic or sulfate-reducing bacteria predominate.[43]
Eh	Increasing pH generally lowers Eh.
Salinity	pH-induced dissolution increases salinity; pH-induced precipitation decreases salinity.
Reservoir matrix	Acidic solutions tend to dissolve carbonates and clays; highly alkaline solutions tend to dissolve silica and clays. Greater pH generally increases cation-exchange capacity of clays.
Temperature	pH-driven exothermic (heat-releasing) reactions will increase fluid temperature; pH-driven endothermic (heat-consuming) reactions will decrease fluid temperature.
Pressure	Will not influence pressure unless pH-induced reactions result in a significant change in the volume of reaction products.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

Very small changes in acidity greatly affect chemical reactions and the form of chemical species in solution. For example, the hydrolysis half-life of hydrogen cyanide is greater than 100,000 years at pH 4 but drops to about 10 years at pH 9.[39]

Buffer capacity is a measure of how much the pH changes when a strong acid or base is added to a solution. A highly buffered solution will show little change; conversely, the pH of a solution with low buffering capacity will change rapidly. Weak acids or bases buffer a solution, and the higher their concentration in solution, the greater the buffering capacity. Alkalinity (usually expressed in calcium carbonate equivalents required to neutralize acid to a specified pH) is a measure of the buffering capacity of a solution.[65]

Acid–base reactions of buffers act either to add or to remove hydrogen ions to or from the solution so as to maintain a nearly constant equilibrium concentration of H^+. For example, carbon dioxide acts as a buffer when it dissolves in water to form carbonic acid, which dissociates to carbonate and bicarbonate ions:

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longleftrightarrow HCO_3^- + H^+ \longleftrightarrow CO_3^{2-} + 2H^+ \tag{20.5}$$

At equilibrium, the concentration of H^+ will remain constant. When a strong acid (represented by H^+ or HA) is introduced into solution, the concentration of H^+ is increased. The buffer compensates by reacting with the excess H ions, moving the direction of the above reaction to the left. By combining with bicarbonate and carbonate ions to form the nonionic carbonic acid, equilibrium is reestablished at a pH nearly the same as that existing before. The buffer capacity in this case is determined by the total concentration of carbonate and bicarbonate ions. When no more carbonate or bicarbonate ions are available to combine with excess H^+ ions, the buffer capacity has been exceeded and pH will change dramatically upon addition of further acid.

20.4.1.2 Eh and Other Redox Indicators

The term Eh, which is the oxidation–reduction potential (often referred to as redox potential), is an expression of the tendency of a reversible redox system to be oxidized or reduced. It is especially significant in its influence on biodegradation processes. The energy of oxidation (electron-escaping tendency) present in a reversible oxidation–reduction system (in volts [V] or millivolts [mV]) is measured as the potential difference between a standard hydrogen electrode and the system being measured. Large positive values (up to ca. +800 mV) indicate an oxidizing tendency, and large negative values (down to ca. –500 mV) indicate a strong reducing tendency. Eh values of +200 mV and lower indicate reducing conditions in near-surface soils and sediments.[16]

The Eh of connate waters (water entrapped in the interstices of sediment at the time of deposition) ranges from 0 to –200 mV. For example, formation water from two monitoring wells in the lower limestone of the Florida aquifer near Pensacola ranged from +23 to –32 mV,[67] and formation fluids from a Devonian limestone in Illinois used for injection at a depth of about 3200 ft had an Eh of –154 mV.[16]

Several measures of organic pollutant loading to waters have been developed to indicate the redox status of a system:

1. Biochemical oxygen demand (BOD)
2. Chemical oxygen demand (COD)
3. Total organic carbon (TOC)
4. Dissolved organic carbon (DOC)
5. Suspended organic carbon (SOC)

When values for any of these parameters are high, oxygen is rapidly depleted in groundwaters and reducing conditions will develop. BOD and COD were designed to measure oxygen consumption during the microbial degradation of municipal sewage. They are only semiquantitative indicators of organic loading because measurement procedures for these parameters have no direct geochemical significance.[65] Malcolm and Leenheer[68] recommend the use of DOC and SOC, which are independent of microbial effects, toxic substance, and variability with diverse organic constituents. TOC, when measured as a single parameter (rather than as the sum of DOC and SOC), provides less information for geochemical interpretation.

Reducing conditions predominate in the deep-well environment for several reasons:

1. No source of oxygen replenishment exists.
2. Higher temperatures in the deep-well environment are associated with decreases in Eh.
3. Neutral to slightly alkaline water in the deep-well environment favors lower Eh values.

Deep-well injection of wastes can change, at least temporarily, the Eh of the injection zone. For example, Ragone and coleagues[69] observed a change from reducing to oxidizing conditions when tertiary-treated sewage (reclaimed water) was injected into the Magothy aquifer, Long Island, NY, at a depth of 400 ft. The reclaimed water had 6.6 mg/L dissolved oxygen compared with no dissolved oxygen in the formation water. On the other hand, the Eh of an acidic waste dropped dramatically, from +800 mV to ca. +100 mV, when mixed with siltstone under conditions of low oxygen and simulated deep-well temperature and pressure.[67] Similarly, the Eh of an alkaline waste dropped from +600 mV to ca. +200 mV.[67]

20.4.1.3 Salinity and Specific Conductance

Salinity is defined as the concentration of total dissolved solids (TDS) in a solution, usually expressed in mg/L. The TDS concentration in water is usually determined from the weight of the dry residue remaining after evaporation of the volatile portion of the original solution. Groundwater may be classified into four salinity classes[64]:

1. Slightly saline (1000 to 3000 mg/L)
2. Moderately saline (3000 to 10,000 mg/L)
3. Very saline (10,000 to 35,000 mg/L)
4. Brine (more than 35,000 mg/L) (seawater is about 35,000 mg/L)

Water with a salinity of less than 10,000 mg/L is considered to be a potential underground source of drinking water. By regulatory definition, deep-well injection of hazardous waste can occur only in very saline waters or brines. Actual salinities of waters in currently used deep-well injection zones vary greatly.[70] Normally, the term brine is used to refer to the natural waters in deep-well injection zones. As noted above, however, this term is not technically correct if TDS levels are less than 35,000 mg/L.

Solutions of substances that are good conductors of electricity are called electrolytes. Sodium chloride, the major constituent of seawater, is a strong electrolyte. Most salts, as well as strong acids and bases, are strong electrolytes because they remain in solution primarily in ionic (charged) forms. Weak acids and bases are weak electrolytes because they tend to remain in nonionic forms. Pure water is a nonconductor of electricity.

The conductivity of solutions is measured as specific conductance, which may be expressed as μmhos/cm or mmhos/cm at 25°C. Seawater has a specific conductance of about 50 mmhos/cm. Salinity shows a high correlation with specific conductance at low to moderate TDS levels, but the concentrations of ions in brines are so high that the relationship between concentration and conductance becomes ill-defined.[64]

20.4.1.4 Reservoir Matrix

With few, if any, exceptions, deep-well injection zones will be sedimentary rock, and the reactions that take place when hazardous wastes are injected are determined largely by the physical and chemical properties of that rock. The most important physical properties of sedimentary rocks in relation to deep-well geochemical interactions are texture (the proportions of different sized particles in sediment) and specific surface area. The most important chemical property is mineralogy, defined by the types and proportions of minerals present.

20.4.1.5 Temperature and Pressure

Temperature and pressure are the primary influences on the rate of chemical reactions. Both temperature and pressure increase with depth below the Earth's surface. Consequently, temperatures and pressures in the deep-well environment are significantly higher than those in the near-surface environment.

Geothermal gradients in the subsurface typically range from 1°C per 15 m (50 ft) to 1°C per 45 m (150 ft), with most regions having a gradient of around 1°C per 30 m (100 ft). Tables giving data on temperature gradients for 679 wells located in 23 states can be found in reference 71. Temperature can vary greatly at the same depth in different locations. For example, temperatures at approximately the same depth in Florida differ by almost 26°C.

The velocity of most acid–base and dissolution reactions increases as temperature increases. Higher temperatures generally also increase the rate of redox reactions; however, the effect is difficult to predict exactly because the interactions among competing reactions may offset the effect of the increase. In contrast, higher temperatures usually decrease the amount and rate of adsorption, because these reactions are generally exothermic (heat-producing). An exception has been noted by Choi and Aomine,[72] who found that adsorption rates of pentachlorophenol on soil increase 6% to 12% when samples of three different soils are subjected to an increase in temperature from 4°C to 33°C. Adsorption decreased by 9% in a fourth sample. Laboratory adsorption experiments at constant, simulated deep-well pressure with phenol and 1,2-dichloroethane result in decreased adsorption with increased temperature.[73]

Greater pressures tend to decrease the growth and survival of bacteria, but for certain species increased temperature counters this effect. For example, the growth and reproduction of *E. coli* essentially stops in nutrient cultures at 20°C and 400 atm (40.5 MPa). When the temperature is increased to 40°C, however, growth and reproduction are about the same as at near-surface conditions.[74]

20.4.2 GEOCHEMICAL CHARACTERISTICS OF DEEP-WELL-INJECTION ZONES

This section provides information on the range of environmental conditions that occur in deep-well-injection zones in different geologic regions of the U.S. The section on lithology discusses the types of sedimentary formations that are suitable for deep-well injection and confining layers and provides some information on geologic formations that are used for deep-well injection of wastes. The section on brine chemistry discusses the typical range of chemical characteristics of formation waters found in injection zones.

20.4.2.1 Lithology

Rock that can be mapped over a large area based on mineralogy, fossil content, or other recognizable characteristic is called a formation. The lithology (texture and mineralogy) of a geologic formation influences its suitability for deep-well injection. Sedimentary carbonates and sandstones usually have suitable geologic and engineering characteristics for disposal of hazardous wastes by deep-well injection. These characteristics include sufficient porosity, permeability, thickness, and extent to permit use as a liquid-storage reservoir at safe injection pressures.[75] In 1981, 62% of the injection wells in the U.S. were drilled into two types of reservoir rocks, either consolidated sandstone or unconsolidated sands that had not yet been altered by cementation to form strongly cohesive sandstone. The latter were usually of Tertiary age. At that time (1981), 34% of all wells used limestones and dolomites as reservoir rock and 4% used miscellaneous formations.

Sedimentary-rock formations that overlie the injection formation are called confining layers. To prevent injected wastes from migrating to higher strata or to potential underground sources of drinking water, a confining layer must have certain geologic and engineering characteristics[3,76,77]:

1. Sufficient thickness and area to prevent upward migration of wastes
2. Low porosity and permeability and the ability to maintain low porosities and permeabilities when interacting with wastes that may dissolve minerals through neutralization
3. Lack of natural continuous fracturing or faulting, and resistance to artificial fracturing in response to injection pressures
4. No abandoned unplugged or improperly plugged wells

Sedimentary rocks that are most likely to meet the first three criteria are unfractured shale, clay, siltstone, anhydrite, gypsum, and salt formations. Massive limestones and dolomites (i.e., carbonates with no continuous fracturing and solution channels) can also serve as confining layers. Their suitability must be determined on a case by case basis. The fourth criterion has no relationship to lithology.

Formations from all geologic periods have been used for deep-well injection, but Paleozoic rocks are used for most injection zones (53%), followed by Tertiary-age formations (39%). Older Paleozoic rocks have been more frequently used for injection primarily because they tend to be more deeply buried. However, the more recent Tertiary-age Gulf Coast sediments are also very thick, and most injection in rocks of this age takes place there.

Figure 20.4 provides a general indication of site suitability based on geologic factors.

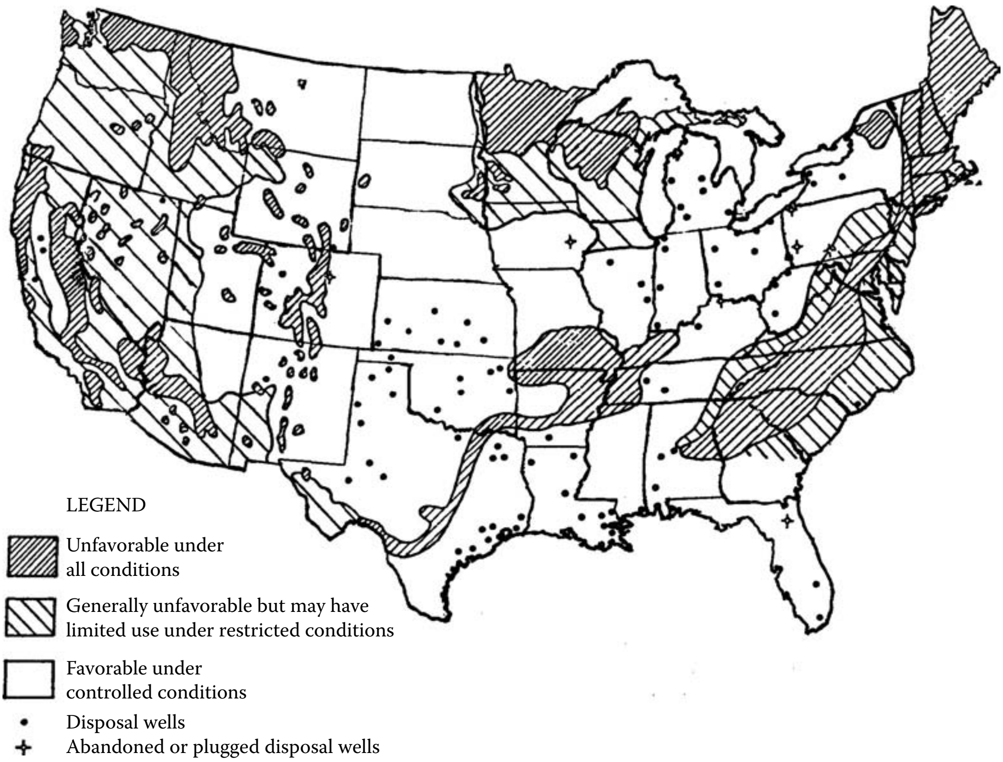


FIGURE 20.4 Site suitability for deep-well injection and locations of industrial waste disposal wells. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

20.4.2.2 Brine Chemistry

Brines are classified according to their chemical constituents. At least nine distinct types are recognized by petroleum geologists, but most brines encountered in injection operations are either Na-Cl or Na-Ca-Cl brines.[78] None is similar to seawater, and the geochemical mechanisms by which such brines develop are not well-understood. Three mechanisms have been proposed to explain the high concentrations of dissolved solids and the chemical composition of brines, but at present there is no consensus on their relative importance in explaining brine chemistry.[78] The dominant mechanism at work in a deep-well environment has important implications for the hydrodynamic conditions affecting the movement of injected wastes. The mechanisms and their implications are summarized in Table 20.13. The salinity, pH, and chemical composition of the very saline and briny waters into which hazardous wastes are injected can vary greatly, both among geologic basins and within a single formation.

The maximum salinities in the Tertiary section of the Gulf of Mexico basin (the most extensively used strata for deep-well injection) reach almost four times that of seawater. The Michigan basin has the highest salinity, reaching 400,000 mg/L TDS, more than 11 times that of seawater. In Florida, however, where seawater circulates through the Floridan aquifer, maximum salinities tend to be controlled by the salinity of the seawater.[79]

The Frio formation, in Texas, receives more hazardous waste by volume through deep-well injection than any other geologic formation in the U.S. The average salinity of this formation is about twice that of seawater (72,185 mg/L TDS), but individual samples range from a low of 10,528 mg/L TDS (barely above the salinity cutoff for potential USDWs) to a high of more than 118,000 mg/L TDS. Data from sites in Illinois and North Carolina indicate the presence of very saline water (around 20,000 mg/L TDS, but still less saline than seawater).

The pH of formation waters in the Frio formation varies widely from moderately acidic (5.7) to moderately alkaline (8.2), with nearly neutral averages (6.8). The pH of formation waters from other injection sites tends to be more alkaline, ranging from slightly alkaline (Belle Glade, Florida, pH 7.5) and moderately alkaline (Wilmington, North Carolina, pH 8.6), to very alkaline (Marshall, Illinois, pH 7.1 to 10.7).

20.4.3 INFLUENCE OF ENVIRONMENTAL FACTORS ON WASTE/RESERVOIR COMPATIBILITY

This section focuses on environmental conditions that may result in physical or chemical incompatibilities between wastes and reservoirs. Determining the potential for incompatibility is a part of the geochemical fate assessment that must be undertaken for any injection project because of possible

TABLE 20.13
Implications of Brine-Formation Mechanisms on Movement of Injected Wastes

Mechanism	Brine Type	Implications
Residual left after precipitation of evaporites (salt deposits).	Na-Ca-Cl	Brines are as old as the formation in which they occur; stagnant conditions exist.
Solution of halite present as bedded or domal salt-evaporite deposits.	Na-Cl Na-Ca-Cl	Active hydrologic conditions exist, although neither the mechanism nor the rate of fluid movement is indicated.
Reverse osmosis. Basinal waters forced through low-permeability shales, leaving the high-pressure side.	Na-Cl Na-Ca-Cl	Active hydrologic conditions exist because large volumes of water would have to pass brine through a basin to reach observed brine concentrations.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

TABLE 20.14
Processes Significant in Different Types of Waste–Reservoir Interactions

Interaction	Process
Waste with *in situ* fluids	Precipitation may result from incompatible brine. Hydrolysis may detoxify wastes. Complexation may increase or decrease mobility depending on condition. Oxidation or reduction of wastes may occur.
Waste with rock	Dissolution by highly acidic or alkaline wastes may threaten well and rock integrity. Gases generated by dissolution of carbonates may cause immiscible phase separation and well blowout. Adsorption on mineral surfaces may immobilize wastes. Clays may be mobilized and clog pores.
Waste/brine with rock	Waste/brine precipitates may clog pores. Successive adsorption/desorption reactions mayoccur at a particular location as waste/brine mixtures of varying proportions come in contact with the rock.
Microbiota	May form mats that clog pores near the injection well. May transform waste to nontoxic or other toxic forms.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

operational problems that may result from waste/reservoir incompatibility. The following are the major operational problems that can occur[3]:

1. Well plugging
2. Casing/confining layer failure
3. Well blowout

In extreme situations, incompatibility between injection fluids and reservoir components can be so great that deep-well disposal will not be the most cost-effective approach to waste disposal. In other situations, such remedial measures as pretreatment or controlling fluid concentrations or temperatures can permit injection even when incompatibilities exist. In addition to operational problems, waste–reservoir incompatibility can cause wastes to migrate out of the injection zone (casing/confining-layer failure) and even cause surface-water contamination (well blowout).

Four major types of chemical interactions are important when evaluating compatibility:

1. Waste interactions with brine
2. Waste interactions with rock
3. Waste–brine mixture interactions with rock
4. Microbiological interactions with the waste/brine/rock system

Each interaction involves numerous chemical processes. The dominance of a specific interaction depends on the type of waste, the characteristics of the brine and rock in the reservoir, and environmental conditions. Table 20.14 describes some of the more common processes that may result in incompatibility.

20.4.3.1 Well Plugging

The term well plugging refers to any of a variety of processes that reduce the permeability of the injection formation or the screens that are placed in the well's injection interval. When permeability is reduced, injection rates must be reduced or injection pressures increased. Table 20.15 lists a number of ways in which plugging may occur. One or more of these situations will probably take place in most injection wells; the number and severity of reactions will determine whether serious operational problems arise. If plugging is confined to the immediate vicinity of the injection well,

TABLE 20.15
Causes of Well Plugging and Possible Remedial Actions

Cause	Possible Action
Particulate solids and/or colloids.	Filter before injection.
Bacterial growth on well screen and formation.	Treat with bactericides.
Emulsification of two fluid phases.	Do not exceed solubility limits of organic wastes in water.
Precipitates resulting from mixing of injection and reservoir fluids.	Use pretreatment or buffer of non reactive water.
Expansion and dispersion of water-sensitive clays	Avoid injection of low-salinity solutions in water-sensitive (particularly montmorillonite) formations. Use clay stabilizers.
Migration of fines (very small particles) released by dissolution.	Neutralize before injection.
Reprecipitation of dissolved material (iron or calcium sulfate).	Use pretreatment.
Change in wettability or reduction in pore dimensions by adsorption (organics with large molecular weight).	Difficult to remedy.
Flow of unconsolidated sands into bore.	Use gravel-pack well screen. Inject a slug of brine after every period of interrupted flow.
Scaling on injection equipment by precipitation from injection fluid.	Use pretreatment; flush with solutions to remove accumulated scale.
Entrapped gases.	Remove gases from waste before injection or treat to prevent gas formation in the injection zone.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

wastes will not migrate into the injection zone until permeability is reestablished by physical or chemical means (see Table 20.15). Partial reductions in permeability may allow wastes to move into the injection zone but at increased pressures. This latter situation may contribute to well-casing or confining-layer failure. Clay swelling, mobilization of fine particles by dissolution, and precipitation are the common causes of well plugging.

20.4.3.2 Well-Casing and Confining-Formation Failure

Interactions between corrosive wastes and casing and packing can threaten the integrity of a well if proper materials have not been used in construction. Of equal concern is the potential for failure of the confining zone due to physical or chemical effects. For example, dissolution of an overlying carbonate confining layer may allow upward migration of wastes. This process was observed when hot acidic wastes were injected in a Florida well.

Chemically active injected fluids can also have negative impacts on the mechanical properties of the reservoir rock. For example, adsorption of aluminum and iron hydroxides and ferric chloride on quartz and other silicates can weaken the surface silicon–oxygen bonds by hydrolysis, reducing the surface energy, surface cohesion, and breaking strength of the formation. In addition, stress changes caused by increased injection pressures can fracture rock, forming permeability channels in a confining formation through which injected fluids could escape.[80]

20.4.3.3 Well Blowout

Gases entrapped in pore spaces resulting from phase separation of gases from liquids can reduce the permeability of a formation. This process was the major cause of clogging at groundwater recharge wells in the Grand Prairie Region in Arkansas.[81] Normally, pressures in deep-well-injection zones are high enough to keep gases in solution, so phase separation is not a problem. However, it is possible for permeability to be reduced by air entrainment at the same time gases are generated by reactions between the injected waste and reservoir formation. The resulting pressure then forces waste and reservoir fluid up the injection well to the surface, causing a well blowout.

The hazard of well blowout is greatest if hydrochloric acid wastes exceeding certain temperature and concentration limits are injected into a carbonate formation. When carbonate dissolves in acid, carbon dioxide is formed. Normally, this gas remains dissolved in the formation waters at deep-well temperatures and pressures, but if the temperature exceeds 88°F or acid concentration exceeds 6% HCl, carbon dioxide will separate from the formation waters as a gas. The resulting gas accumulation can increase pressures to a point where, if injection stops or drops below the subsurface carbon dioxide pressure, a blowout can occur.

20.4.4 INFLUENCE OF THE DEEP-WELL ENVIRONMENT ON BIODEGRADATION

Biodegradation of hazardous organic compounds in groundwaters has been the subject of much research in recent years. Ghiorse and Wilson[82] provide good general reviews of the topic. Unpolluted near-surface aquifers typically contain enough oxygen for aerobic processes to prevail. For example, Ghiorse and Wilson[82] summarize biodegradation data on 38 trace organic contaminants in subsurface materials from pristine sites. At most sites aerobic degradation is observed. In contrast, the deep-well-injection environment is typically anaerobic.

20.4.4.1 Occurrence of Microbes

Messineva[83] classifies subsurface sediments and rocks into geochemically active and geochemically inactive categories, based on microbial activity. Geochemically active sediments and rocks tend to be heterogeneous, containing organic material, nitrogen, and phosphorus, and support indigenous bacteria populations. Geochemically inactive formations do not maintain *in situ* microbial populations and lack fermentive properties when microorganisms are added. Such rocks are typically homogeneous, well-sorted clays.[83] Sinclair and Ghiorse[84] describe similar relationships between microbiological activity and the saturated zone in near-surface aquifers: gravelly sand was the most biologically active and clayey layers the least.

It is now generally accepted that microorganisms are ubiquitous in the deep subsurface, although, as noted, not all strata are biologically active.[85] Microorganisms have adapted to the complete range of environmental conditions that exist on and below the Earth's surface. They have been observed at pressures up to 1760 kg/cm^2 (25,000 psi), temperatures up to 100°C, and salt concentrations up to 300,000 mg/L.[86]

Most pre-1970 research on microorganisms in the deep-surface was done by petroleum microbiologists. Dunlap and McNabb[87] summarize data from 30 studies reporting isolation of microorganisms from deep-subsurface sediments. Because deep-well injection zones in the Gulf Coast region (where most deep-well injection of hazardous wastes occurs) are commonly associated with petroleum-producing strata, this research probably has some relevance. Kuznetsov and colleagues,[86] in an analysis of 50 samples of oilfield waters in Russia, found methanogenic organisms in 23 samples.

Ghiorse and Wilson[82] reviewed 14 studies characterizing subsurface microorganisms in pristine aquifers; only three studies involve samples deeper than 300 m below the surface. Olson and colleagues[88] found sulfate-reducing and methanogenic bacteria in waters from wells 1800 m deep in the Madison Limestone in Montana. In a comparison of microbial activity in the Bucatanna clay at 410 m near Pensacola, Florida, with that in the shallow Fort Polk aquifer, Louisiana, it was found that the biomass had to be about half that in the shallow aquifer and that there was a greater evidence of the byproducts of anaerobic bacterial activity.

Ehrlich and colleagues[89] examined microbial populations in samples of industrial wastes containing acrylonitrile and inorganic sodium salts (nitrate, sulfate, and thiocyanate) that had been injected to a depth of 375 to 425 m at a second waste-injection facility at Pensacola, Florida. Samples were obtained by allowing the injected waste to backflow, with a maximum estimated aquifer residence time of 107 h. Denitrifying bacteria dominated in the waste/formation-water mixture (10^5 to $>10^6$ organisms/mL), although substantial populations of both aerobes and anaerobes were also present (10^3 to 10^6 organisms/mL).

20.4.4.2 Degradation of Organic Compounds in Anaerobic Conditions

The three most significant groups of bacteria that may mineralize hazardous organic compounds are as follows:

1. Denitrifiers, which reduce nitrate to nitrogen
2. Sulfate reducers, which reduce sulfate to hydrogen sulfide
3. Methanogens, which reduce carbon dioxide to methane

Biodegradation of organic compounds under denitrifying conditions has been the least-studied of the three groups. Ehrlich and colleagues[89] inferred that acrylonitrile injected into a carbonate aquifer was completely degraded because the waste was not found in samples taken from a monitoring well where the waste arrived about 260 d after injection began, or in any subsequent samples. Bouwer and McCarty[90] observed partial to almost complete degradation of carbon tetrachloride (>95%), bromodichloromethane (>55%), dibromochloromethane (>85%), and bromoform (>90%) in laboratory batch experiments simulating denitrifying conditions. Compounds studied that did not show significant degradation under these conditions include chlorinated benzenes, ethylbenzene, naphthalene, chloroform, 1,1,1-trichloroethane, and 1,2-dibromomethane. Phthalic acids, phenol, tri-sodium nitrilotriacetate, and o- and m-xylene[3] are other compounds for which degradation has been observed under denitrifying conditions.

Degradation of organic compounds by sulfate-reducing bacteria has been studied mostly in the context of petroleum deposits.[91,92] These microbes are good scavengers of organic waste products regardless of the source of the waste. Novelli and ZoBell[91] reported finding some strains of sulfate-reducing bacteria that use hydrocarbons, beginning with decane and higher forms, paraffin oil and paraffin wax. In this study, the aromatic hydrocarbons—benzene, xylene, anthracene, and naphthalene—are not degraded, nor are aliphatic hydrocarbons, hydrocarbons with molecular weight lower than that of decane, or hydrocarbons of the naphthene series (cyclohexane). Rosenfeld[92] reported that high-molecular-weight aliphatic hydrocarbons are quickly decomposed by sulfate-reducing bacteria. However, the thinking is that molecular oxygen is required to degrade saturated hydrocarbons and that the experiments in the above-cited papers did not fully simulate anoxic conditions.

Degradation of organic compounds by methanogens has been the most extensively studied of the three groups. Methanogenic bacteria can readily degrade a number of monocyclic aromatics, phenol and some chlorophenols, benzene, ethyl benzene and a number of C_1 and C_2 halogenated aliphatic compounds.[3] However, the amount of degradation depends on the specific compound and conditions favorable for bacteria that can adapt to degrade the compound.

Biodegradation in groundwater systems may involve complex interactions among many types of bacteria, including denitrifying, sulfate-reducing, methanogenic, and others. Whether complete mineralization occurs depends on the compound, environmental conditions at the site, and the microorganisms that are best adapted to those conditions.

Iron- and manganese-reducing and ammonia-producing bacteria may also be significant in biochemical reactions that occur in the subsurface environment. Iron and manganese oxides are usually broken down through microbial reduction. Consequently, the possibility of this process should be considered when evaluating chemical reactions of iron and manganese species in the deep-well environment. Lovley[93] reviews the literature on biomineralization of organic matter with the reduction of ferric iron, and Ehrlich[94] reviews the literature on manganese oxide reduction through anaerobic respiration.

20.4.4.3 Microbial Ecology

The dissolved organic carbon content of subsurface waters is sufficient to maintain a small but diverse population of microorganisms. Denitrifiers, sulfate-reducers, and methanogens are likely to be present in low numbers in most groundwater unless conditions strongly favoring one group exist. Consequently, when a potential energy source in the form of an organic contaminant enters the water, the group most capable of utilizing the substrate at the environmental conditions existing in the aquifer will adapt and increase in population, while the population of other indigenous microbes will remain small or possibly be eliminated.

Effects of salinity

Typical salinities in deep-well injection zones range from about 20,000 to 70,000 mg/L, which is within the optimum range (50,000 to 60,000 mg/L) for halophilic organisms.[86] Many nonhalophilic bacteria can also live within this range. For example, a test of 14 microbe genera representing widely varying groups showed that most grew in salt concentrations of up to 60,000 mg/L.[95] Nitrification readily occurs at high salinities. Rubentschik[96] observed the conversion of ammonia to nitrate at concentrations of 150,000 mg/L NaCl, and isolated a culture of *Nitrosomonas* showing optimal growth at 40,000 mg/L. However, very high concentrations may slow denitrification. Hof[95] found that it took more than three times as long for the same amount of gas to be generated from denitrification at 300,000 mg/L NaCl as at 30,000 mg/L NaCl (10 vs. 3 d).

Effects of pressure

In general, growth and reproduction of both aerobic and anaerobic bacteria occurring at near-surface conditions decrease with increasing pressures.[74] However, certain barophilic (pressure-loving) bacteria have adapted to the temperature and pressure conditions in the deep-well environment. For example, aliphatic acids (acetate ions) are degraded by methanogenic bacteria in oilfield waters as long as temperatures are lower than 80°C.[97] Additionally, ZoBell and Johnson[74] found that certain sulfate-reducing bacteria isolated from oil-well brines located several thousand feet below the surface are metabolically more active when compressed to 400 to 600 atm (40.5 to 60.8 MPa) than at 1 atm. On the other hand, the pressures in deep-well waste injection formations may be sufficiently high to kill or otherwise severely affect the metabolic activity of microbes from surface habitats that may be indigenous to the injected wastes.[98]

Interactions among microbial groups

Decomposition of organic matter in anaerobic environments often depends on the interaction of metabolically different bacteria. Degradation in this situation is a multistep process in which complex organic compounds are degraded to short-chain acids by facultative bacteria and then to methane and carbon dioxide by methanogenic bacteria. In these interactions, methanogens may function as electron sinks during organic decomposition by altering electron flow in the direction of hydrogen production.[99] The altered flow of interspecies hydrogen transfer that occurs during coupled growth of methanogens and nonmethanogens may result in increased substrate utilization; different proportions of reduced end products; increased growth of both organisms; and displacement of unfavorable reaction equilibria.[99]

Redox conditions favoring denitrification lie somewhere between those for aerobic and methanogenic decomposition. However, denitrification and methanogenesis are not entirely mutually exclusive. Ehrlich and colleagues[100] observed evidence of both denitrifying and methanogenic bacteria in phenol-depleted zones of a creosote-contaminated aquifer and concluded that the denitrifying bacteria contributed to degradation. In this study, denitrifiers and iron reducers were the dominant anaerobes in contaminated wells. Methane production was highest in the closest wells downgradient from the contaminated site, indicating the development of redox zones with methanogenic conditions strongest where contaminant concentrations were highest, changing to stronger denitrifying conditions where contaminant concentrations were lower.

Studies by the U.S. Geological Survey at the Wilmington, NC, deep-well waste-injection facility also provide evidence of simultaneous degradation of organics by denitrifying and methanogenic organisms.[101,102] When the dilute waste front, containing organic acids, formaldehyde, and methanol, reached the first observation well, production of gases increased dramatically. For a period of about 6 weeks, about half the gas volume was methane and about a quarter, nitrogen. Two weeks later, nitrogen had increased to 62% and methane dropped to 33%, and after another three weeks nitrogen had increased to 68%, and methane had dropped to 12%. These relationships indicate that the methanogens were more sensitive to the increases in waste concentration as the dilute front passed the observation well and more concentrated waste reached the site. The inhibiting effects of sulfates on methane production would seem to indicate that sulfate-reduction will take place in preference to methanogenesis as long as sulfates are present.

20.5 GEOCHEMICAL CHARACTERISTICS OF HAZARDOUS WASTES

This section relates the chemical characteristics of inorganic and organic hazardous wastes to the important fate-influencing geochemical processes occurring in the deep-well environment.

20.5.1 INORGANIC VERSUS ORGANIC HAZARDOUS WASTES

Hazardous wastes are broadly classified as either organic or inorganic. Carbon is the central building block of organic wastes, whereas inorganic wastes are compounds formed by elements other than carbon (except for a few carbon-containing compounds such as metal carbonates, metal cyanides, carbon oxides, and metal carbides). Heavy metals may straddle the definition; although usually associated with inorganics, they can also be incorporated into organic compounds. In fact, organic forms of heavy metals, such as dimethyl mercury, are often more toxic than inorganic compounds formed by the same metal.

A major difference between organic and inorganic hazardous wastes is that, with the exception of cyanide, inorganics cannot be destroyed by being broken down into nonhazardous component parts, because at least one element in the compound is toxic. Inorganic hazardous wastes containing toxic elements can be transformed from a more to a less toxic form, but can never be transformed to a nontoxic form.

Toxic organic compounds (with the exception of organometallic compounds containing toxic metals), however, may be rendered harmless in some cases by being broken down into their inorganic components: carbon, hydrogen, oxygen, and other nontoxic elements. Most hazardous organic substances must be manufactured under carefully controlled conditions and are highly unlikely to form from the basic elements of hydrogen, oxygen, and others under uncontrolled deep-well environmental conditions. Therefore, once these wastes have completely broken down, their detoxification can be considered permanent.

Another major difference between inorganic and organic compounds is the number of compounds. Inorganic elements that exhibit toxic properties at levels of environmental concern number in the dozens, and only ten are regulated as hazardous wastes under the UIC program (arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, thallium, and cyanide). Additionally, the number of inorganic compounds that any individual toxic element may form is limited (fewer than 50). On the other hand, the extreme versatility of carbon as a building block for organic compounds means that literally millions are possible, and the number that exhibit toxic properties is probably on the order of thousands or tens of thousands.

Regardless of whether a waste is classified as organic or inorganic, it must have certain physical and chemical properties to be suited for deep-well injection. Because water is the medium for injection, injected wastes, whether organic or inorganic, will typically be liquid or water-soluble or miscible, and relatively nonvolatile.

20.5.2 CHEMICAL PROPERTIES OF INORGANIC HAZARDOUS WASTES

The only means by which inorganic wastes can be rendered nonhazardous are dilution, isolation (as in deep-well injection), in some cases changes in oxidation state, and neutralization. Acidic wastes made up one-fifth of the injected waste volume and involved one-third of the injection wells in 1983. Most of the volume was from inorganic acids (hydrochloric, sulfuric, and nitric). Acid–base characteristics and neutralization were discussed in detail earlier, so the remainder of this section will focus on heavy metals and other hazardous inorganics (selenium and cyanide).

Inorganic elements can be broadly classified as metals and nonmetals. Most metallic elements become toxic at some concentration. Nine elements (arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, and thallium) and cyanide are defined as hazardous inorganics for the purposes of deep-well injection.

In aqueous geochemistry, the important distinguishing property of metals is that, in general, they have a positive oxidation state (donate electrons to form cations in solution), but nonmetals have a negative oxidation state (receive electrons to form anions in solution). In reality, there is no clear dividing line between metals and nonmetals. For example, arsenic, which is classified as a nonmetal, behaves like a metal in its commonest valence states and is commonly listed as such. Other nonmetals, such as selenium, behave more like nonmetals.

Metals are divided into light (also called alkali-earth metals) and heavy. All toxic metals are heavy metals except for beryllium and barium. Additionally, other categories of elements that are or may be significant chemically as dissolved species in deep-well-injection zones include the following:

1. *Alkali-earth metals*: sodium, magnesium, potassium, calcium, and strontium
2. *Heavy metals*: manganese, iron, and aluminum, which may be significant in precipitation reactions
3. *Nonmetals*: carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, chlorine, bromine, and iodine

20.5.2.1 Major Processes and Environmental Factors Affecting Geochemical Fate of Hazardous Inorganics

The major processes affecting the geochemical fate of hazardous inorganics are acid–base adsorption–desorption, precipitation–dissolution, complexation, hydrolysis, oxidation–reduction, and catalytic reactions. The significance of these processes to inorganic wastes is discussed only briefly here; additional information on individual elements is given in Table 20.16.

Acid–base equilibrium is very important to inorganic chemical reactions. Adsorption–desorption and precipitation–dissolution reactions are also of major importance in assessing the geochemical fate of deep-well-injected inorganics. Interactions between and among metals in solution and solids in the deep-well environment can be grouped into four types[3]:

1. Adsorption (including both physical adsorption and ion exchange) by clay minerals and silicates
2. Adsorption and coprecipitation by hydrous iron and manganese oxides
3. Complexation by organic substances such as fulvic and humic acids
4. Precipitation or coprecipitation by incorporation in crystalline minerals

TABLE 20.16
Geochemical Properties of Listed Metals and Nonmetals

Property	Forms/Conditions
Mobility	Cr is very mobile in neutral to alkaline conditions. As is more mobile under anaerobic than aerobic conditions and in alkaline conditions. Pb^{2+2} is relatively immobile except in highly acidic environments.
Strong adsorption on Fe and Mn oxides and hydrous oxides	Cd, Cr(IV), Hg, Ni, Se.
Precipitation	$Cd + H_2S \rightarrow CdS$. Cr + organic material → insoluble (aerobic conditions) precipitates. Cr(III) hydroxide, carbonate, and sulfide precipitate ($pH > 6$); Cr(VI) does not precipitate in these conditions. Pb typically precipitates as $Pb(OH)_2$, $PbCO_3$, $Pb_5(PO_4)_3OH$. NaCl increases solubility. Ni carbonates, hydroxides, and sulfides are relatively insoluble; Ni oxides in acidic solution may precipitate with neutralization.
Oxidation–reduction	Many selenium compounds can be reduced to produce elemental selenium when exposed to organic matter in subsurface environment.
Bioconversion	$As(OH)_3$ to $As(CH_3)_3$ (anaerobic); Hg (inorganic) to methyl mercury (anaerobic).

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

Solution complexation is of major importance for the fate of metals in the deep-well environment. Soluble metal ions in solution can be divided into three major groups: simple hydrated metal ions,[103] metals complexed by inorganic anions, and organometallic complexes.[104] The stability of complexes between metals and organic matter is largely independent of ligand, and follows the following general relationships[105]:

1. Monovalent ions: Ag > Tl > Na > K > Pb > Cs
2. Divalent ions: Pt > Pd > Hg > UO_2 > Cu > Ni > Co > Pb > Zn > Cd > Fe > Mn > Sr > Ba
3. Trivalent ions: Fe > Ge> Sc > In > Y > Pl > Ce > La

Hydration reactions between metal ions and water affect mobility and adsorption but not toxicity. Hydrolysis is particularly important in the chemistry of cyanide.

Oxidation–reduction reactions may affect the mobility of metal ions by changing the oxidation state. The environmental factors of pH and Eh (oxidation–reduction potential) strongly affect all the processes discussed above. For example, the type and number of molecular and ionic species of metals change with a change in pH (see Figures 20.5–20.7). A number of metals and nonmetals (As, Be, Cr, Cu, Fe, Ni, Se, V, Zn) are more mobile under anaerobic conditions than aerobic conditions, all other factors being equal.[104] Additionally, the high salinity of deep-well injection zones increases the complexity of the equilibrium chemistry of heavy metals.[106]

Förstner and Wittmann[107] reported the following observations about the general mobility of heavy metals in groundwater:

1. Mobility tends to increase with increasing salinity because alkali- and alkaline-earth cations compete for adsorption sites on solids.
2. A change in redox conditions (lower Eh) can partly or completely dissolve Fe and Mn oxides and liberate other coprecipitated metals.
3. When natural or synthetic complexing agents are added, soluble metal complexes may form.

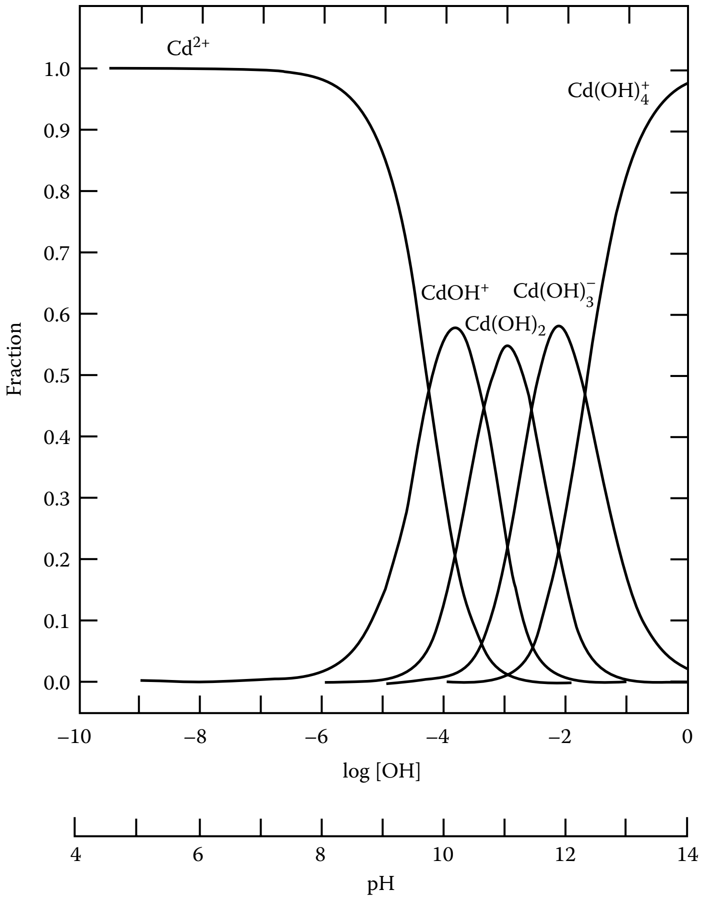


FIGURE 20.5 Distribution of molecular and ionic species of divalent cadmium at different pH values. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

20.5.2.2 Known Properties of Listed Hazardous Inorganics

An extensive body of literature is available on the chemistry of listed inorganic wastes, although most of it is oriented toward near-surface environments. For example, Förstner and Wittmann[107] present a good overview of the aqueous geochemistry of metal contaminants, and the various reports of the National Research Council of Canada provide summaries of the geochemistry of individual metals. Fuller[105] contains over 200 citations on the movement of metals in soil, and Moore and Ramamoorthy[108] devote individual chapters to the chemistry of As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn in natural waters. One source that does discuss the chemistry of listed wastes in the deep-well environment is Strycker and Collins.[109] The information on listed inorganic wastes is summarized in Table 20.16.

20.5.3 CHEMICAL PROPERTIES OF ORGANIC HAZARDOUS WASTES

Because carbon atoms can form strong bonds with one another while combining with other elements, the number of organic compounds is enormous. More than two million such compounds have been described and characterized,[3] which is more than ten times the total number of known compounds of all other elements except hydrogen.

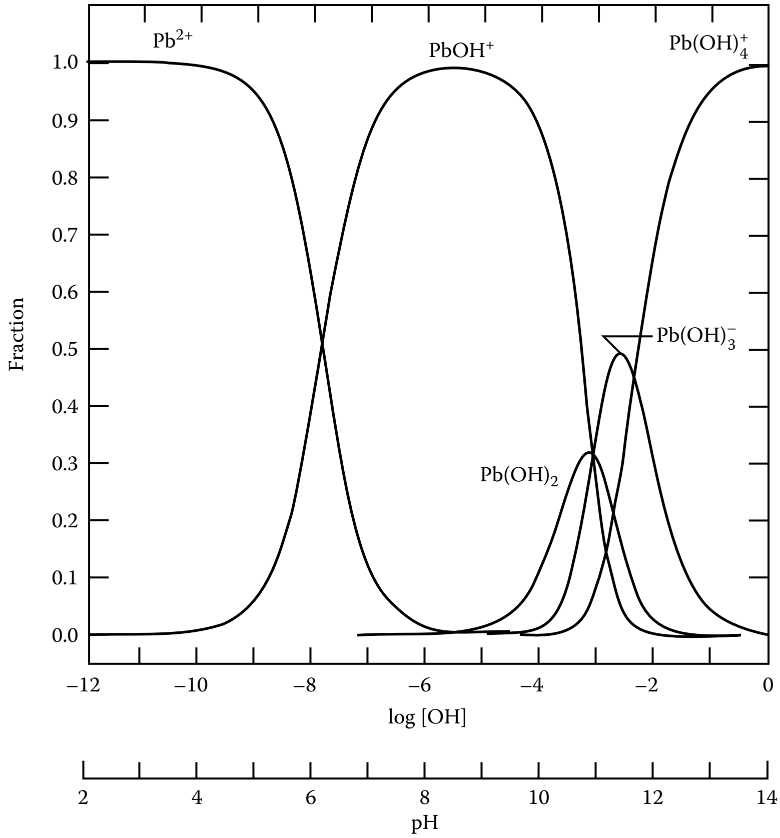


FIGURE 20.6 Distribution of molecular and ionic species of divalent lead at different pH values. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

Organic compounds can be broadly grouped into hydrocarbons (compounds formed from only carbon and hydrogen atoms) and their derivatives, in which a hydrogen atom is replaced with another atom or group of atoms, such as a functional group (e.g., an atom or atom group that imparts characteristic chemical properties to the organic molecules containing it). Structurally, organic compounds can also be classified as straight-chain compounds, branched-chain compounds, and cyclic compounds. Another classification of organic compounds divides these compounds between aromatics (those with a six-member ring structure in which single and double carbon bonds alternate) and aliphatics (those containing chains or nonaromatic rings of carbon atoms). There are seven major groups of hazardous organics:

1. Halogenated aliphatic hydrocarbons
2. Halogenated ethers
3. Monocyclic aromatics
4. Phthalate esters
5. Polycyclic aromatic hydrocarbons
6. Nitrogenous compounds
7. Pesticides

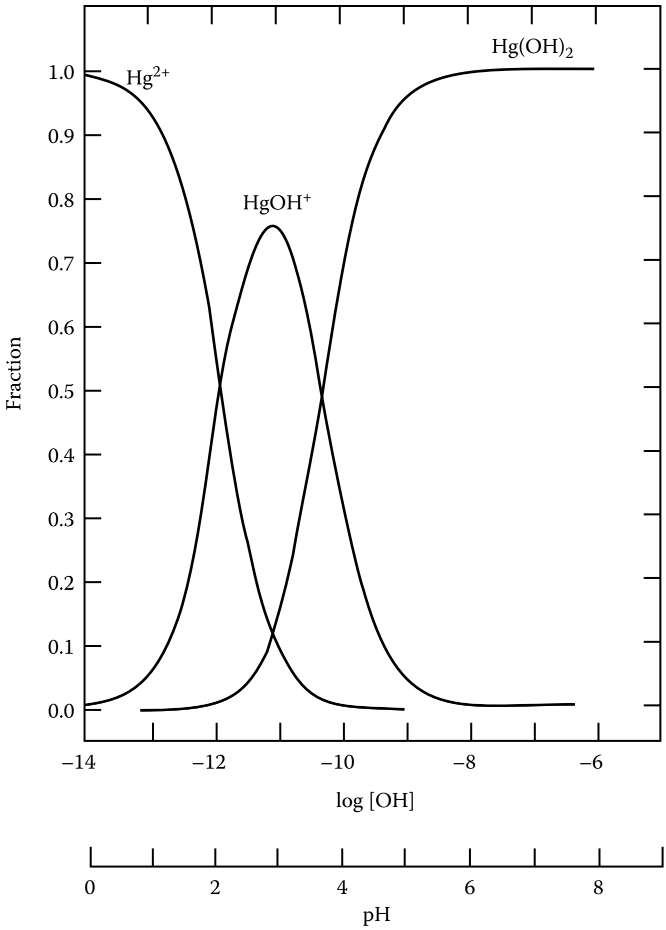


FIGURE 20.7 Distribution of molecular and ionic species of divalent mercury at different pH values. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

20.5.3.1 Halogenated Aliphatic Hydrocarbons

Hazardous halogenated aliphatic hydrocarbons include mostly straight-chain hydrocarbons (alkanes containing single bonds, such as methane and ethane, and alkenes containing one double bond between carbon atoms, such as ethene and propene) in which one or more hydrogen atoms are replaced by atoms of the halogen group of elements (fluorine, chlorine, or bromine). Moore and Ramamoorthy[110] reviewed the behavior of aliphatic hydrocarbons in natural waters.

Tabak and colleagues[111] found most compounds in the group to be subject to significant degradation under experimental aerobic conditions. At least ten of the compounds are subject to biodegradation under anaerobic conditions. Britton[112] discusses microbial degradation of aliphatic hydrocarbons in more detail.

20.5.3.2 Halogenated Ethers

Ethers are either aliphatic (chain-structure) or aromatic (ring-structure) hydrocarbons containing an oxygen atom connected to two carbon atoms by single bonds. In halogenated ethers, one or more halogens (chlorine or bromine) replace hydrogen in the aliphatic or aromatic portion of the molecule. This group contains mostly aliphatic ethers except for 4-chlorophenyl phenyl ether and 4-bromophenyl phenyl ether, which are aromatic hydrocarbons.

Adsorption is very likely to be a more significant process for the aromatic halogenated ethers than for the aliphatic halogenated ethers. Hydrolysis is important for two of the aliphatic ethers: *bis*(chloromethyl) ether and 2-chloroethyl vinyl ether. The group appears generally resistant to biodegradation, although under certain conditions several may be degraded.

20.5.3.3 Monocyclic Aromatic Hydrocarbons and Halides

As mentioned, aromatic hydrocarbons have a six-member ring structure in which single and double carbon bonds alternate. This ring structure tends to be stable, so chemical reactions tend to result in the substitution of hydrogen atoms for another atom or functional group. Five of these compounds are hydrocarbons (benzene, ethylbenzene, toluene, phenol, and 2,4-dimethyl phenol) and the rest are halogenated or nitrogenated derivatives of benzene, toluene, and phenol. Moore and Ramamoorthy[110] reviewed the behavior of monocyclic aromatics and phenols in natural waters.

Adsorption may be important for most of the compounds in this group, whereas hydrolysis may not be a significant process except for pentachlorophenol. Tabak and colleagues[111] found that significant degradation with rapid or gradual adaptation occurred for 15 of a listed 23 compounds. Anaerobic degradation has been reported for five compounds in this group (benzene, ethylbenzene, phenol, 2-chlorophenol, and 2,4-dichlorophenol). Chapman[113] discusses in some detail the reaction sequence used for the bacterial degradation of phenolic compounds; Gibson and Subramanian[114] provide a general review of microbial degradation of aromatic hydrocarbons; and Reinke[115] reviews microbial degradation of halogenated aromatics.

20.5.3.4 Phthalate Esters

Esters contain a single oxygen atom attached to a single carbon atom by a single bond, and a second oxygen atom attached to the same carbon atom by a double bond. Phthalate esters form when aliphatic hydrocarbon groups replace the acidic hydrogen atoms in phthalic acid (benzenedicarboxylic acid). All phthalate esters are subject to adsorption and are readily biodegraded under aerobic conditions, but apparently not under anaerobic conditions. Ribbons and colleagues[116] review mechanisms for microbial degradation of phthalates. Hydrolysis half-lives of four phthalate esters (dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, and di-*n*-octyl phthalate) are on the order of thousands of days, which may be significant in the timeframe of deep-well injection.

20.5.3.5 Polycyclic Aromatic Hydrocarbons

Polycyclic (also called polynuclear) aromatic hydrocarbons (PAHs) are composed of multiple rings connected by shared carbon atoms (i.e., separate rings are combined by sharing two carbon atoms). All these compounds are pure hydrocarbons except for the two benzo-fluoranthenes, polychlorinated biphenyls (PCBs), and 2-chloronaphthalene. Moore and Ramamoorthy[110] review the behavior of PAHs in natural waters.

Adsorption and biodegradation under aerobic conditions are significant for the entire group, but PAHs are generally resistant to anaerobic degradation. Safe[117] reviews the literature on microbial degradation of PCBs. Hydrolysis is not significant for any compounds in the group.

20.5.3.6 Nitrogenous Compounds

The diverse nitrogenous compounds group is composed of substances that have in common the substitution of one or more nitrogen-containing functional groups for hydrogen in the structure. Amines are derivatives of ammonia and contain a nitrogen atom bonded to at least one carbon atom. Nitrosamines are amines with a nitro ($-NO_2$) functional group; two are aliphatic (dimethylnitrosamine and di-*n*-propyl nitrosamine) and one is aromatic (diphenylnitrosamine). The two benzidines and 1,2-diphenyl hydrazine are aromatic amines. Acrylonitrile contains the nitrile (–CN) functional group. Adsorption is a significant process for all four of the aromatic amines; hydrolysis is not. Compounds in the group are generally not amenable to biodegradation. Acrylonitrile, however, is readily mineralized by anaerobic denitrifying bacteria.

20.5.3.7 Pesticides

By definition, any pesticide has toxic effects on organisms. Listed pesticides are those that combine high toxicity with resistance to degradation in the environment. Moore and Ramamoorthy[109] review the behavior of chlorinated pesticides in natural waters.

Most of the common 15 hazardous pesticides are chlorinated hydrocarbons. Adsorption can be an important process for most. All except DDT, endosulfan, and heptachlor resist hydrolysis, and most are also resistant to biodegradation. Kearney and Kaufman[118] review conditions under which chlorinated pesticides are biodegraded.

20.6 METHODS AND MODELS FOR PREDICTING THE GEOCHEMICAL FATE OF DEEP-WELL-INJECTED WASTES

20.6.1 Basic Approaches to Geochemical Modeling

The geochemical interactions possible between an injected waste and the reservoir rock and its associated fluids can be quite complex. Thus a combination of computer modeling, laboratory experimentation, and field observation will inevitably be necessary to satisfy current regulatory requirements for a geochemical no-migration deep-well injection. This section covers the computer methods and models available for predicting geochemical fate.

The American Society for Testing and Materials (ASTM)[119] has developed a standard protocol for evaluating environmental chemical-fate models, along with the definition of basic modeling terms, shown in Table 20.17. Predicting fate requires natural phenomena to be described mathematically.

TABLE 20.17
Definitions of Terms Used in Chemical Fate Modeling

Term	Definition
Algorithm	The numerical technique embodied in the computer code.
Calibration	A test of a model with known input and output information that is used to adjust or estimate factors for which data are not available.
Computer code	The assembly of numerical techniques, bookkeeping, and control languages that represents the model from acceptance of input data and instruction to delivery of output.
Model	An assembly of concepts in the form of a mathematical equation that portrays understanding of a natural phenomenon.
Sensitivity	The degree to which the model result is affected by changes in a selected input parameter.
Validation	Comparison of model results with numerical data independently derived from experiment or observation of the environment.
Verification	Examination of the numerical technique in the computer code to ascertain that it truly represents the conceptual model and that there are no inherent numerical problems associated with obtaining a solution.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

The expression of chemical fate can be computerized using a code to perform the computations and predict the results when inputs simulating conditions of interest are provided. Two critical aspects of the use of computer codes for predicting geochemical fate are the verification and validation of the models on which the codes are based.

In addition to the limited availability of validation, the following are some of the problems found in computer and mathematical modeling[120]:

1. The data on thermodynamic properties of many relevant water-miscible organic species are either incomplete or unavailable.
2. Many minerals are solid solutions (e.g., clays, amphiboles, and plagioclase feldspars). Solid-solution models are either not available or appropriate algorithms have not been incorporated into computer codes.
3. Models describing the adsorption of water-miscible organic compounds on natural materials have not been correlated with field observations under typical injection-zone conditions. Few computer codes contain algorithms for calculating the distribution of species between the adsorbed and aqueous states.
4. Calcium-sodium-chloride-type brines (which typically occur in deep-well-injection zones) require sophisticated electrolyte models to calculate their thermodynamic properties. Many parameters for characterizing the partial molal properties of the dissolved constituents in such brines have not been determined. (Molality is a measure of the relative number of solute and solvent particles in a solution and is expressed as the number of gram-molecular weights of solute in 1000 g of solvent.) Precise modeling is limited to relatively low salinities (where many parameters are unnecessary) or to chemically simple systems operating near 25°C.
5. Computer codes usually calculate only the thermodynamically most stable configuration of a system. Modifications can simulate nonequilibrium, but there are limitations on the extent to which codes can be manipulated to simulate processes that are kinetically (rate) controlled; the slow reaction rates in the deep-well environment compared with groundwater movement (i.e., failure to attain local homogeneous or heterogeneous reversibility within a meter or so of the injection site) create particular problems.
6. Little is known about the kinetics of dissolution, precipitation, and oxidation–reduction reactions in the natural environment. Consequently, simulating the kinetics of even more complicated injection- zone chemistry is very difficult.

Bergman and Meyer[121] point out a particularly relevant problem with mathematical models. The relative reliability of mathematical models (compared with physical models based on empirical field or laboratory studies) decreases rapidly as the number of environmental pollutants being modeled increases (see Figure 20.8). Consequently, mathematical models tend to be less cost-effective for complex wastestreams than physical (empirical) models.

20.6.2 Specific Methods and Models

Most of the chemical processes discussed before (acid–base equilibria, precipitation–dissolution, neutralization, complexation, and oxidation–reduction) are interrelated; that is, reactions of one type may influence other types of reactions, and consequently must be integrated into aqueous- and solution-geochemistry computer codes.

20.6.2.1 Aqueous- and Solution-Geochemistry Computer Codes

More than 50 computer codes that calculate chemical equilibrium in natural waters or similar aqueous systems are described in the literature.[122] Most are not suitable for modeling the deep-well

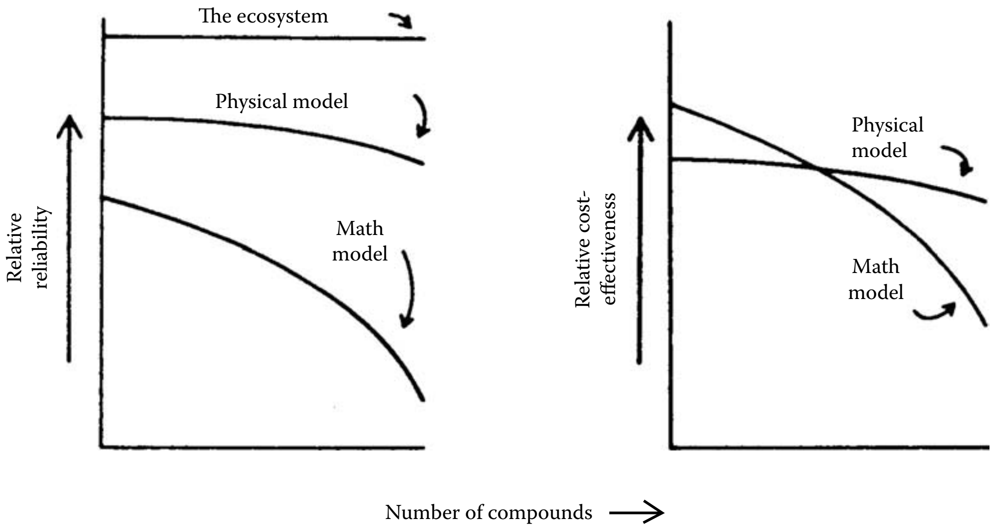


FIGURE 20.8 Relative tradeoffs between physical (microcosm) and mathematical models as affected by effluent complexity. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

injection of hazardous wastes, because they are limited to simulating reactions under one or more of the following conditions:

1. Ambient temperatures (25°C)
2. Low pressures (1 atm)
3. Relatively low salinities

When the simulation of deep-well temperatures, pressures, and salinities is imposed as a condition, the number of codes that may be of value is reduced to a much smaller number. Nordstrom and Ball[121] recommend six references as covering virtually all the mathematical, thermodynamic, and computational aspects of chemical-equilibrium formulations (see references 123–128). Recent references on modeling include references 45, 63, 70, 129, and 130.

20.6.2.2 Adsorption

Mineral surfaces on which adsorption may occur are diverse and complex, and the mechanisms by which a hazardous constituent may attach to the solid surface vary substantially. Therefore, theoretical models that can be used readily to predict adsorption for a variety of compounds over a range of conditions are difficult to develop. Table 20.18 summarizes the applicability of three major methods for predicting adsorption in the deep-well environment. These methods include the following:

1. Adsorption isotherms
2. The clay ion-exchange model
3. The triple-layer model

Adsorption isotherms

The simplest and most widely used method for predicting adsorption is to measure adsorption isotherms (the variations in the amount of a substance adsorbed at different concentrations measured at a constant temperature). Empirical constants can be calculated from such measurements.

TABLE 20.18
Applicability of Methods and Models for Predicting Adsorption in the Deep-Well Environment

Method/Model	Applicability
Methods	
Adsorption isotherms	Relatively easy to measure. The main disadvantage is that the empirical coefficients may change with changing environmental conditions, requiring measurement.
Linear distribution coefficient	Applicable only at very dilute concentrations of organic compounds and where >0.1% organic matter is present. Usefulness is uncertain.
Langmuir	Underlying assumptions for the derivation of the equation typically will not apply.
Freundlich	Limited available data on adsorption under simulated deep-well conditions are best described by the formula; however, the disadvantage of all adsorption isotherms applies.
Models	
Clay ion-exchange model	May be useful for predicting adsorption of heavy metals. Aqueous-phase-activity solid-solution model coefficients can be obtained from distribution-of-species models. Estimating clay-phase activity coefficients is more problematic.
Triple-layer model	Of limited value because of the complexity of adsorption sites, unpredictable interactions among adsorbents, and complications introduced by high salinities.

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

The amount of adsorption at concentrations other than those that were measured can then be predicted using the empirical constants in an appropriate formula. The correct application of this method requires acknowledging such effects as matrix and temperature.

Three types of adsorption isotherms are discussed in this section:

1. The linear distribution coefficient
2. The Langmuir adsorption isotherm
3. The Freundlich adsorption isotherm

The distribution coefficient assumes that adsorption is linear (i.e., the amount of adsorption is directly proportional to the concentration of the compound in solution) and is actually a special case of the Langmuir and Freundlich isotherms, which are nonlinear.[31,32]

The simplest type of isotherm is the linear-distribution coefficient, K_d.[121] It is also called the partition coefficient, K_p.[58] The equation for calculating adsorption at different concentrations is

$$S = K_d C \tag{20.6}$$

where S = amount adsorbed (μg/g solid), C = concentration of adsorbed substance in solution (μg/mL), and K_d = linear distribution coefficient = partition coefficient = K_p.

This equation is widely used to describe adsorption in soil and near-surface aquatic environments. Another widely used linear coefficient is the organic-carbon partition coefficient K_{oc}, which is equal to the distribution coefficient divided by the percentage of organic carbon present in the system as proposed by Hamaker and Thompson.[131]

$$K_{oc} = \frac{K_d}{\%\ \text{organic carbon}} \tag{20.7}$$

Sabljiã[132] presents very accurate equations for predicting the K_{oc} of both polar and nonpolar organic molecules based on molecular topology, provided the organic matter percentage exceeds 0.1%. Karickhoff[133] discusses in detail adsorption processes of organic pollutants in relation to K_{oc}.

Winters and Lee[134] describe a physically based model for adsorption kinetics for hydrophobic organic chemicals to and from suspended sediment and soil particles. The model requires determination of a single effective diffusivity parameter, which is predictable from compound solution diffusivity, the octanol–water partition coefficient, and the adsorbent organic content, density, and porosity.

Major problems are associated with using the linear distribution coefficient for describing adsorption–desorption reactions in groundwater systems. Some of these problems include the following[135,136]:

1. The coefficient actually measures multiple processes (reversible and irreversible adsorption, precipitation, and coprecipitation). Consequently, it is a purely empirical number with no theoretical basis on which to predict adsorption under differing environmental conditions or to give information on the types of bonding mechanisms involved.
2. The waste-reservoir system undergoes a dynamic chemical evolution in which changing environmental parameters may result in variations of K_d values by several orders of magnitude at different locations and at the same location at different times.
3. All methods used to measure the K_d value involve some disturbance of the solid material and consequently do not accurately reflect *in situ* conditions.

The Langmuir equation was originally developed to describe adsorption of gases on homogeneous surfaces and is commonly expressed as follows:

$$\frac{C}{S} = \frac{1}{kS_{\max}} + \frac{1}{CS_{\max}} \tag{20.8}$$

where $S_{\max}$ = maximum adsorption capacity (μg/g soil), k = Langmuir coefficient related to adsorption bonding energy (mL/g), S = amount adsorbed (μg/g solid), and C = concentration of adsorbed substance in solution (μg/mL).

A plot of C/S versus $1/C$ allows the coefficients k and $S_{\max}$ to be calculated. When $kC \ll 1$, adsorption will be linear, as represented by Equation 20.6.

The Langmuir model has been used to describe adsorption behavior of some organic compounds at near-surface conditions.[137] However, three important assumptions must be made:

1. The energy of adsorption is the same for all sites and is independent of degree of surface coverage.
2. Adsorption occurs only on localized sites with no interactions among adjoining adsorbed molecules.
3. The maximum adsorption capacity ($S_{\max}$) represents coverage of only a single layer of molecules.

In a study of adsorption of organic herbicides by montmorillonite, Bailey and colleagues[138] found that none of the compounds conformed to the Langmuir adsorption equation. Of the 23 compounds tested, only a few did not conform well to the Freundlich equation.

The assumptions mentioned above for the Langmuir isotherm generally do not hold true in a complex heterogeneous medium such as soil. The deep-well environment is similarly complex and consequently the studies of adsorption in simulated deep-well conditions[139,140] have followed the form of the Freundlich equation:

$$S = KC^N \tag{20.9}$$

where S and C are as defined in Equation 20.6, and K and N are empirical coefficients.

Taking the logarithms of both sides of Equation 20.9:

$$\log S = \log K + N \log C \tag{20.10}$$

Thus, log–log plots of S versus C provide an easy way to obtain the values for K (the intercept) and N (the slope of the line). The log–log plot can be used for graphic interpolation of adsorption at other concentrations, or, when values for K and N have been obtained, the amount of adsorption can be calculated from Equation 20.9. Figure 20.9 shows an example of adsorption isotherms for phenol adsorbed on Frio sandstone at two different temperatures. Note that when $N = 1$, Equation 20.9 simplifies to Equation 20.6 (i.e., adsorption is linear).

The Langmuir equation has a strong theoretical basis, whereas the Freundlich equation is an almost purely empirical formulation because the coefficient N has embedded in it a number of thermodynamic parameters that cannot easily be measured independently.[120] These two nonlinear isotherm equations have most of the same problems discussed earlier in relation to the distribution-coefficient equation. All parameters except adsorbent concentration C must be held constant when measuring Freundlich isotherms, and significant changes in environmental parameters, which would be expected at different times and locations in the deep-well environment, are very likely to result in large changes in the empirical constants.

An assumption implicit in most adsorption studies is that adsorption is fully reversible. In other words, once the empirical coefficients are measured for a particular substance, Equations 20.6 to 20.10 describe both adsorption and desorption isotherms. This assumption is not always true. Collins and Crocker[140] observed apparently irreversible adsorption of phenol in flowthrough adsorption experiments involving phenol interacting on a Frio sandstone core under simulated deep-well

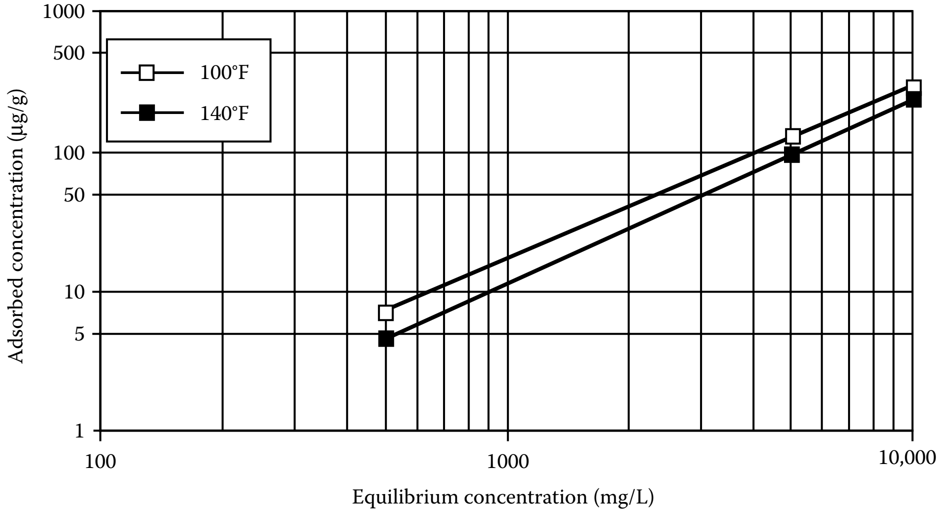


FIGURE 20.9 Freundlich isotherm for phenol adsorbed on Frio Core. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

temperatures and pressures. If adsorption–desorption is not fully reversible, it may be necessary to use separate Freundlich adsorption- and desorption-isotherm equations to model these processes in the deep-well environment.[120]

Clay ion-exchange model

As noted above, adsorption isotherms are largely derived empirically and give no information on the types of adsorption that may be involved. Scrivner and colleagues[39] have developed an adsorption model for montmorillonite clay that can predict the exchange of binary and ternary ions in solution (two and three ions in the chemical system). This model would be more relevant for modeling the behavior of heavy metals that actively participate in ion-exchange reactions than for organics, in which physical adsorption is more important.

The clay ion-exchange model assumes that the interactions of the various cations in any one clay type can be generalized and that the amount of exchange will be determined by the empirically determined cation-exchange capacity (CEC) of the clays in the injection zone. The aqueous-phase activity coefficients of the cations can be determined from a distribution-of-species code. The clay-phase activity coefficients are derived by assuming that the clay phase behaves as a regular solution and by applying conventional solution theory to the experimental equilibrium data in the literature.[3]

Scrivner and colleagues[39] compared the ion-exchange model predictions with several sets of empirical data. The model predictions are very accurate for binary-exchange reactions involving the exchange of nickel ions for sodium and potassium ions on illite and less accurate for ternary reactions involving hydrogen, sodium, and ammonia ions. The deep-well environment, however, is very likely to have multiple exchangeable species (such as Na^+, K^+, Ca^{2+}, and Mg^{2+}), and injected wastes commonly have elevated concentrations of more than one heavy metal. These concentrations result in complex ion-exchange interactions that probably exceed the capabilities of the model.

Triple-layer model

One of the more sophisticated models for describing adsorption phenomena in aqueous solutions is the triple-layer model (TLM), also called the Stanford General Model for Adsorption (SGMA) because it has been developed, refined, and tested over a number of years by faculty and researchers at Stanford University.[141–143] The TLM separates the interface between the aqueous phase and the adsorbent surface into three layers: surface layer, inner diffuse layer, and outer diffuse layer. Each has an electrical potential, charge density, capacitance, and dielectric constant. Hydrogen ions are assumed to bind at the surface plane; electrolyte ions (such as Na^+) bind at the inner diffuse plane. The surface is assumed to be coated with hydroxyl groups (OH^-), with each surface site associated with a single hydroxyl group. The hydroxyl-occupied surface sites may either react with other ions in solution or dissociate according to a series of reactions, with each having an associated equilibrium constant. Experimental terms relate the concentrations of the ions at their respective surface planes to those in the bulk solution. The sum of the charges of the three layers is assumed to be zero (i.e., the triple layer is electrically neutral). For all its sophistication, TLM is of limited value for predicting adsorption in deep-well environments[120]:

1. Site-binding constants have been determined for only a limited range of simple oxides with only one type of surface site. Multiple-surface site minerals occurring in the deep-well environment such as silicates, aluminosilicates, and complex oxides (such as manganese oxide) will require much more complex TLMs.
2. Fixed-charge minerals such as clay are even more complex than the multiple-surface site minerals, and both ion exchange and other types of adsorption must be measured to characterize absorption reactions fully.
3. Minerals with different adsorptive properties in the injection zone may interact to produce results different from those that would be obtained if each mineral were tested separately. No satisfactory model has been developed that predicts adsorption properties of mixtures based on the properties of individual adsorbents.

4. The TLM is based on laboratory measurements of adsorption on materials that are suspended in solution. No satisfactory methods for measuring and interpreting the adsorptive properties of intact host rock have been developed for TLM application.
5. The TLM has been developed using studies based on solutions of relatively low concentrations of dissolved compounds. The very saline and briny conditions found in the deep-well environment may require an entirely different model.

20.6.2.3 Biodegradation

This section examines two quantitative models for predicting biodegradation: the kinetic rate expressions and the biofilm model. It also examines several qualitative models for describing biodegradation in the deep-well environment.

Kinetic rate expressions

When microorganisms use an organic compound as a sole carbon source, their specific growth rate is a function of chemical concentration and can be described by the Monod kinetic equation. This equation includes a number of empirical constants that depend on the characteristics of the microbes, pH, temperature, and nutrients.[54] Depending on the relationship between substrate concentration and rate of bacterial growth, the Monod equation can be reduced to forms in which the rate of degradation is zero order with substrate concentration and first order with cell concentration, or second order with concentration and cell concentration.[144]

The Monod equation assumes a single carbon source. The difficulty in handling multiple carbon sources, which are typical in nature, has led to the use of an empirical biodegradation rate constant k_1:

$$S = k_1 BC \tag{20.11}$$

where B = bacterial concentration, k_1 = an empirical biodegradation rate constant. This equation is of the same form as Equation 20.6 for linear adsorption. Predicting biodegradation using such a rate constant is complicated when multiple biodegradable compounds are present. For example, phenol and naphthalene are both rapidly biodegraded in single-compound laboratory shake-flask experiments when seeded with bacteria from an oil-refinery settling pond, but when the two compounds are combined, naphthalene is not degraded until the phenol is gone.[3]

When a compound is cometabolized (degraded but not used as a nutrient), a second-order biodegradation coefficient can be used to estimate, k_{B}:

$$k_{\mathrm{B}} = k_{\mathrm{B2}} B \tag{20.12}$$

where k_{B} = first-order biodegradation coefficient, k_{B2} = second-order biodegradation coefficient, and B = bacterial concentration.

Mills and colleagues[58] describe the use of these formulations to predict aerobic biodegradation in surface waters and present methods of adjusting for temperature and nutrient limitations. This approach to predicting biodegradation is problematic because it is difficult to obtain empirical coefficients in the deep-well setting.

Baughman and colleagues[145] derive a second-order kinetic rate expression as a special case of the Monod kinetic equation. It appears to describe biodegradation of organics in natural surface waters reasonably well:

$$-\mathrm{d}C/\mathrm{d}t = k[B][C] \tag{20.13}$$

Paris and colleagues[144] found that degradation of several pesticides in samples from over 40 lakes and rivers fits this second-order model of microbial degradation.

General degradation rate models of organics in soils have been described by Hamaker,[146] Larson,[147] and Rao and Jessup.[148] In most instances, biodegradation is the major, but not necessarily the only, process affecting the rate of degradation.

Biofilm model

The most sophisticated model available for predicting biodegradation of organic contaminants in subsurface systems is the biofilm model, presented by Williamson and McCarty[149,150] which has been refined over several years by researchers at Stanford University and the University of Illinois/Urbana.[151–157]

The biofilm model is based on two important features of the groundwater environment:

1. The nutrient concentrations tend to be low.
2. The solid matrix has a high specific surface area.

These characteristics favor the attachment of bacteria to solid surfaces in the form of biofilm so that nutrients flowing in the groundwater can be used. The presence of low nutrient levels in the groundwater also implies that bacteria must regularly use many different compounds as energy sources and, consequently, may select organic contaminants more readily as nutrients.

The basic biofilm model[149,150] idealizes a biofilm as a homogeneous matrix of bacteria and the extracellular polymers that bind the bacteria together and to the surface. A Monod equation describes substrate use; molecular diffusion within the biofilm is described by Fick's second law; and mass transfer from the solution to the biofilm surface is modeled with a solute-diffusion layer. Six kinetic parameters (several of which can be estimated from theoretical considerations and others of which must be derived empirically) and the biofilm thickness must be known to calculate the movement of substrate into the biofilm.

Rittmann and McCarty[152,153] have developed equations for incorporating bacterial growth into the model, allowing the steady-state utilization of substrate materials to be predicted. They also show theoretically and verify experimentally that there is a substrate concentration threshold $S_{\min}$ below which no significant activity occurs. McCarty and colleagues[154] introduce the idea of secondary substrate utilization by a biofilm, in which microbes can metabolize trace compounds ($S < S_{\min}$) in the presence of another substrate that is in sufficient concentrations to support biofilm growth. Bouwer and McCarty[155] incorporate steady-state utilization of secondary substrates into the model by coupling the biofilm mass (controlled by degradation of the primary substrate) with concentration and individually determine rate parameters for each secondary substrate. Laboratory tests of degradation on a variety of chlorinated benzenes, nonchlorinated aromatics, and halogenated aliphatics as secondary substrates agree reasonably well with predicted values.[155] The later refinement of the model incorporates the effects of adsorption of material substrate to the surface on which the biofilm is attached, but is restricted to biofilm on activated carbon.[156,157]

When water containing substrate concentrations greater than $S_{\min}$ is injected into the subsurface, the model predicts that biofilm development will occur only in the first meter or so of the injection zone.[151] Low concentrations of hazardous compounds will be significantly degraded as secondary substrates only if they are readily biodegraded in the biofilm zone. Any amount not biodegraded in the biofilm zone will tend to persist once it leaves the zone of concentrated biological activity. When substrate concentrations are not sufficient to sustain biofilm development, Bouwer and McCarty[155] suggest that a simple biodegradation coefficient such as that discussed earlier (Equation 20.11) is probably adequate.

Qualitative models

Several qualitative models for biodegradation in the deep-well environment have been suggested. They do not allow quantitative predictions to be made, but they do provide insight into the types of biodegradation processes that may occur. These models have not been expressed quantitatively to

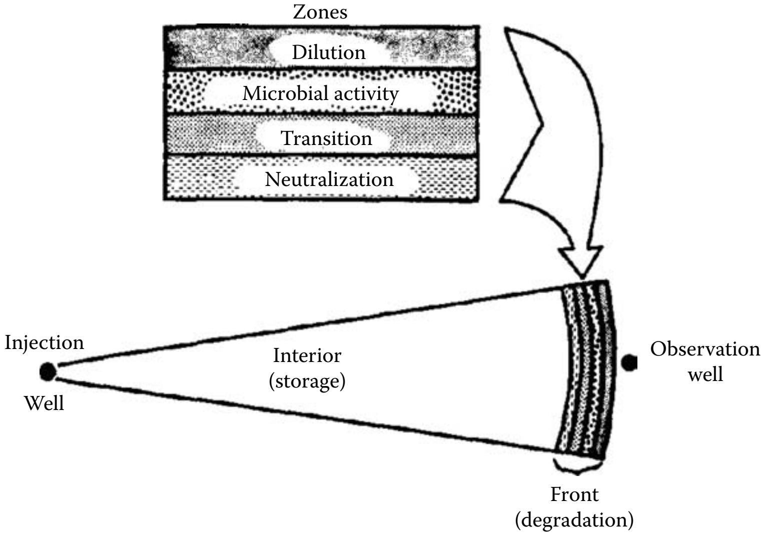


FIGURE 20.10 Proposed geochemical model of waste after injection into the subsurface. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

simulate degradation, although relatively simple codes using first-order biodegradation constants k_B could probably be developed without much difficulty. In the absence of quantitative models for predicting biodegradation, laboratory simulations must be used to assess biodegradation potential.

The conceptual geochemical model of acidic waste after injection into the subsurface, proposed by Leenheer and Malcolm,[102] involves a moving front of microbial activity with five zones as shown in Figure 20.10:

1. The dilute zone, controlled by diffusion
2. A zone where substrate concentrations are sufficiently high to allow significant microbial activity
3. The transition zone, where increasing waste concentrations create unfavorable conditions for microbial growth
4. The neutralization zone, where abiotic chemical reactions predominate
5. The waste storage zone where undiluted waste no longer reacts with the host rock.

This model implies that the rate of injection far exceeds the zone's capacity for biodegradation. Bouwer and McCarty[155] suggest a qualitative model that represents nonbiofilm microbial biodegradation over increasing distances from the injection point. This model follows the redox reaction sequence. This model implies that most compounds not degraded in their appropriate zone will move through the groundwater system without significant additional degradation. The model also implies, however, that those compounds that are biodegraded by methanogenesis will continue to move through the groundwater until degradation is complete.

20.6.2.4 Hydrolysis

Hydrolysis is easily predicted, provided that the rate constants for a compound are known. The rate of abiotic hydrolysis is given by

$$R = -k_H C_T \tag{20.14}$$

where R = the rate of hydrolysis (mol/L/s or μg/L/s), k_H = specific hydrolysis rate constant (L/s), C_T = the dissolved plus adsorbed phase concentration of compound C (mol/L or μg/L).

The hydrolysis rate constant k_H is actually the sum of three rate constants:

$$k_H = k_n + k_a[H^+] + k_b[OH^-] \tag{20.15}$$

where k_n = the natural hydrolysis rate constant for the pH independent reactions of a chemical with water (L/s), k_a = the acid-catalyzed hydrolysis rate constant (L/mol/s), $[H^+]$ = the concentration of hydrogen ion (mol/L), k_b = the base-catalyzed hydrolysis rate constant (L/mol/s), $[OH^-]$ = the concentration of hydroxide ion (mol/L).

Note that in an acid solution, $k_b = 0$, and in an alkaline solution, $k_a = 0$. k_H can be adjusted to include the effects of adsorption by multiplying ($k_a[H^+] + k_b[OH^-]$) times the decimal fraction of the total amount of a dissolved compound, C.[58] At any fixed pH, the half-life of a substance is independent of concentration and can be calculated with the equation

$$t_{1/2} = 0.693/k_h \tag{20.16}$$

Hydrolysis is strongly pH-dependent, with k_a dominant at low pH and k_b dominant at high pH; at pH 7, k_n can often be most important. However, the detailed relationship of pH and rate depends on the specific values of k_n, k_a, and k_b. If these rate constants are known, then the hydrolysis rate at any pH can be readily calculated. Mabey and Mill[158] provide these data for a large number of organic compounds, and Ellington[159–161] provides data on about 70 regulated hazardous pollutants.

Mills[58] describes step-by-step procedures for calculating k_H, and Scrivner and colleagues[39] describe in detail the modeling of cyanide and nitrite hydrolysis in the deep-well environment.

20.6.2.5 Chemical Transport

Basic approaches and important models of chemical transport will be addressed briefly. Three major approaches can be used to modeling chemical transport:

1. *Retardation-factor models*, which incorporate a simple retardation factor derived from a linear- or linearized-distribution coefficient
2. *Integrated models*, in which all mass, momentum, and energy transfer equations, including those in which chemical reactions participate, are solved simultaneously for each time step in the evolution of the system
3. *Two-step models*, which first solve mass momentum and energy balances for each time step and then reequilibrate the chemistry using a distribution-of-species code.

Empirically determined retardation factors (either partition coefficients or breakthrough curve measurements, which are the change in solute concentration measured over time in laboratory or field experiments) have been widely used because of their inherent simplicity.[162] Modeling of specific geochemical partition and transformation processes is not necessary if the retardation factor can be determined empirically.

The problems with linear-distribution coefficients apply equally to any retardation factor derived from them. Field measurements can be made but are expensive to obtain and highly site specific. Nevertheless, retardation factors provide some insight into organic chemical transport.

Integrated and two-step chemical-transport models incorporate distribution-of-species or reaction-progress codes into hydrologic transport codes. The few studies in which the two approaches have been tested using the same set of field data have agreed reasonably well; thus one approach does not have an obvious advantage over the other. The two-step approach tends to be computationally less intensive than the integrated approach but may have difficulty maintaining mass balance when rapid precipitation and dissolution occur.[120]

A number of models of both types have been described in the literature. Of the models, DYNAMIX would appear to have the greatest potential for use in simulating chemical transport in the deep-well environment because it incorporates the reaction-progress code PHREEQE, which can handle deep-well temperatures. PHREEQE, however, does not incorporate pressure equilibria.

20.7 CASE STUDIES OF DEEP-WELL INJECTION OF INDUSTRIAL WASTE

This section discusses how field studies can be used in geochemical fate assessment and includes six cases of deep-well-injection facilities, documenting the geochemistry of the injected hazardous and other industrial wastes. Each case study is organized in the same format, with section headings as follows:

1. *Injection Facility Overview* describes the type of facility, its current status, and the characteristics of the injected wastes, and presents a brief history of injection and monitoring activities, including the distance traveled by the waste.
2. *Injection/Confining-Zone Lithology and Chemistry* provides information on the geology and chemistry of the injection zone formation fluids.
3. *Chemical Processes Observed* briefly describes the types of interactions and major physical effects that have been observed at the site and evaluates their significance.

Table 20.19 summarizes information about each study, including the location of the well, the lithology of the injection zone, waste characteristics, and the major geochemical processes observed. Current commercial-hazardous-waste, deep-well-injection facilities can be found on the Environment, Health and Safety Online (EHSO) web site.[163]

Field studies are an important complement to geochemical modeling and to laboratory studies. The following are two ways to investigate the interactions between injected wastes and reservoir material:

1. Direct observation of the injection zone and overlying aquifers using monitoring wells
2. Backflushing of the injected waste

In both instances, samples of the fluids in the zone are collected at intervals to characterize the nature of geochemical reactions and to track changes over time.

Monitoring wells drilled into the injection zone at selected distances and directions from the injection well allow direct observation of formation water characteristics and the interactions that occur when the waste front reaches the monitoring well. When placed near the injection well in the aquifer above the confining layer, monitoring wells can detect the upward migration of wastes caused by casing or confining-layer failure. Foster and Goolsby[164] describe detailed methods for constructing monitoring wells.

Monitoring wells have several advantages, in that time-series sampling of the formation over extended periods is easy and the passage of the waste front can be observed precisely. Disadvantages include cost and the potential for upward migration of wastes if monitoring well casings fail. A monitoring well at the Monsanto plant had to be plugged when unneutralized waste reached it because of fears that the casing would corrode. The three Florida case studies and the North Carolina case study illustrate the usefulness of monitoring wells.

Backflushing of injected wastes can also be a good way to observe waste/reservoir geochemical interactions. Injected wastes are allowed to backflow (if formation pressure is above the elevation of the wellhead) or are pumped to the surface. Backflowed wastes are sampled periodically (and reinjected when the test is completed); the last sample taken will have had the longest residence time in the injection zone. Keely[165] and Keely and Wolf[166] describe this technique for characterizing

TABLE 20.19
Summary of Case Studies

Location	Lithology	Wastes	Processes Observed
Florida			
Pensacola (Monsanto)	Limestone	Nitric acid Inorganic salts Organic compounds	Neutralization Bacterial denitrification
Pensacola (American Cyanamid)	Limestone	Acrylonitrile Sodium salts (nitrate, sulfate thiocyanate)	Bacterial denitrification No retardation of thiocyanate ions
Belle Glade	Carbonate	Hot acid Organic plant wastes	Neutralization Bacterial sulfate reduction Methane production
North Carolina			
Wilmington	Sand Silty sand Limestone	Organic acids Formaldehyde Methanol	Neutralization Dissolution–precipitation Complexation Adsorption Bacterial sulfate and iron reduction Methane production
Illinois			
Tuscola	Dolomite	Hydrochlorite acid	Neutralization Dissolution CO_2 gas production
Texas			
Not specified	Miocene sand	1. Organic acids Organic compounds 2. Alkaline salts Organic compounds	Precipitation Adsorption (inferred)

Source: U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.

contamination of near-surface aquifers and suggest using logarithmic time intervals for chemical sampling. The three Florida studies all present results from backflushing experiments.

The advantages of backflushing are reduced cost compared with that of monitoring wells and reduced sampling time (sampling takes place only during the test period). Disadvantages include less precise time- and distance-of-movement determinations and the need to interrupt injection and to have a large enough area for backflushed fluid storage before reinjection.

20.7.1 Case Study No. 1: Pensacola, FL (Monsanto)

20.7.1.1 Injection-Facility Overview

Monsanto operates one of the world's largest nylon plants on the Escambia River about 13 miles north of Pensacola, Florida. The construction, operations, and effects of the injection-well system at this site have been extensively documented by the U.S. Geological Survey in cooperation with the Florida Bureau of Geology. Pressure and geochemical effects are reported by Goolsby,[67] Faulkner and Pascale,[167] and Pascale and Martin.[168] Additional microbiological data are reported by Willis and colleagues[169] and Elkan and Horvath.[170] Major chemical processes observed at the site include neutralization, dissolution, biological denitrification, and methanogenesis.

The waste is an aqueous solution of organic monobasic and dibasic acids, nitric acid, sodium and ammonium salts, adiponitrile, hexamethylenediamine, alcohols, ketones, and esters.[67] The waste also contain cobalt, chromium, and copper, each in the range of 1 to 5 mg/L. Wastestreams with different characteristics, produced at various locations in the nylon plant, are collected in a large holding tank; this composite waste is acidic. The specific characteristics of the waste varied somewhat as a result of process changes (e.g., after 1968 more organic acids and nitric acid were added). Until mid-1968, wastes were partially neutralized by pretreatment. After that, unneutralized wastes were injected. No reason was reported for suspending treatment. Goolsby[67] reports pH measurements ranging from a high of 5.6 in 1967 (at which time the pH was raised before injection by adding aqueous ammonia) to a low of 2.4 in 1971, and Eh ranging from +300 mV in 1967 to +700 mV in 1971. The chemical oxygen demand in 1971 was 20,000 mg/L.

Monsanto began injecting wastes into the lower limestone of the Floridan aquifer in 1963. In mid-1964, a second well was drilled into the formation about 300 m (1000 ft) southwest of the first. A shallow monitoring well was placed in the aquifer above the confining layer about 30 m (100 ft) from the first injection well, and a deep monitoring well was placed in the injection zone about 400 m (1300 ft) south of both injection wells. The deep monitoring well (henceforth referred to as the near-deep monitoring well) was plugged with cement in 1969. In late 1969 and early 1970, two additional deep monitoring wells were placed in the injection formation, 2.4 km (1.5 miles) south-southeast (downgradient) and 3 km (1.9 miles) north-northwest (upgradient) of the site. From 1963 to 1977, about 50 billion liters (13.3 billion gal) of waste were injected. During the same period, injection pressures ranged from 8.8 to 16.5 kg/cm^2 (125 to 235 psi). Since then, a third injection well has been added.

Ten months after injection of neutralized wastes began, chemical analyses indicated that dilute wastes had migrated 1300 ft to the nearest deep monitoring well. Injection of unneutralized wastes began in April 1968. Approximately 8 months later, unneutralized wastes reached the near-deep monitoring well, indicating that the neutralization capacity of the injection zone between the injection wells and the monitoring well had been exceeded. At this point, the monitoring well was plugged with cement from bottom to top because operators were concerned that the acidic wastes could corrode the steel casing and migrate upward.[67] The rapid movement of the waste through the limestone indicated that most of it migrated through a more permeable section, which was about 20 m (65 ft) thick. By mid-1973, 10 years after injection began, a very dilute waste front arrived at the south monitoring well, 2.4 km (1.5 miles) away. As of early 1977, there was no evidence that wastes had reached the upgradient monitoring well. The shallow monitoring well remained unaffected during the same period.

Increases in permeability caused by limestone dissolution approximately doubled the injection index (the amount of waste that can be injected at a specified pressure). As of 1974, the effects of the pressure created by the injection were calculated to extend more than 40 miles radially from the injection site.[167] An updip movement of the freshwater/saltwater interface in the injection-zone aquifer, which lies less than 32 km (20 miles) from the injection wells, was also observed.

20.7.1.2 Injection/Confining-Zone Lithology and Chemistry

The lower limestone of the Floridan aquifer is used as the injection zone (at 430 to 520 m), and the Bucatunna clay member of the Byram formation (about 67 m thick) serves as the confining layer. Figure 20.11 shows the stratigraphy of the area, and Figure 20.12 shows the local stratigraphy and the monitoring well installations. The formation water in the injection zone is a highly saline (11,900 to 13,700 mg/L TDS) sodium-chloride solution. The Eh of samples collected from two monitoring wells located in the injection formation ranged from +23 to –32 mV, indicating reducing conditions in the injection zone that would favor anaerobic biodegradation.

The injection zone contains about 7900 mg/L chloride, but less than 32 km (20 miles) northeast of the injection site, chloride concentrations are less than 250 mg/L. Under natural conditions, water

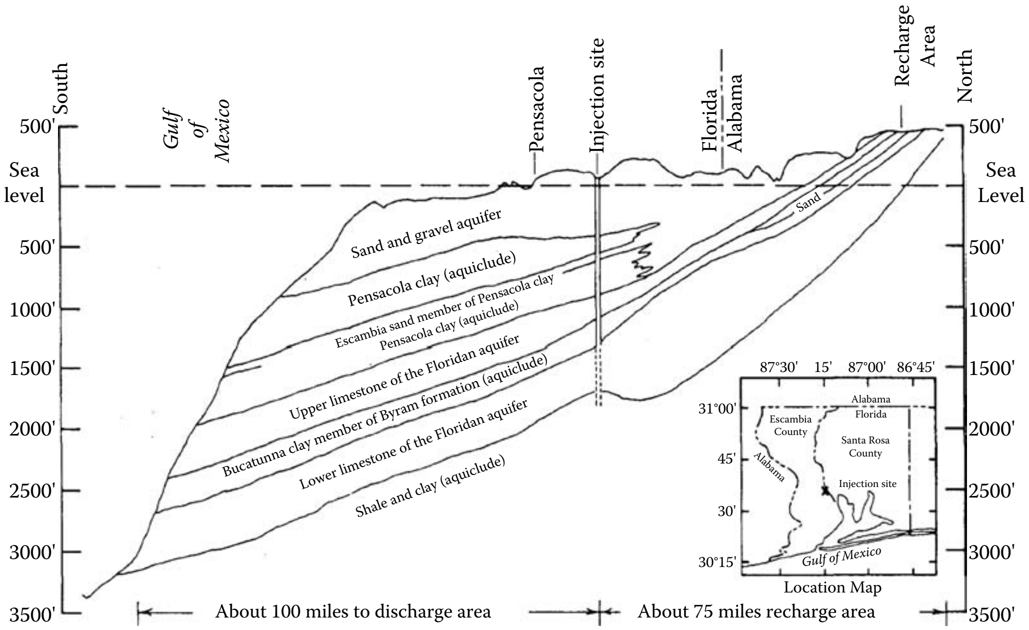
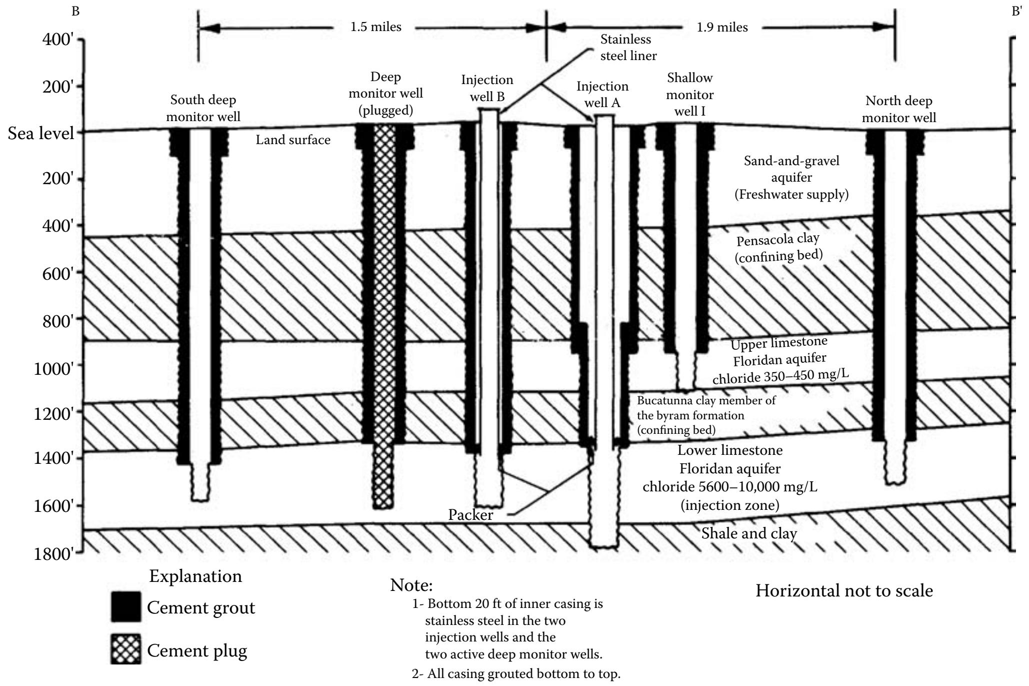


FIGURE 20.11 Generalized north–south geologic section through Southern Alabama and Northwestern Florida. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)



Note:
1- Bottom 20 ft of inner casing is stainless steel in the two injection wells and the two active deep monitor wells.
2- All casing grouted bottom to top.

FIGURE 20.12 Monsanto Injection Facility hydrogeologic cross-section. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

in the injection zone moves slowly south-southwestward toward the Gulf of Mexico, where it is assumed to discharge about 160 km (100 miles) offshore. The pre-injection hydraulic gradient was about 0.25 m/km (1.3 ft/mile).

20.7.1.3 Chemical Processes Observed

As a result of dissolution of the limestone by the partly neutralized acid wastes, calcium concentrations more than doubled in the near-deep monitoring well 10 months after injection started in 1963.[67] In early 1966, however, they dropped to background levels (about 200 mg/L), possibly in response to biochemical decomposition of the waste. In September 1968, after about 300 million gallons of the acidic, unneutralized waste had been injected, the calcium concentration began to increase again. An abrupt increase in calcium to 2700 mg/L accompanied by a decrease in pH to 4.75 in January 1969 led to the decision to plug the near-deep monitoring well.

In an attempt to find out how fast the waste was reacting with limestone, a 3-h backflushing experiment, in which waste was allowed to flow back out of the injection well, yielded some unexpected results. The increase in pH of the neutralized waste could not be fully accounted for by the solution of limestone as determined from the calcium content of the backflushed liquid; the additional neutralization apparently resulted from reactions between nitric acid and alcohols and ketones in the original waste induced by increased pressure in the injection zone compared to surface conditions.[41]

The lack of nitrates (which were present at levels of 545 to 1140 mg/L in the waste) in the near-deep monitoring well, combined with the presence of nitrogen gas, indicated that degradation by denitrifying bacteria had taken place.[67] Backflushing shortly before injecting unneutralized wastes confirmed denitrification. Nitrate concentrations decreased rapidly as the backflushed waste was replaced by formation water. Similar backflushing experiments conducted after unneutralized wastes were injected, however, provided no evidence of denitrification, indicating that microbial activity was suppressed in the portion of the zone containing unneutralized wastes.

Elkan and Horvath[170] performed a microbiological analysis of samples taken from the north and south deep monitoring wells in December 1974, about 6 months after the dilute waste front had reached the south well. Both denitrifying and methanogenic bacteria were observed. The lower numbers and species diversity of organisms observed in the south monitoring well compared with those in the north well indicated suppression of microbial activity by the dilute wastes.

Between September 1973 and March 1977 bicarbonate concentrations increased from 282 mg/L to 636 mg/L and dissolved organic carbon increased from 9 mg/L to 47 mg/L. These increases were accompanied by an increase in the dissolved-gas concentration and a distinctive odor like that of the injected wastes. The pH, however, remained unchanged. During the same period, dissolved methane increased from 24 mg/L to 70 mg/L, indicating increased activity by methanogenic bacteria. The observation of denitrification in the near-deep monitoring well and methanogenesis in the more distant south monitoring well fit the redox-zone biodegradation model.

Significant observations made at this site are:

1. Organic contaminants (as measured by dissolved organic carbon) continue to move through the aquifer even when acidity has been neutralized.
2. Even neutralized wastes can suppress microbial populations.

20.7.2 CASE STUDY NO. 2: PENSACOLA, FL (AMERICAN CYANAMID)

20.7.2.1 Injection-Facility Overview

American Cyanamid Company operates a plant near Milton, Florida, which lies about 12 miles northeast of Pensacola and about 8 miles east of the Monsanto plant discussed in the previous sections. Chemical changes caused by the injection of acidic wastes from this plant have been reported by Ehrlich and colleagues[89] and Vecchioli and colleagues,[171] with the former citation providing the most complete information on the site. This case study illustrates the complexity of assessing the geochemical fate of mixed wastes. Acrylonitrile was detoxified by biological reduction, whereas sodium thiocyanate remained unaltered.

The facility combines acidic wastestreams from various plant operations in a holding pond where they are mixed and aerated. The waste is pumped from the pond and neutralized with sodium hydroxide. The neutralized wastes are treated with alum to flocculate suspended solids and then passed through mixed-media filters. A small amount of hydrogen peroxide solution (amount unspecified) is added before filtration to inhibit microbial growth on the filters. The pretreated waste that is injected contains high concentrations of sodium nitrate, sodium sulfate, sodium thiocyanate (an inorganic cyanide compound), and various organic compounds, including acrylonitrile (a listed hazardous waste). The average pH of the waste is 5.8, and the average chemical oxygen demand is 1690 mg/L.

A primary injection well and a standby well are situated about 460 m (1500 ft) apart. A shallow monitoring well is located near the primary injection well in the upper limestone Floridan aquifer that overlies the confining Bucatunna clay. Two deep monitoring wells in the injection zone are located 300 m (1000 ft) southwest and 2492 m (8170 ft) northeast of the primary injection well.

Waste injection began in June 1975, and waste was first detected in the downgradient southwest deep monitoring well about 260 days later. To analyze the waste's physical and chemical properties after injection, the primary injection well was allowed to backflow into a holding pond for 5 days in November 1977. This waste was sampled periodically (and reinjected when the test was completed). About 4 years after injection began; dilute waste arrived at the standby injection well 476 m (1560 ft) south of the primary well.

20.7.2.2 Injection/Confining-Zone Lithology and Chemistry

The injection well is in the same area as the Monsanto well, so the geology and native water chemistry are very similar to that described before. Figure 20.13 shows the stratigraphy of the immediate area

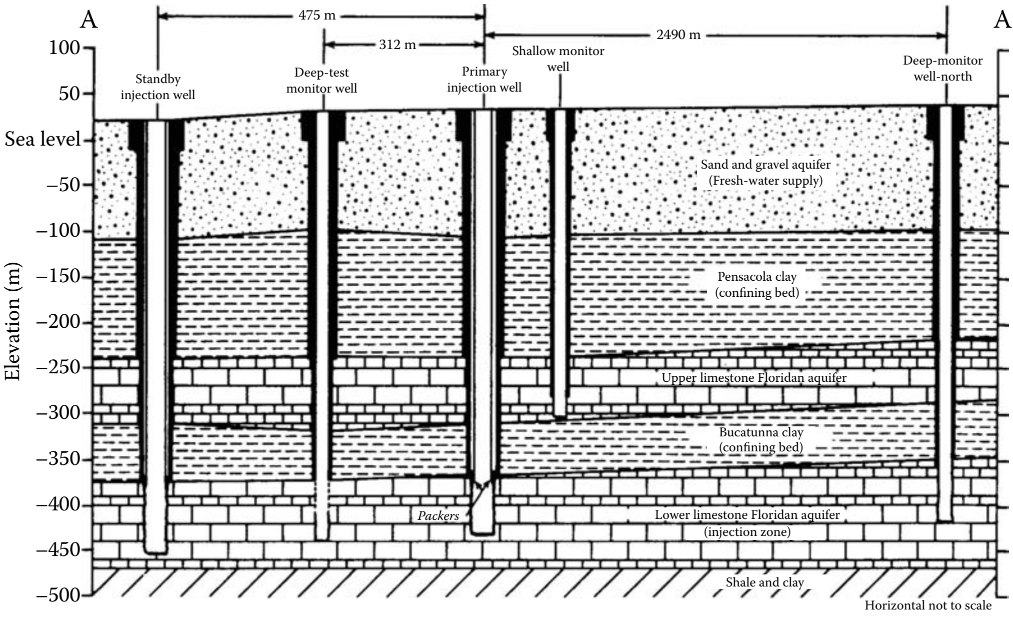


FIGURE 20.13 American Cyanamid Injection Facility hydrogeologic cross-section. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

and distances between the injection and monitoring wells. The lower limestone of the Floridan aquifer is used as the injection zone (1230 to 1440 ft), and the confining Bucatunna clay is about 50 m (165 ft) thick. TDS levels range from 12,000 to 12,700 mg/L, with chloride ion concentrations of 6700 mg/L. The pH ranges from 7.3 to 7.6, and temperature from 30°C to 32°C. Caliper and flowmeter tests made in the injection wells suggest that the waste moves almost exclusively within the top 18 m (55 ft) of the lower limestone. The preinjection groundwater flow direction is south-southwest.

20.7.2.3 Chemical Processes Observed

The Eh of the injected waste dropped rapidly from +40 mV to –80 mV in the first 40 h after injection began and remained at about –80 mV thereafter. Denitrifying bacteria detoxified the acrylonitrile by mineralizing the compound, breaking it down into bicarbonate and ammonia. The nitrates were degraded to nitrogen gas. The backflow test produced data indicating that these transformations were about 90% complete within 25 m (82 ft) of the injection well and virtually 100% complete within 100 m (328 ft). These results are an example of a biodegradation-dispersion curve. Denitrifying-bacteria densities increased from traces (101 organisms/100 mL in the native groundwater) to large populations (10 to 10^8 organisms/100 mL) in injected wastes that had been in the aquifer for several days.

Sodium thiocyanate (NaSCN) was first detected in the closest monitoring well (300 m away) 260 days after injection began. Ammonium ions (a reaction product of biomineralization) did not appear as a contaminant until 580 days after initial injection. This delay was probably the result of ion exchange or other adsorption processes and may be an example of an adsorption–dispersion curve. Because sodium thiocyanate in the waste remained unchanged during its movement through the injection zone, it was used to detect the degree of mixing that took place between the waste liquid and native water in an observation well. Thus the appearance of sodium thiocyanate as well as an increase in chemical oxygen demand in the standby well 4 years after injection began signaled the arrival of wastes at that location.

This case study is interesting in that one hazardous waste (acrylonitrile) was quickly rendered nonhazardous after injection, whereas another (sodium thiocyanate) showed no evidence of decomposition during the duration of the study. The implication for geochemical fate assessment is that research should focus on the compounds likely to be most resistant to decomposition or immobilization, as they will be the ones most critical in demonstrating containment in a no-migration petition.

20.7.3 Case Study No. 3: Belle Glade, FL

20.7.3.1 Injection-Facility Overview

The Belle Glade site, located southeast of Lake Okeechobee in south-central Florida, illustrates some of the problems that can develop with acidic-waste injection when carbonate rock is the confining layer. Contributing factors to the contamination of the aquifer above the confining zone were the dissolution of the carbonate rock and the difference in density between the injected wastes and the formation fluids. The injected waste was less dense than the groundwater because of its lower salinity and higher temperature.[172]

The injected fluids include the effluent from a sugar mill and the waste from the production of furfural, an aldehyde processed from the residues of processed sugar cane. The waste is hot (about 75°C to 93°C), acidic (pH 2.6 to 4.5), and has high concentrations of organics, nitrogen, and phosphorus.[173] The waste is not classified as hazardous under 40 CFR 261, and the well is currently regulated by the State of Florida as a nonhazardous injection well. The organic carbon concentration exceeds 5000 mg/L.

The well was originally cased to a depth of 456 m (1495 ft), and the zone was left as an open hole to a depth of 591 m (1939 ft). The depth of the zone has been increased twice. Seasonal injection (fall, winter, and spring) began in late 1966; the system was inactive during late summer.

Injection rates ranged from 25 to 50 L/h (400 to 800 gal/min), and wellhead injection pressures ranged from 2.1 to 4.2 kg/cm^2 (30 to 60 psi). By 1973, injection had become more or less continuous. From 1966 to 1973, more than 4.16 billion liters (1.1 billion gal) of waste had been injected.[172]

At the time injection began, a shallow monitoring well was placed 23 m (75 ft) south of the injection well in the upper part of the Floridan aquifer above the confining layer. A downgradient, deep monitoring well was placed in the injection zone 300 m (1000 ft) southeast of the injection well. Another shallow well, located 3.2 km (2 miles) southeast of the injection site at the University of Florida's Everglades Experiment Station, has also been monitored for near-surface effects.

Acetate ions from the injected waste were detected in the deep monitoring well 300 m (1000 ft) southeast of the injection well in early 1967, a matter of months after injection began.[174] In 1971, about 27 months after injection began; evidence of waste migration was detected at a shallow monitoring well in the upper part of the Floridan aquifer. Dissolution of the carbonate confining layer by the acidic waste was the main reason for the upward migration. However, the lower density of the injected wastes compared with that of the formation waters (0.98 g/mL vs. 1.003 g/mL) served to accelerate the rate of upward migration.[174] In an attempt to prevent further upward migration, the injection well was deepened to 684 m (2242 ft), and the inner casing was extended and cemented to 591 m (1938 ft). When waste injection was resumed, evidence of upward migration to the shallow aquifer was observed only 15 months later. By late 1973, 7 years after injection began, the waste front was estimated to have migrated 1 to 1.6 km (0.6 to 1 mile) from the injection well.[173]

The injection well was deepened a third time, to a depth of 900 m (3000 ft).[175] A new, thicker confining zone of dense carbonate rock separates the current injection zone from the previous zone. As of early 1989, the wastes were still contained in the deepest injection zone. For details on acid injection into carbonate rock refer to Clark.[176]

20.7.3.2 Injection/Confining-Zone Lithology and Chemistry

The wastes are injected into the lower part of the carbonate Floridan aquifer, which is extremely permeable and cavernous. The natural direction of groundwater flow is to the southeast. The confining layer is 45 m (150 ft) of dense carbonate rocks. The chloride concentration in the upper part of the injection zone is 1650 mg/L, increasing to 15,800 mg/L near the bottom of the formation.[172] The sources used for this case study did not provide any data on the current injection zone. The native fluid was basically a sodium-chloride solution but also included significant quantities of sulfate (1500 mg/L), magnesium (625 mg/L), and calcium (477 mg/L).

20.7.3.3 Chemical Processes Observed

Neutralization of the injected acids by the limestone formation led to concentrations of calcium, magnesium, and silica in the waste solution that were higher than those in the unneutralized wastes. Anaerobic decomposition of the organic matter in the injected waste apparently occurred through the action of both sulfate-reducing and methanogenic bacteria. Sulfate-reducing bacteria were observed in the injected wastes that were allowed to backflow to the surface. Sulfate levels in the native groundwater declined by 45%, and the concentration of hydrogen sulfide increased by 1600%. Methane fermentation (reduction of CO_2 to CH_4) was also inferred from the presence of both gases in the backflow fluid, but the presence of methanogenic bacteria was not confirmed. Increased hydrogen sulfide concentrations produced by the bacteria during biodegradation and the subsequent decrease in sulfate/chloride ratio in the observation wells were taken as indicators of upward and lateral migration. Migration into the shallow monitoring well was also indicated by a decline in pH from around 7.8 to 6.5, caused by mixing with the acidic wastes.

Chemical analyses of the backflowed injected waste that had been in the aquifer for about 2.5 months (for which some dilution had occurred) indicated that COD was about half that of the original waste. Samples that had been in residence for about 5 months had a COD approximately one-quarter that of the original waste (12,200 mg/L in the original waste compared with 4166 mg/L in the samples). The percent reduction in COD resulting from bacterial action rather than dilution was not estimated.

20.7.4 CASE STUDY NO. 4: WILMINGTON, NC

20.7.4.1 Injection-Facility Overview

The Hercules Chemical, Inc. (now Hercufina, Inc.), facility, 4 miles north of Wilmington, North Carolina, attempted deep-well injection of its hazardous wastes from May 1968 to December 1972, but had to discontinue injection because of waste–reservoir incompatibility and unfavorable hydrogeologic conditions. The U.S. Geological Survey conducted extensive geochemical studies of this site until the well was abandoned.[102,177–179] Biodegradation processes were also studied.[170] More geochemical-fate processes affecting injected organic wastes have been documented at this site than at any other.

Hercules Chemical produced an acidic organic waste derived from the manufacture of dimethyl terphthalate, which is used in the production of synthetic fiber. The average dissolved organic carbon concentration was about 7100 mg/L and included acetic acid, formic acid, p-toluic acid, formaldehyde, methanol, terphthalic acid, and benzoic acid. The pH ranged from 3.5 to 4.0. The waste also contained traces (less than 0.5 mg/L) of 11 other organic compounds, including dimethyl phthalate, a listed hazardous waste.

From May 1968 to December 1972, the waste was injected at a rate of about 300,000 gal/d. The first injection well was completed to a depth of 259 to 313 m (850 to 1025 ft) (i.e., cased from the surface to 259 m with screens placed in the most permeable sections of the injection zone to a depth of 313 m). One shallow observation well was placed 15 m (50 ft) east of the injection site at a depth of 210 m (690 ft). Four deep monitoring wells were also placed in the injection zone, one at 15 m (50 ft) and three at 45 m (150 ft) from the injection well.

The injection well became plugged after a few months of operation because of the reactive nature of the wastes and the low permeability of the injection zone. The actual plugging process was caused both by reprecipitation of the initially dissolved minerals and by plugging of pores by such gaseous products as carbon dioxide and methane. When the first well failed, a second injection well was drilled into the same injection zone about 5000 ft north of the first, and injection began in May 1971. Nine additional monitoring wells (three shallow, and six deep) were placed at distances ranging from 450 to 900 m (1500 to 3000 ft) from the second injection well. Injection was discontinued in 1972 after the operators determined that the problems of low permeability and waste–reservoir incompatibility could not be overcome. Monitoring of the waste movement and subsurface environment continued into the mid-1970s in the three monitoring wells located 450 to 600 m (1500 to 2000 ft) from the injection wells.

Within 4 months, the waste front had passed the deep observation wells located within 45 m (150 ft) of the injection well. About 9 months after injection began; leakage into the aquifer above the confining layer was observed. This leakage was apparently caused by the increased pressures created by formation plugging and by the dissolution of the confining beds and the cement grout surrounding the well casing of several of the deep monitoring wells, caused by organic acids.

Eight months after injection began in the second injection well, wastes had leaked upward into the adjacent shallow monitoring well. The leak apparently was caused by the dissolution of the cement grout around the casing. In June 1972, 13 months after injection began in the second well, the waste front reached the deep monitoring well located 450 m (1500 ft) northwest of the injection well. Waste injection ended in December 1972. As of 1977, the wastes were treated in a surface facility.[170]

20.7.4.2 Injection/Confining-Zone Lithology and Chemistry

The injection zone consisted of multiple Upper Cretaceous strata of sand, silty sand, clay, and some thin beds of limestone (see Figure 20.14). The clay confining layer was about 30 m (100 ft) thick.

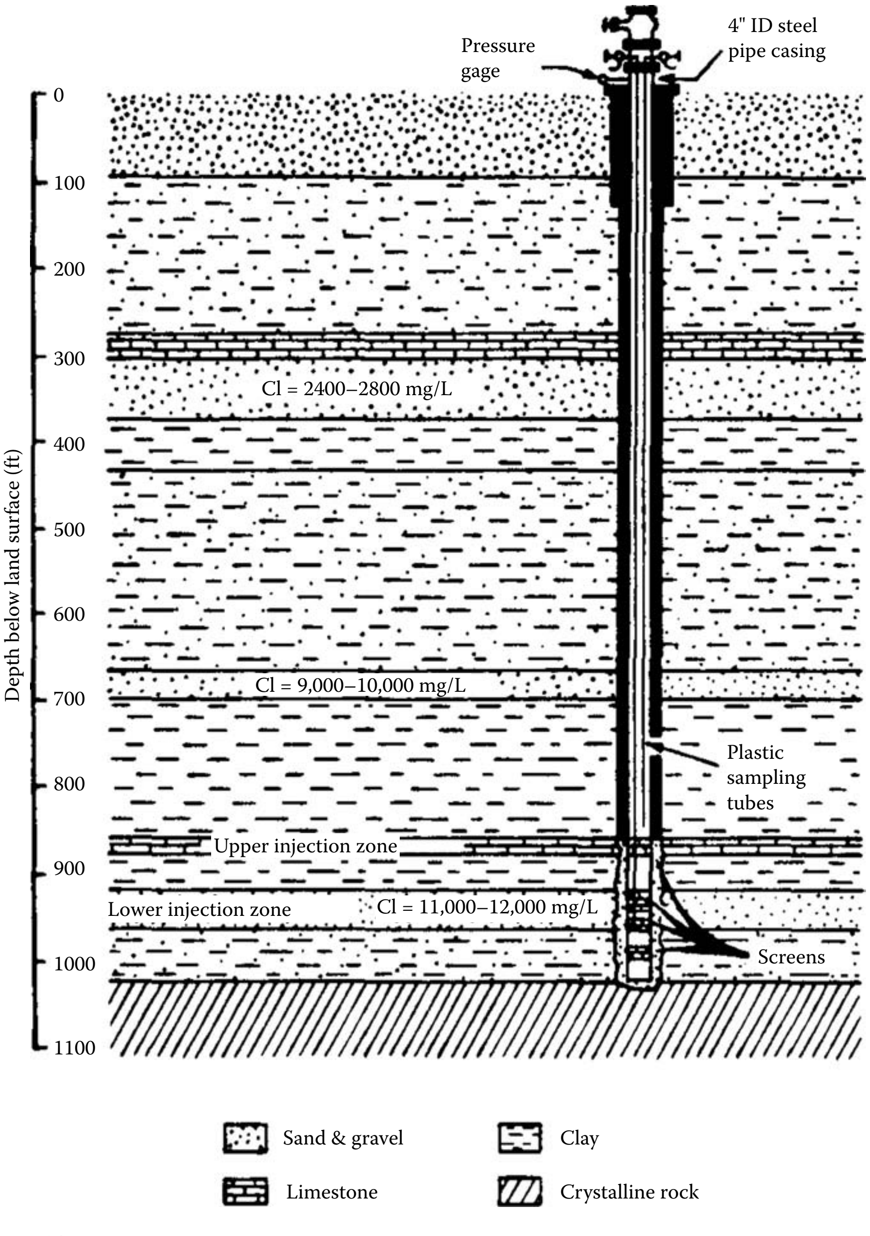


FIGURE 20.14 Diagram showing construction features and lithologic log of North Observation Well, Wilmington, NC. (From U.S. EPA, Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: A Reference Guide, EPA/625/6-89/025a, U.S. EPA, Cincinnati, OH, June 1990.)

The TDS concentration in the injection-zone formation water was 20,800 mg/L, with sodium chloride the most abundant constituent.

20.7.4.3 Chemical Processes Observed

A number of chemical processes were observed at the site[178,179]:

1. The waste organic acids dissolved carbonate minerals, alumino-silicate minerals, and iron/manganese-oxide coatings on the primary minerals in the injection zone.

2. The waste organic acids dissolved and formed complexes with iron and manganese oxides. These dissolved complexes reprecipitated when the pH increased to 5.5 or 6.0 because of neutralization of the waste by the aquifer carbonates and oxides.
3. The aquifer mineral constituents adsorbed most waste organic compounds, with the exception of formaldehyde. Adsorption of all organic acids except phthalic acid increased with a decrease in waste pH.
4. Phthalic acid was complexed with dissolved iron. The concentration of this complex decreased as the pH increased because the complex coprecipitated with the iron oxide.
5. Biochemical waste transformation occurred at low waste concentrations, resulting in the production of methane. Additional microbial degradation of the waste resulted in the reduction of sulfates to sulfides and ferric ions to ferrous ions.

When the dilute waste front reached the North Observation Well in June 1972 microbial populations rapidly increased in this well, with methanogenesis being the major degradative process.[180] Elkan and Horvath[170] found greater numbers and species diversity of microorganisms in the observation well, which contained dilute wastes, than in the observation well, which was uncontaminated. In laboratory experiments, however, DiTommaso and Elkan[180] found that bacterial growth was inhibited as the concentration of waste increased and could not decompose the waste at the rate it was being injected.

This case study illustrates the importance of dissolution/precipitation reactions in determining waste– reservoir compatibility. Adsorption was observed to immobilize most of the organic constituents in the waste except for formaldehyde. As with the Monsanto case study, biodegradation was an important process when wastes were diluted by formation waters, but the process became inhibited when undiluted waste reached a given location in the injection zone.

20.7.5 Case Study No. 5: Illinois Hydrochloric Acid-Injection Well

20.7.5.1 Injection-Facility Overview

This case study is an example of a well blowout resulting from the neutralization of acid by carbonate rock. Kamath and Salazar[181] and Panagiotopoulos and Reid[182] both discuss the same incident. Although they do not specify the location, Brower and colleagues[183] identify the site as the Cabot Corporation injection well, near Tuscola, Illinois.

The waste hydrochloric acid (HCl) injected at the site was a byproduct of a combustion process at 1633°C (2972°F). When not recovered, the acidic stream was dumped into holding ponds where it was cooled to about 24°C (75°F) before injection. The concentration of injected acid typically varied from 0.5 to 5% HCl, but ranged as high as about 30%. (The pH of injected acid that backflowed during one blowout incident ranged from 0.5 to 1.3.)

The injection well was cased to a depth of about 1495 m (4900 ft) and extended into dolomite to a total depth of 1617 m (5300 ft). Injection began in the early 1960s and averaged around 340 L/min (90 gal/min). The natural fluid level was 60 m (200 ft) below the wellhead, and wastes were injected using gravity flow; that is, the pressure head of the well when filled to the surface with fluid was sufficient to inject fluids without pumping under pressure.[181]

Between 1973 and 1975, several blowouts caused surface water pollution and fish kills. The most serious occurred in 1975 after unusually high concentrations of HCl (ca. 30%) were injected intermittently for several weeks. The well refused to accept additional acid under gravity flow. At first the operators thought the well bore had become plugged, and they pumped a concentrated calcium-chloride solution down the hole to dissolve precipitates that might have formed. Shortly thereafter the well tubing broke, pressure suddenly rose to 37 kg/cm^2 (450 psi), and a section of the upper tubing was ejected through the wellhead along with acid and annulus fluids. Backflow was stopped for a while by draining cold water from a fire hydrant into the well at 190 L/min

(50 gal/min). The well erupted again the next day, however, with a 3-m (10-ft) gusher discharging at 946 L/min (250 gal/min). The blowout was brought under control 2 d later when a blowout preventer was installed.

20.7.5.2 Injection/Confining-Zone Lithology and Chemistry

The injection zone was a cavernous dolomite, and the native groundwater was very saline, with TDS levels ranging from 21,000 to 26,000 mg/L. No information was provided on the confining layer, but it is discussed in the work by Brower and colleagues[183] in detail.

20.7.5.3 Chemical Processes Observed

The HCl dissolved the dolomite, forming carbon dioxide (CO_2) gas. Under normal circumstances this gas remains in solution, but if the temperature of the acid or the acid concentration exceed certain limits, CO_2 evolves as a gas and accumulates in the upper portion of the cavity. The escape of even small amounts of CO_2 into the injection pipe can serve as a driving force to reverse the flow of the injected liquids, because as the CO_2 rises, pressure decreases and the gas expands.

There is some disagreement as to which parameter is most critical to gas blowout. Based on analysis of CO_2 phase behavior at different temperatures and pressures, Kamath and Salazar[181] concluded that gas blowout becomes hazardous if the temperature of the injected HCl exceeds 88°F. Panagiotopoulos and Reid[182] concluded that HCl concentration is the critical factor and that HCl concentrations exceeding 6% will evolve CO_2 gas and create a blowout hazard. Both sets of investigators explained the circumstances of this case study in terms of their respective models.

20.7.6 CASE STUDY NO. 6: TEXAS PETROCHEMICAL PLANT

20.7.6.1 Injection-Facility Overview

This case study involves an unnamed petrochemical plant located about 15 miles inland from the Texas Gulf Coast, described by Donaldson and Johansen.[184] It illustrates two approaches to injecting incompatible wastestreams to prevent well plugging by precipitation: surface treatment and multiple injection wells.

The plant began full-scale operation in 1962 and produced acetic, adipic, and propionic acids; acetaldehyde; butanol; hexamethyldiamine; vinyl acetate; nylon; and other chemical products from petroleum-base stocks. The effluent was collected at waste treatment facilities as two separate mixtures. Because mixing two wastestreams produced considerable precipitation, the wastestreams were processed and injected separately into two wells.

Organic constituents in the first wastestream totaled about 14,000 mg/L (acetaldehyde, acetaldol, acetic acid, butanol-1, butyraldehyde, chloroacetaldehyde, crotonaldehyde, phenol, and propionic acid) and about 5200 mg/L inorganic constituents. The pH ranged from 4 to 6, and TDS ranged from 3000 to 10,000 mg/L.

The second wastestream contained amines and nitrates generated from the manufacture of nylon, hydrocarbon solvents used in processing, and other minor constituents. Organic constituents (amyl alcohol, cyclohexane, dodecane, hexanol, 1-hexylamine, 1,6-hexylamine, methanol, and valeric acid) totaled about 4700 mg/L. Inorganic constituents in the second wastestream totaled about 21,350 mg/L, including 7500 mg/L nitrate and 4600 mg/L nitrite. The second wastestream was basic, with a pH ranging from 8 to 10. The composition of the wastes changed over time when processes changed or a new unit was installed. Several new process wastes (unspecified) that were incompatible with either wastestream were made compatible by adjusting the pH and diluting them.

Injection began in both wells in mid-1963. The injection zone for Well No. 1 was 13.7 m (45 ft) thick beginning at about 1037 m (3400 ft) below the surface. Well No. 2 was located 824 m (2700 ft) north of Well No. 1, and the injection zone was located between 991 and 1083 m (3520 and 3550 ft).

Donaldson and Johansen[184] mention no monitoring wells at the site. About 6 years after injection began, pressure interference from the two injection wells was observed. During the same period, the fluid front from Well No. 1 was about 223 m (730 ft) from the well bore.

20.7.6.2 Injection/Confining-Zone Lithology and Chemistry

The injection formation was loosely consolidated, fine-grained Miocene sand. The confining strata between the base of the freshwater aquifer and the injection zone included about 366 m (1200 ft) of relatively impermeable shale and clay beds with individual zone thickness ranging from 3 to 75 m (10 to 245 ft).

20.7.6.3 Chemical Processes Observed

Well head pressures increased when injection was stopped at Well No. 1 for more than 24 h, apparently caused by a combination of precipitation reactions and backflow of sand. Injecting a slug of brine after every period of interrupted flow solved this problem. Movement of the main organic constituents (*n*-hexylamine, butanal, butanol, and phenol) was assumed to be slowed by adsorption. This conclusion was based on laboratory adsorption experiments by involving a different geologic formation (Cottage Grove sandstone); no direct observations were made of the injected waste. For current hazardous waste injection wells in Texas, the reader can refer to Texas Environmental Profiles web site for on-line resources for the State of Texas.[185]

NOMENCLATURE

B	Bacterial concentration
C	Concentration of adsorbed substance in solution, μg/mL
C_T	Dissolved plus adsorbed phase concentration of compound C, mol/L or μg/L
$[H^+]$	Concentration of hydrogen ion, mol/L
k	Langmuir coefficient related to adsorption bonding energy (mL/g)
k_1	Empirical biodegradation rate constant
k_a	Acid-catalyzed hydrolysis rate constant, L/mol/s
k_b	Base-catalyzed hydrolysis rate constant, L/mol/s
k_B	First-order biodegradation coefficient
k_{B2}	Second-order biodegradation coefficient
k_H	Specific hydrolysis rate constant, L/s
k_n	Natural hydrolysis rate constant for the pH-independent reactions of a chemical with water, L/s
K	Empirical coefficient
K_d	Distribution coefficient
K_{oc}	Organic-carbon partition coefficient
K_p	Partition coefficient
N	Empirical coefficient
$[OH^-]$	Concentration of hydroxide ion, mol/L
R	Rate of hydrolysis, mol/L/s or μg/L/s
S	Amount adsorbed (μg/g solid)
S_{max}	Maximum adsorption capacity (μg/g soil)
$t_{1/2}$	Half-life of a substance

ACRONYMS

ASTM	American Society for Testing and Materials
BOD	Biochemical oxygen demand

CEC	Cation-exchange capacity
COD	Chemical oxygen demand
DNAPL	Dense nonaqueous-phase liquid
Eh	Oxidation–reduction potential
EHSO	Environment, Health and Safety Online
EP	Extraction procedure
LNAPL	Light nonaqueous-phase liquid
NAPL	Nonaqueous-phase liquid
PAH	Polycyclic aromatic hydrocarbon
RCRA	Resource Conservation and Recovery Act
SOC	Suspended organic carbon
TDS	Total dissolved solids
TLM	Triple-layer model
TOC	Total organic carbon
USDW	Underground Source of Drinking Water
U.S. EPA	U.S. Environmental Protection Agency

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21 Waste Management in the Pulp and Paper Industry

Nazih K. Shammas

CONTENTS

21.1 INTRODUCTION

21.1.1 BACKGROUND

The paper and allied products industry comprises three types of facilities: pulp mills that process raw wood fiber or processed fiber to make pulp; paper and board mills that manufacture paper or board; and converting facilities that use these primary materials to manufacture more specialized products such as writing paper, napkins, and other tissue products. The process of converting paper is not a source of water or air pollution, as is the case for the first two facilities. This chapter focuses primarily on the greatest areas of environmental concern within the pulp and paper industry: those from pulping processes.

The specific components in the pulp and paper industry include the following[1,2]:

1. *Pulp mills.* These separate the fibers of wood or other materials, such as rags, linters, wastepaper, and straw, in order to create pulp. Mills may use chemical, semichemical, or mechanical processes, and may create coproducts such as turpentine and tall oil. Most pulp mills bleach the pulp they produce, and, when wastepaper is converted into secondary fiber, it is deinked. The output of some pulp mills is not used to make paper, but to produce cellulose acetate or to be dissolved and regenerated in the form of viscose fibers or cellophane.
2. *Paper mills.* These are primarily engaged in manufacturing paper from wood pulp and other fiber pulp, and may also manufacture converted paper products. Establishments primarily engaged in integrated operations of producing pulp and manufacturing paper are included in this industry if primarily shipping paper or paper products.
3. *Paperboard mills.* These are primarily engaged in manufacturing paperboard, including paperboard coated on a paperboard machine, from wood pulp and other fiber pulp; they may also manufacture converted paperboard products.
4. *Paperboard containers and boxes.* These establishments are engaged in the manufacture of corrugated and solid fiber boxes and containers from purchased paperboard. The principal commodities of this industry are boxes, pads, partitions, display items, pallets, corrugated sheets, food packaging, and nonfood (e.g., soaps, cosmetics, and medicinal products) packaging.

5. *Miscellaneous converted paper products.* These establishments produce a range of paper, paperboard, and plastic products with purchased material. Common products include paper and plastic film packaging, specialty paper, paper and plastic bags, manila folders, tissue products, envelopes, stationery, and other products.

One important characteristic of the pulp and paper industry is the interconnection of operations between pulp mills and downstream processing of pulp into paper, paperboard, and building paper. Another important characteristic of the pulp and paper industry is that the range of processes, chemical inputs, and outputs used are used in pulp manufacture. On the whole, pulp mill processes are chemical intensive and have been the focus of past and ongoing pollution prevention rulemaking. There are also numerous manufacturers of finished paper and paperboard products from paper and paperboard stock. Some companies are involved in both the manufacture of primary products and converting, particularly in the production of tissue products, corrugated shipping containers, folding cartons, flexible packaging, and envelopes.

21.1.2 CHARACTERIZATION OF THE PULP AND PAPER INDUSTRY

The pulp and paper industry produces primary products—commodity grades of wood pulp, printing and writing papers, sanitary tissue, industrial-type papers, containerboard, and boxboard—using cellulose fiber. The two steps involved are pulping and paper or paperboard manufacturing.

21.1.2.1 Pulping

Pulping is the process of separating wood chips into individual fibers by chemical, semichemical, or mechanical methods. The particular pulping process used affects the strength, appearance, and intended use characteristics of the resultant paper product. Pulping is the major source of environmental impacts from the pulp and paper industry. There are more than a dozen different pulping processes in use in the U.S.; each process has its own set of process inputs, outputs, and resultant environmental concerns.[3] Table 21.1 provides an overview of the major pulping processes and the main products that they produce. Kraft pulp, bleached and unbleached, is used to manufacture the majority of paper products. Together, chemical pulping processes account for 84% of the pulp produced in the U.S.[1] Figure 21.1 presents the relative outputs of the major pulping processes.

A bleached kraft pulp mill requires 15,140 to 45,420 L (4000 to 12,000 gal) of water and 8.56 to 12.22 million chu (14 to 20 million Btu) of energy per ton of pulp, of which ca. 4.44 to 5.56 million chu (8 to 10 million Btu) are typically derived from biomass-derived fuel from the pulping process itself.[4] Across all facilities, the pulp, paper, and allied products industry is the largest consumer of process water and the third largest consumer of energy (after the chemicals and metals industries).[5,6] The large amounts of water and energy used, as well as the chemical inputs, lead to a variety of environmental concerns.

21.1.2.2 Paper and Paperboard Manufacturing

The paper or paperboard manufacturing process is similar for all types of pulp. Pulp is spread out as extremely dilute slurry on a moving endless belt of filtering fabric. Water is removed by gravity and vacuum, and the resulting web of fibers is passed through presses to remove more water and consolidate the web. Paper and paperboard manufacturers use nearly identical processes, but paperboard is thicker (more than 0.3 mm).

21.1.3 INDUSTRY SIZE AND GEOGRAPHIC DISTRIBUTION

The pulp and paper industry is characterized by very large facilities; of the 514 pulp and paper mills reported by the Bureau of the Census in 1998, 343 (67%) had 100 or more employees. Across all of

TABLE 21.1
Description of Pulping Processes

Pulping Process	Description/Principal Products
Dissolving kraft	Highly bleached and purified kraft process wood pulp suitable for conversion into products such as rayon, viscose, acetate, and cellophane
Bleached papergrade kraft and soda Unbleached kraft	Bleached or unbleached kraft process wood pulp usually converted into paperboard, coarse papers, tissue papers, and fine papers such as business, writing and printing
Dissolving sulfite	Highly bleached and purified sulfite process wood pulp suitable for conversion into products such as rayon, viscose, acetate, and cellophane
Papergrade sulfite	Sulfite process wood pulp with or without bleaching used for products such as tissue papers, fine papers, and newsprint
Semichemical	Pulp is produced by chemical, pressure, and occasionally mechanical forces with or without bleaching used for corrugating medium (cardboard), paper, and paperboard
Mechanical pulp	Pulp manufacture by stone groundwood, mechanical refiner, thermo-mechanical, chemi-mechanical, or chemi-thermomechanical means for newsprint, coarse papers, tissue, molded fiber products, and fine papers
Secondary fiber deink	Pulps from recovered paper or paperboard using a chemical or solvent process to remove contaminants such as inks, coatings, and pigments used to produce fine, tissue, and newsprint papers
Secondary fiber nondeink	Pulp production from recovered paper or paperboard without deinking processes to produce tissue, paperboard, molded products, and construction papers
Nonwood chemical pulp	Production of pulp from textiles (e.g., rags), cotton linters, flax, hemp, tobacco, and abaca to make cigarette wrap papers and other specialty paper products

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

these facilities, there are 172,000 employees who produced USD 59 billion in shipments (in 1998 dollars). In 2000, the industry employed 182,000 people and produced USD 79 billion in shipments. In contrast, the downstream facilities (container and specialty product manufacturers) tend to be more numerous but smaller. More than 75% of these facilities have fewer than 100 employees. Table 21.2 presents the employment distribution for both pulp and paper facilities and downstream manufacturers

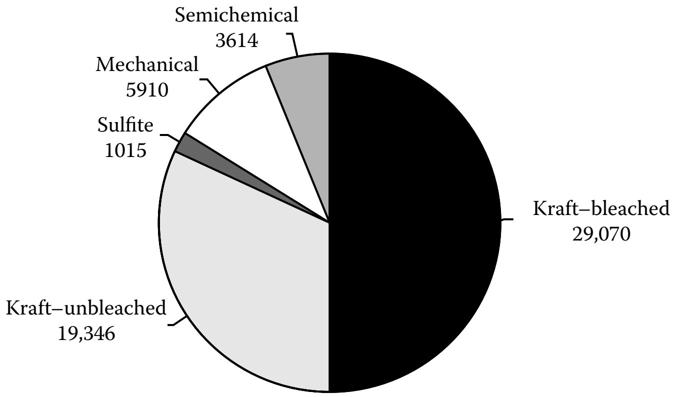

FIGURE 21.1 U.S. pulp production in 1000 t (year 2000). (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

TABLE 21.2
Size of Paper and Allied Products Facilities

	Employees per Facility (% of Total)			
Industry	**1–19**	**20–99**	**100–499**	**>499**
Pulp mills	3 (7%)	14 (34%)	18 (44%)	6 (15%)
Paper mills	6 (2%)	63 (24%)	107 (41%)	83 (32%)
Paperboard mills	8 (4%)	77 (36%)	96 (45%)	33 (15%)
Paperboard containers and boxes	748 (26%)	1311 (46%)	782 (27%)	14 (<1%)
Misc. converted paper products	1383 (44%)	1116 (36%)	597 (19%)	70 (2%)

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

in 1997 (the most recent data available) as reported by the U.S. Census Bureau.[7] Because recent years have seen some facility closures, the current number of facilities may be somewhat lower.

The integrated pulp and paper industry is among the top 10 U.S. manufacturing industries in value of shipments. The industry shipments amount to 146 billion USD with an employment of 609,480. Individual pulp and paper mills employ only 28% of the workers in the industry, but produce over 40% of the shipments.[8]

The geographic distribution of pulp and paper mills varies according to the type of mill. As there are tremendous variations in the scale of individual facilities, tallies of the number of facilities may not represent the level of economic activity (nor possible environmental consequences). Pulp mills are located primarily in regions of the country where trees are harvested from natural stands or tree farms, such as the Southeast, Northwest, Northeast, and North Central regions.[9] Pulp mills that process recycled fiber are generally located near sources of waste paper. Paper mills, however, are more widely distributed. They are located near pulping operations or near converting markets. The distribution of paperboard mills reflects the location of manufacturing in general, as such operations are the primary market for paperboard products. Figure 21.2 presents the locations of pulp and paper mills in the U.S.

21.1.4 ECONOMIC TRENDS

The U.S. produces roughly 30% of the world's paper and paperboard. The pulp and paper industry is one of the most important industries for the balance of trade in the U.S. This trade balance increased through most of the 1990s. In 1999, exports were USD 8.5 billion. In recent years, however, exports have been declining and imports have been increasing. Between 1997 and 2000, exports declined 5.5% and imports increased by more than 20%. The declining exports and increasing imports are partly due to a strong dollar in this period and the recent slow down of the U.S. economy.[1]

The U.S. industry has several advantages over the rest of the world market: modern mills, a highly skilled work force, a large domestic market, and an efficient transportation infrastructure. Major export markets for pulp are Japan, Italy, Germany, Mexico, and France. The U.S. Department of Commerce anticipates exports to grow faster than production for domestic markets through 2004. World Trade Organization (WTO) efforts to reduce tariffs include those on pulp and paper products; if these are successful, the U.S. industry expects pulp and paper export rates to increase even further.

However, pulp and paper are commodities and therefore prices are vulnerable to global competition. Countries such as Brazil, Chile, and Indonesia have built modern, advanced pulp facilities. These countries have faster-growing trees and lower labor costs. Latin American and European countries are also adding papermaking capacity. Because of this increased foreign competition, imports of paper to the U.S. market are expected to increase 3% annually through 2004.[10] In order

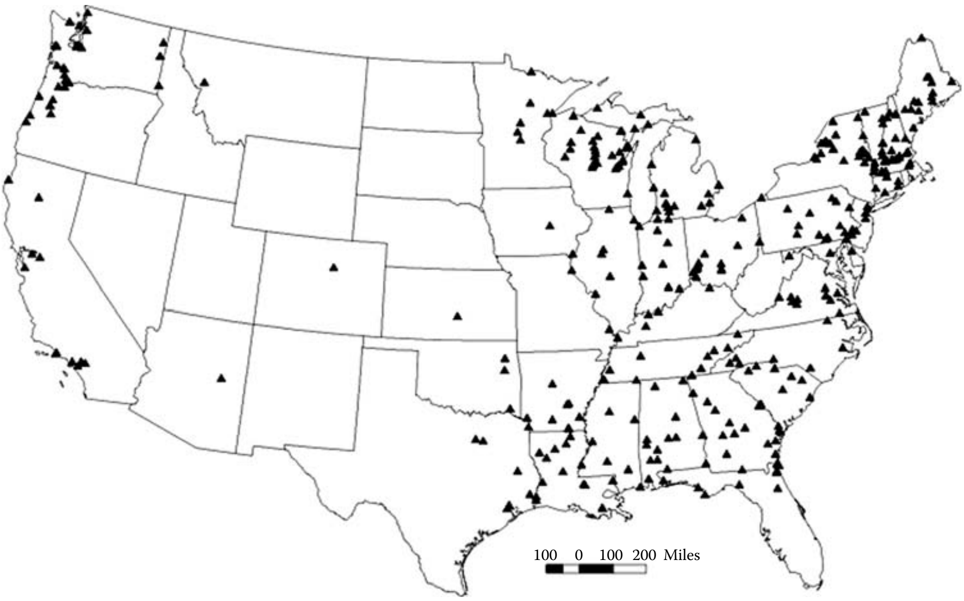

FIGURE 21.2 Geographic distribution of pulp, paper, and cardboard mills. (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

to compensate for this increasingly competitive market, pulp and paper companies have undertaken a considerable number of mergers and acquisitions between 1997 and 2002.

Historically, U.S. pulp and paper companies have invested heavily in capital improvements to their facilities. Capital investments in recent years, however, are well below historic levels due to the difficult market conditions. For the first time, industry capacity actually declined in 2001.[1] Because few new mills are being built, most capital expenditures are for plant expansions, upgrades, and environmental protection initiatives at existing facilities. Throughout the time period 1985–1999, capital improvements related to environmental protection claimed from 4% to 22% of the total investments, with significant increases in the early and late 1990s.[1]

A major movement within the pulp and paper industry has been an increased focus on the use of recovered paper. Nearly 50% of paper is now recovered and used either as recycled paper or as products such as home insulation. Furthermore, recovered paper contributes to U.S. exports; roughly ten million tons of recovered paper were exported in 2000.[1]

21.2 PROCESS DESCRIPTION

21.2.1 PROCESSES IN THE PULP AND PAPER INDUSTRY

Simply put, paper is manufactured by applying a watery suspension of cellulose fibers to a screen that allows the water to drain and leaves the fibrous particles behind in a web. Most modern paper products contain nonfibrous additives, but otherwise they fall within this general definition. Only a few paper products for specialized uses are created without the use of water, using dry forming techniques. The production of pulp is the major source of environmental impacts from the pulp and paper industry.

Processes in the manufacture of paper and paperboard can, in general terms, be divided into three steps:

1. Pulp making
2. Pulp processing
3. Paper/paperboard production

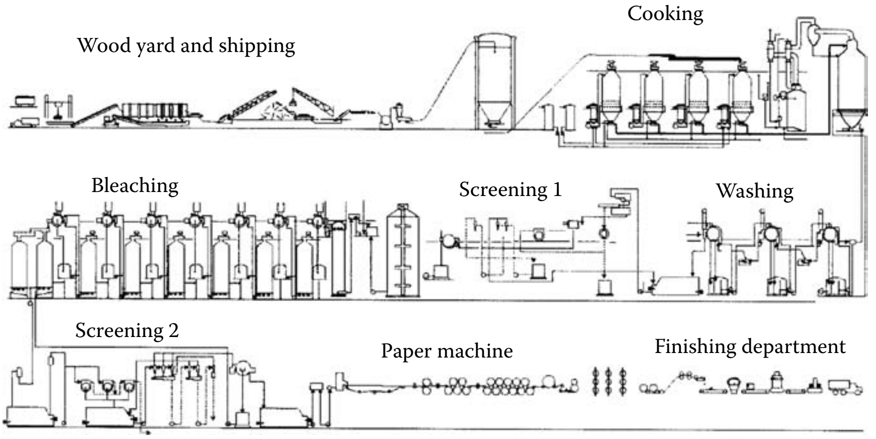

FIGURE 21.3 Simplified flow diagram of an integrated mill. (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

Paper and paperboard production processes are similar. After the fibers are separated and impurities have been removed, the pulp may be bleached to improve brightness and processed to a form suitable for paper-making. At the paper-making stage, the pulp can be combined with dyes, strength-building resins, or texture-adding filler materials, depending on its intended end product. Afterwards, the mixture is dewatered, leaving the fibrous constituents and pulp additives on an endless fabric belt. The fibers bond together as the web passes through a series of presses and around heated drum driers. Additional additives may be applied to the moving web. The final paper product is usually spooled on large rolls for storage (see Figure 21.3). If more information on paper making processes is desired, reference 3 is recommended.

21.2.1.1 Pulp Manufacturing

Table 21.3 presents an overview of wood pulping types by the method of fiber separation, resultant fiber quality, and percent of 1998 U.S. pulp production.[11,12] Many mills perform multiple pulping processes at the same site, most frequently nondeink secondary fiber pulping and paper-grade kraft

TABLE 21.3
General Classification of Wood Pulping Processes

Process Category	Fiber Separation Method	Fiber Quality	Examples	% of Total 1998 U.S. Wood Pulp Production
Mechanical	Mechanical energy	Short, weak, unstable, impure fibers	Stone groundwood, refiner mechanical pulp	10
Semichemical	Combination of chemical and mechanical treatments	"Intermediate" pulp properties (some unique properties)	High-yield kraft, high-yield sulfite	6
Chemical	Chemicals and heat	Long, strong, stable fibers	Kraft, sulfite, soda	84

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

pulping.[3] The following three basic types of wood-pulping processes are detailed below, followed by a discussion of secondary fiber pulping techniques:

1. Chemical pulping
2. Semichemical pulping
3. Mechanical pulping

Various technologies and chemicals are used to manufacture pulp, but most pulp manufacturing systems contain the process sequence shown in Table 21.4. Overall, most of the pollutant releases associated with pulp and paper mills occur at the pulping and bleaching stages where the majority of chemical inputs occur.

Furnish composition

According to the National Census,[13] wood is used in some form by approximately 95% of pulp and paper manufacturers. Wood can be in a variety of forms and types. Wood logs, chips, and sawdust are used to make pulp. Due to different physical and chemical properties, however, certain pulping processes are more efficient when used on specific wood types. The species of wood used has a profound influence on the characteristics of the pulp. In general, softwood fibers are longer than those from hardwood and have thinner cell walls. The longer fibers of softwood produce papers of greater strength, particularly tear strength.

Secondary fibers comprise the next most common furnish constituent. Secondary fibers consist of preconsumer fibers (e.g., mill waste fibers, which were always recycled internally) and postconsumer fiber, which is what is generally referred to as recycled paper. Postconsumer fiber sources are diverse, but the most common are newsprint and corrugated boxes. Although secondary fibers are not used in as great a proportion as wood furnish, ca. 70% of pulp and paper manufacturers use some secondary fibers in their pulp production and ca. 200 mills (40% of the total number of mills) rely exclusively on secondary fibers for their pulp furnish.[11,14] Secondary fibers must be processed to remove contaminants such as glues, coatings, or bindings, and, depending on the end product, may or may not be processed to remove ink or brighten the pulp.

Secondary fiber use is increasing in the pulp and paper industry due to the increasing prices of virgin pulp and the continuing improvement in deinking technology. Environmental concerns have led to consumer acceptance of lower brightness of products made from recycled paper, and government specifications set a minimum level of product quality. Recovered fiber accounted for 75% of the industry's increase in fiber consumption between 1990 and 2000.[15] The utilization of secondary

TABLE 21.4
Pulp Manufacturing Process Sequence

Process Sequence	Description
Fiber furnish preparation and handling	Debarking, slashing, chipping of wood logs and then screening of wood chips/ secondary fibers (some pulp mills purchase chips and skip this step)
Pulping	Chemical, semichemical, or mechanical breakdown of pulping material into fibers
Pulp processing	Removal of pulp impurities, cleaning and thickening of pulp fiber mixture
Bleaching	Addition of chemicals in a staged process of reaction and washing increases whiteness and brightness of pulp, if necessary
Pulp drying and baling (nonintegrated mills)	At nonintegrated pulp mills, pulp is dried and bundled into bales for transport to a paper mill
Stock preparation	Mixing, refining, and addition of wet additives to add strength, gloss, texture to paper product, if necessary

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

fibers, expressed as the ratio of recovered paper consumption to the total production of paper and paperboard, is ca. 39% and is climbing slowly.[1] In a resource-deficient country such as Japan, the secondary fiber utilization rate is ca. 50%, whereas the average utilization rate in Europe is ca. 40%.[16] Due to losses of fiber substance and strength during the recycling process, a 50% utilization rate is considered the present maximum overall utilization rate for fiber recycling.[12]

Until recently, secondary fiber was not used for higher quality paper products. Contaminants (e.g., inks, paper colors) are present, so production of low-purity products is often the most cost-effective use of secondary fibers. Approximately 68% of all secondary fiber in the U.S. is presently used for multi-ply paperboard or the corrugating paper used to manufacture corrugated cardboard.[15] Recently, continuing improvement of deinking processes together with the demand created by environmental concerns have resulted in an increasing use of deinked fiber for newsprint or higher-quality uses, such as office copier paper.

Other sources of fibers include cotton rags and linters, flax, hemp, bagasse, tobacco, and synthetic fibers such as polypropylene. These substances are not used widely, however, as they are typically for low-volume, specialty grades of paper.

The types of furnish used by a pulp and paper mill depend on the type of product produced and what is readily available. Urban mills use a larger proportion of secondary fibers due to the post-consumer feedstock being close at hand. More rurally located mills are usually close to timber sources and thus may use virgin fibers in a greater proportion.

Furnish preparation

Wood is prepared for pulp production by a process designed to supply a homogeneous pulping feedstock. In the case of roundwood furnish (logs), the logs are cut to manageable size and then debarked. At pulp mills integrated with lumbering facilities, acceptable lumber wood is removed at this stage. At these facilities, any residual or waste wood from lumber processing is returned to the chipping process; in-house lumbering rejects can be a significant source of wood furnish at a facility. The bark of those logs not fit for lumber is usually either stripped mechanically or hydraulically with high pressure water jets in order to prevent contamination of pulping operations. Depending on the moisture content of the bark, it may then be burned for energy production. If not burned for energy production, bark can be used for mulch, ground cover, or to make charcoal.

Hydraulic debarking methods may require a drying step before burning. Usually, hydraulically removed bark is collected in a water flume, dewatered, and pressed before burning. Treatment of wastewater from this process is difficult and costly, however, whereas dry debarking methods can channel the removed bark directly into a furnace.[12] In part because of these challenges, hydraulic debarking has decreased in significance within the industry.[1]

Debarked logs are cut into chips of equal size by chipping machines. Chippers usually produce uniform wood pieces 20 mm long in the grain direction and 4 mm thick. The chips are then put on a set of vibrating screens to remove those that are too large or small. Large chips stay on the top screens and are sent to be recut, while the smallest chips are usually burned with the bark. Certain mechanical pulping processes, such as stone groundwood pulping, use roundwood; however, the majority of pulping operations require wood chips. Nonwood fibers are handled in ways specific to their composition. Steps are always taken to maintain fiber composition and thus pulp yield.

Chemical pulping

Chemical pulps are typically manufactured into products that have high quality standards or require special properties. Chemical pulping separates the fibers of wood by dissolving the lignin bond holding the wood together. Generally, this process involves the cooking/digesting of wood chips in aqueous chemical solutions at elevated temperatures and pressures. There are two major types of chemical pulping used in the U.S., which differ in the chemicals employed and in the waste produced:

1. Kraft/soda pulping
2. Sulfite pulping

Kraft pulping processes produced approximately 83% of all U.S. pulp tonnage during 2000 according to the American Forest and Paper Association.[1] The success of the process and its widespread adoption are due to several factors. First, because the kraft cooking chemicals are selective in their attack on wood constituents, the pulps produced are notably stronger than those from other processes (kraft is German for "strength"). The kraft process is also flexible, in so far as it can be applied to many different types of raw materials (i.e., hard or soft woods) and can tolerate contaminants frequently found in wood (e.g., resins). Lignin removal rates are high in the kraft process—up to 90%—allowing high levels of bleaching without pulp degradation. Finally, the chemicals used in kraft pulping are readily recovered within the process, making it very economical and reducing potential environmental releases.

The kraft process uses a sodium-based alkaline pulping solution (liquor) consisting of sodium sulfide (Na_2S) and sodium hydroxide (NaOH) in 10% solution. This liquor (white liquor) is mixed with the wood chips in a reaction vessel (digester). The output products are separated wood fibers (pulp) and a liquid that contains the dissolved lignin solids in a solution of reacted and unreacted pulping chemicals (black liquor). The black liquor undergoes a chemical recovery process to regenerate white liquor for the first pulping step. Overall, the kraft process converts ca. 50% of input furnish into pulp.

The kraft process evolved from the soda process. The soda process uses an alkaline liquor of only sodium hydroxide (NaOH). The kraft process has virtually replaced the soda process due to the economic benefits of chemical recovery and improved reaction rates (the soda process has a lower yield of pulp per pound of wood furnish than the kraft process).

Sulfite pulping was used for approximately 2% of U.S. pulp production in 2000.[1] Softwood is the predominant furnish used in sulfite pulping processes. However, only nonresinous species are generally pulped, particularly when a light colored pulp is required. This process is used, for example, almost exclusively for the manufacture of viscose.[17] To manufacture sulfite pulp, wood chips are boiled under pressure in large digesters with calcium sulfite, ammonium sulfite, magnesium sulfite, or sodium sulfite. The sulfite pulping process relies on acid solutions of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-) to degrade the lignin bonds between wood fibers. In sulfite pulping most water pollution arises from spent liquor, condensates, bleach plant effluents, and accidental discharges.

Sulfite pulps have less color than kraft pulps and can be bleached more easily; however, they are not as strong. The efficiency and effectiveness of the sulfite process is also dependent on the type of wood furnish and the absence of bark. For these reasons, the use of sulfite pulping has declined in comparison to kraft pulping over time.

Semichemical pulping

Semichemical pulping comprised 6% of U.S. pulp production in 1993.[1] Semichemical pulp is often very stiff, making this process common in corrugated container manufacture. This process primarily uses hardwood as furnish.

The major process difference between chemical pulping and semichemical pulping is that semichemical pulping uses lower temperatures, more dilute cooking liquor or shorter cooking times, and mechanical disintegration for fiber separation. At most, the digestion step in the semichemical pulping process consists of heating pulp in sodium sulfite (Na_2SO_3) and sodium carbonate (Na_2CO_3). Other semichemical processes include the Permachem process and the two-stage vapor process. The yield of semichemical pulping ranges from 55 to 90%, depending on the process used, but pulp residual lignin content is also high so bleaching is more difficult.

Mechanical pulping

Mechanical pulping accounted for 9% of U.S. pulp production in 2000.[1] Mechanically produced pulp is of low strength and quality. Such pulps are used principally for newsprint and other nonpermanent paper goods. Mechanical pulping uses physical pressures instead of chemicals to separate furnish fibers. The processes include the following:

1. Stone groundwood
2. Refiner mechanical
3. Thermo-mechanical

4. Chemi-mechanical
5. Chemi-thermo-mechanical

The stone groundwood process simply involves mechanical grinding of wood in several high-energy refining systems. The refiner mechanical process involves refining wood chips at atmospheric pressure. The thermo-mechanical process uses steam and pressure to soften the chips before mechanical refining. In the chemi-mechanical process, chemicals can be added throughout the process to aid the mechanical refining. The chemi-thermo-mechanical process involves the treatment of chips with chemicals for softening followed by mechanical pulping under heat and pressure. Mechanical pulping typically results in high pulp yields, up to 95% when compared to chemical pulping yields of 45–50%, but energy usage is also high. To offset its structural weakness, mechanical pulp is often blended with chemical pulp.

Secondary fiber pulping

Secondary fiber pulping accounted for 39% of domestic pulp production in 2000.[1] Nearly 200 mills rely exclusively on recovered paper for pulp furnish, and ca. 80% of U.S. paper mills use recovered paper in some way.[14] In addition, consumption of fiber from recovered paper is growing more than twice as fast as overall fiber consumption. Secondary fibers are usually presorted before they are sold to a pulp and paper mill. If not, secondary fibers are processed to remove contaminants before pulping occurs. Common contaminants consist of adhesives, coatings, polystyrene foam, dense plastic chips, polyethylene films, wet strength resins, and synthetic fibers. In some cases, contaminants of greater density than the desired secondary fibers are removed by centrifugal force while light contaminants are removed by flotation systems. Centri cleaners are also used to remove material less dense than fibers (wax and plastic particles).[18]

Inks, another contaminant of secondary fibers, may be removed by heating a mixture of secondary fibers with surfactants. The removed inks are then dispersed in an aqueous medium to prevent redeposition on the fibers. Continuous solvent extraction has also been used to recover fibers from paper and board coated with plastics or waxes.

Secondary fiber pulping is a relatively simple process. The most common pulper design consists of a large container filled with water, which is sometimes heated, and the recycled pulp. Pulping chemicals (e.g., sodium hydroxide, NaOH) are often added to promote dissolution of the paper or board matrix. The source fiber (corrugated containers, mill waste, and so on) is dropped into the pulper and mixed by a rotor. Debris and impurities are removed by two mechanisms: a ragger and a junker. The ragger withdraws strings, wires, and rags from the stock secondary fiber mixture. A typical ragger consists of a few "primer wires" that are rotated in the secondary fiber slurry. Debris accumulates on the primer wires, eventually forming a "debris rope," which is then removed. Heavier debris is separated from the mixture by centrifugal force and falls into a pocket on the side of the pulper. The junker consists of a grappling hook or elevator bucket. Heat, dissolution of chemical bonds, shear forces created by stirring and mixing, and grinding by mechanical equipment may serve to dissociate fibers and produce a pulp of desired uniformity.

Contaminant removal processes depend on the type and source of secondary fiber to be pulped. Mill paper waste can be easily repulped with minimal contaminant removal. Recycled postconsumer newspaper, on the other hand, may require extensive contaminant removal, including deinking, prior to reuse. Secondary fiber is typically used in lower-quality applications such as multiply paperboard or corrugating paper.

21.2.1.2 Pulp Processing

After pulp production, pulp processing removes impurities[12] such as uncooked chips, and recycles any residual cooking liquor via the washing process (Figure 21.4). Pulps are processed in a wide variety of ways, depending on the method that generated them (e.g., chemical, semichemical). Some pulp processing steps that remove pulp impurities include screening, defibering, and deknotting. Pulp may also be thickened by removing a portion of the water. At additional cost, pulp may be

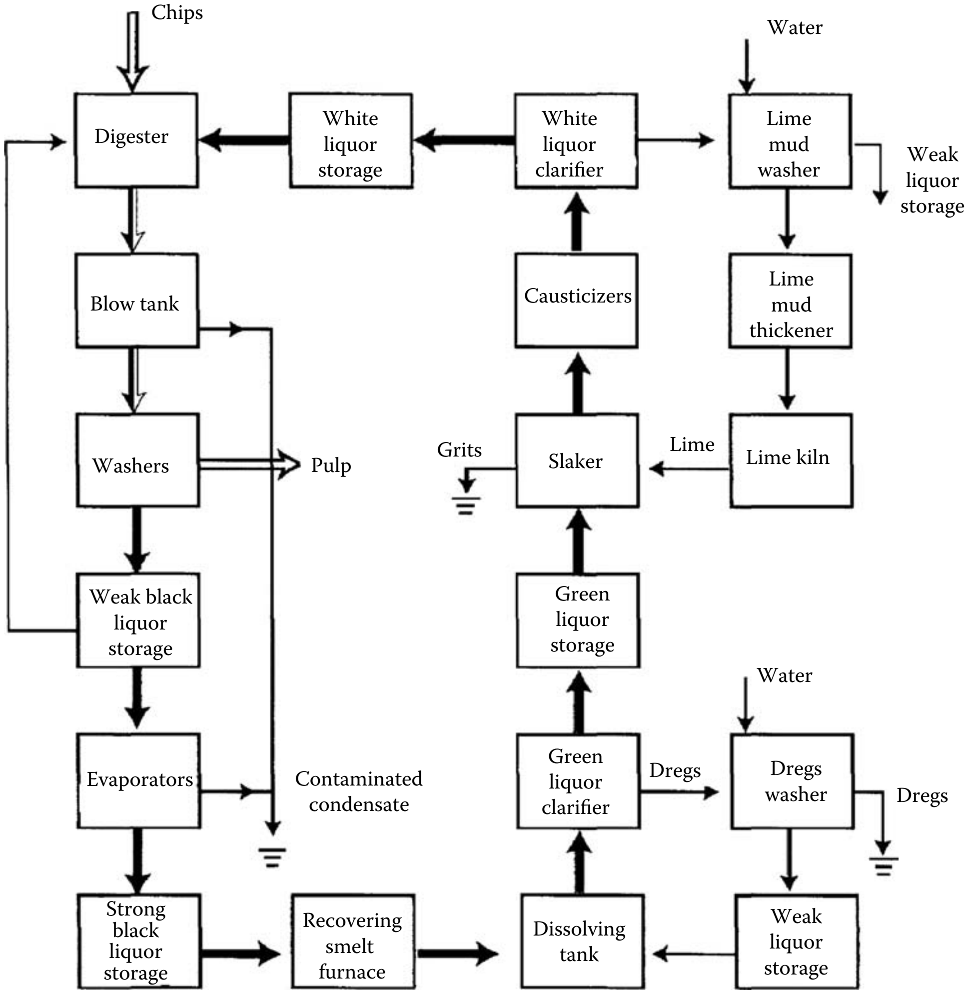

FIGURE 21.4 The kraft pulping process (with chemical recovery). (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

blended to ensure product uniformity. If pulp is to be stored for long periods of time, drying steps are necessary to prevent fungal or bacterial growth.[1]

Residual spent cooking liquor from chemical pulping is washed from the pulp using brown stock washers. Efficient washing is critical to maximize the return of cooking liquor to chemical recovery and to minimize the carryover of cooking liquor (known as brown stock washing loss) into the bleach plant, because excess cooking liquor increases consumption of bleaching chemicals. Specifically, the dissolved organic compounds (lignins and hemicelluloses) contained in the liquor will bind to the bleaching chemicals and thus increase bleach chemical consumption. In addition, these organic compounds are the precursors to chlorinated organic compounds (e.g., dioxins, furans). The most common washing technology is rotary vacuum washing, carried out sequentially in two or four washing units. Other washing technologies include diffusion washers, rotary pressure washers, horizontal belt filters, wash presses, and dilution/extraction washers.

Pulp screening removes the remaining oversized particles such as bark fragments, oversized chips, and uncooked chips. In open screen rooms, wastewater from the screening process receives wastewater treatment prior to discharge. In closed-loop screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. Centrifugal cleaning (also known as liquid cyclone, hydrocyclone, or centricleaning) is used after screening to remove relatively dense contaminants such as sand and dirt. Rejects from the screening process are either repulped or disposed of as solid waste.

Chemical recovery systems

The chemical recovery system is a complex part of a chemical pulp and paper mill and is subject to a variety of environmental regulations. Chemical recovery is a crucial component of the chemical pulping process; it recovers process chemicals from the spent cooking liquor for reuse. The chemical recovery process has important financial and environmental benefits for pulp and paper mills. Economic benefits include savings on chemical purchase costs due to regeneration rates of process chemicals approaching 98%, and energy generation from pulp residue burned in a recovery furnace.[12] Environmental benefits include the recycle of process chemicals and lack of resultant discharges to the environment.

Kraft chemical recovery systems

Although newer technologies are always under development, the basic kraft chemical recovery process has not been fundamentally changed since the issue of its patent in 1884. The stepwise progression of chemical reactions has been refined; for example, black liquor gasification processes are now in use in an experimental phase. The precise details of the chemical processes at work in the chemical recovery process can be found in Smook's Handbook.[12] The kraft chemical recovery process consists of the following general steps:

1. *Black liquor concentration.* Residual weak black liquor from the pulping process is concentrated by evaporation to form "strong black liquor." After brown stock washing in the pulping process the concentration of solids in the weak black liquor is approximately 15%; after the evaporation process, solids concentration can range from 60 to 80%. In some older facilities, the liquor then undergoes oxidation for odor reduction. The oxidation step is necessary to reduce odor created when hydrogen sulfide is stripped from the liquor during the subsequent recovery boiler burning process. Almost all recovery furnaces installed since 1968 have noncontact evaporation processes that avoid these problems, so oxidation processes are not usually seen in newer mills. Common modern evaporator types include multiple effect evaporators as well as a variety of supplemental evaporators. Odor problems with the kraft process have been the subject of control measures.
2. *Recovery boiler.* The strong black liquor from the evaporators is burned in a recovery boiler. In this crucial step in the overall kraft chemical recovery process, organic solids are burned for energy and the process chemicals are removed from the mixture in molten form. Molten inorganic process chemicals (smelt) flow through the perforated floor of the boiler to water-cooled spouts and dissolving tanks for recovery in the recausticizing step. Energy generation from the recovery boiler is often insufficient for total plant needs, so facilities augment recovery boilers with fossil-fuel-fired and wood-waste-fired boilers to generate steam and often electricity. Industry wide, the utilization of pulp wastes, bark, and other paper-making residues supplies 58% of the energy requirements of pulp and paper companies.[11]
3. *Recausticizating.* Smelt is recausticized to remove impurities left over from the furnace and to convert sodium carbonate (Na_2CO_3) into active sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The recausticization procedure begins with the mixing of smelt with "weak" liquor to form green liquor, named for its characteristic color. Contaminant solids, called dregs, are removed from the green liquor, which is mixed with lime (CaO). After the lime mixing step, the mixture, now called white liquor due to its new coloring, is processed to remove a layer of lime mud ($CaCO_3$) that has precipitated. The primary chemicals recovered are caustic (NaOH) and sodium sulfide (Na_2S). The remaining white liquor

is then used in the pulp cooking process. The lime mud is treated to regenerate lime in the calcining process.

4. *Calcining.* In the calcining process, the lime mud removed from the white liquor is burned to regenerate lime for use in the lime mixing step. The vast majority of mills use lime kilns for this process, although a few mills now use newer fluidized bed systems in which the reactants are suspended by upward-blowing air.

Sulfite chemical recovery systems

Numerous sulfite chemical pulping recovery systems are in use today. Heat and sulfur can be recovered from all liquors generated; however, the base chemical can only be recovered from magnesium and sodium base processes. See Smook's Handbook[12] for more information.

21.2.1.3 Bleaching

Bleaching is defined as any process that chemically alters pulp to increase its brightness. Bleached pulps create papers that are whiter, brighter, softer, and more absorbent than unbleached pulps. Bleached pulps are used for white or light colored paper. Unbleached pulp is typically used to produce boxboard, linerboard, and grocery bags. Of the approximately 65.5 million T (72 million tons) of pulp (including recycled pulp) used in paper production in the U.S. in 2000, about 50% is for bleached pulp.[1]

Any type of pulp may be bleached, but the type(s) of fiber furnish and pulping processes used, as well as the desired qualities and end use of the final product, greatly affect the type and degree of pulp bleaching possible. Printing and writing papers comprise ca. 60% of bleached paper production. The lignin content of a pulp is the major determinant of its bleaching potential. Pulps with high lignin content (e.g., mechanical or semichemical) are difficult to bleach fully and require heavy chemical inputs. Bleached pulps with high lignin content are subject to color reversion, loss of brightness when exposed to light. Excessive bleaching of mechanical and semichemical pulps results in loss of pulp yield due to fiber destruction. Chemical pulps can be bleached to a greater extent due to their low (10%) lignin content. For more information, the U.S. EPA reference 19 is recommended. Typical bleaching processes for each pulp type are detailed below.

Chemical pulp bleaching has undergone significant process changes since around 1990. Until that time, nearly every chemical pulp mill that had used bleaching had incorporated elemental chlorine (Cl_2) into some of its processes. Because of environmental and health concerns about dioxins, U.S. pulp mills now use elemental chlorine free (ECF) and total chlorine free (TCF) bleaching technologies. The most common types of ECF and TCF are shown in Table 21.5. The difference

TABLE 21.5
Common Chemicals Used in Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) Bleaching Processes

Bleaching Chemical	Chemical Formula	ECF/TCF
Sodium hydroxide	NaOH	ECF and TCF
Chlorine dioxide	ClO_2	ECF
Hypochlorite	HClO, NaOCl, $Ca(OCl)_2$	ECF
Oxygen	O_2	ECF and TCF
Ozone	O_3	ECF and TCF
Hydrogen peroxide	H_2O_2	ECF and TCF
Sulfur dioxide	SO_2	ECF and TCF
Sulfuric acid	H_2SO_4	ECF and TCF

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

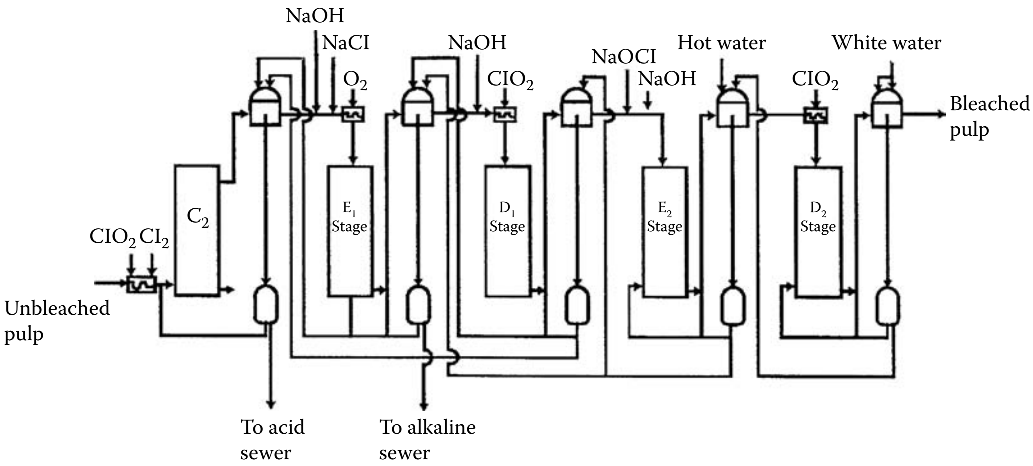

FIGURE 21.5 Typical bleach plant source. (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

between ECF and TCF is that ECF may include chlorine dioxide (ClO_2) and hypochlorite [HClO, NaOCl, and $Ca(OCl)_2$] based technologies. In 2001, ECF technologies were used for about 95% of bleached pulp production, TCF technologies were used for about 1% of bleached pulp production, and elemental chlorine was used for about 4% of production.[20]

Chemical pulp is bleached in traditional bleach plants (see Figure 21.5), where the pulp is processed through three to five stages of chemical bleaching and water washing. The desired whiteness, the brightness of the initial stock pulp, and the plant design determine the number of cycles needed.

Bleaching stages generally alternate between acid and alkaline conditions. Chemical reactions with lignin during the acid stage of the bleaching process increase the whiteness of the pulp. The alkaline extraction stages dissolve the lignin/acid reaction products. At the washing stage, both solutions and reaction products are removed. Chemicals used to perform the bleaching process must have high lignin reactivity and selectivity to be efficient. Typically, 4 to 8% of pulp is lost due to bleaching agent reactions with the wood constituents cellulose and hemicellulose, but these losses can be as high as 18%.[1,2]

Semichemical pulps are typically bleached with hydrogen peroxide (H_2O_2) in a bleach tower.

Mechanical pulps are bleached with hydrogen peroxide (H_2O_2) or sodium hydrosulfite ($NaHSO_3$). Bleaching chemicals are either applied without separate equipment during the pulp processing stage (i.e., in-line bleaching), or in bleaching towers. Full bleaching of mechanical pulps is generally not practical due to bleaching chemical cost and the negative impact on pulp yield.

Deinked secondary fibers are usually bleached in a bleach tower, but may be bleached during the repulping process. Bleach chemicals may be added directly into the pulper. The following are examples of chemicals used to bleach deinked secondary fibers: hypochlorite [HClO, NaOCl, $Ca(OCl)_2$], hydrogen peroxide (H_2O_2), and hydrosulphite ($NaHSO_3$).

21.2.1.4 Stock Preparation

At this final stage, the pulp is processed into the stock used for paper manufacture. Market pulp, which is to be shipped off-site to paper or paperboard mills, is processed little, if at all at this stage. Processing includes pulp blending specific to the desired paper product desired, dispersion in water, beating and refining to add density and strength, and addition of any necessary wet additives. Wet additives are used to create paper products with special properties or to facilitate the paper-making process. Wet additives include resins and waxes for water repellency, fillers such as clays, silicas, talc, inorganic/organic dyes for coloring, and certain inorganic chemicals (calcium sulfate, zinc sulfide, and titanium dioxide) for improved texture, print quality, opacity, and brightness.

21.2.1.5 Processes in Paper Manufacture

The paper and paperboard making process consists of the following general steps:

1. *Wet end operations*: formation of paper sheet from wet pulp
2. *Dry end operations*: drying of paper product, application of surface treatments, and spooling for storage

Wet end operations

The processed pulp is converted into a paper product via a paper production machine, the most common of which is the Fourdrinier paper machine (see Figure 21.6). In the Fourdrinier system,[3] the pulp slurry is deposited on a moving belt (made from polyester forming fabrics) that carries it through the first stages of the process. Water is removed by gravity, vacuum chambers, and vacuum rolls. This waste water is recycled to the slurry deposition step of the process due to its high fiber content. The continuous sheet is then pressed between a series of rollers to remove more water and compress the fibers.

Dry end operations

After pressing, the sheet enters a drying section, where the sheet passes around a series of steam-heated drums. It then may be calendared. In the calendar process the sheet is pressed between heavy rolls to reduce paper thickness and produce a smooth surface. Coatings can be applied to the paper at this point to improve gloss, color, printing detail, and brilliance. Lighter coatings are applied on-machine, and heavy coatings are performed off-machine. The paper product is then spooled for storage.

21.2.1.6 Energy Generation

Pulp and paper mill energy generation is provided in part from the burning of liquor waste solids in the recovery boiler, but other energy sources are needed to make up the remainder of mill energy needs. Over the last 25 years the pulp and paper industry has changed its energy generation methods from fossil fuels to a greater utilization of processes or process wastes. The increase in use of wood wastes from the wood handling and chipping processes (Table 21.6) is one example of this industry-wide movement. During the period 1972 to 1999, the proportion of total industry power generation from the combination of woodroom wastes, spent liquor solids, and other self-generation methods increased from ca. 41% to ca. 58%, while coal, fuel oil, and natural gas use decreased from ca. 54% to ca. 36%.[12,21]

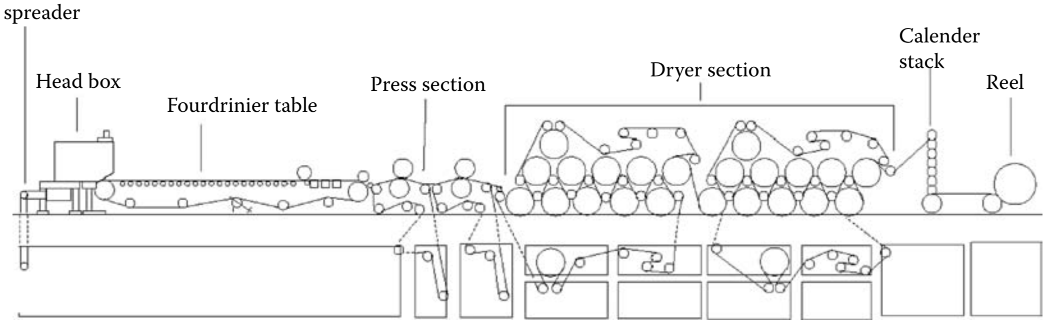

FIGURE 21.6 Fourdrinier paper machine. (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

TABLE 21.6
Estimated Energy Sources for the U.S. Pulp and Paper Industry

Energy Source	1972	1979	1990	1999
Purchased steam	5.4%	6.7%	7.3%	1.5%
Coal	9.8%	9.1%	13.7%	12.5%
Fuel oil	22.3%	19.1%	6.4%	6.3%
Natural gas	21.5%	17.8%	16.4%	17.6%
Other purchased energy	—	—	—	6.7%
Waste wood and wood chips (hogged fuel) and bark	6.6%	9.2%	15.4%	13.5%
Spent liquor solids	33.7%	37.3%	39.4%	40.3%
Other self-generated power	0.6%	0.8%	1.2%	1.6%

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

Power boilers at pulp and paper mills are sources of particulate emissions, SO_2, and NO_x. Pollutants emitted from chemical recovery boilers include SO_2 and total reduced sulfur compounds (TRS).

21.2.2 RAW MATERIAL INPUTS AND POLLUTION OUTPUTS IN THE PRODUCTION LINE

Pulp and paper mills use and generate materials that may be harmful to the air, water, and land:

1. Pulp and paper processes generate large volumes of wastewaters that might adversely affect freshwater or marine ecosystems.
2. Residual wastes from wastewater treatment processes may contribute to existing local and regional disposal problems.
3. Air emissions from pulping processes and power generation facilities may release odors, particulates, or other pollutants.

The major sources of pollutant releases in pulp and paper manufacture occur at the pulping and bleaching stages, respectively. As such, nonintegrated mills (i.e., those mills without pulping facilities on site) are not significant environmental concerns when compared to integrated mills or pulp mills.

21.2.2.1 Water Pollutants

The pulp and paper industry is the largest industrial process water user in the U.S.[5] In 2000, a typical pulp and paper mill used between 15,140 and 45,420 L (4000 to 12,000 gal) of water per ton of pulp produced.[4] General water pollution concerns for pulp and paper mills are effluent solids, biochemical oxygen demand (BOD), and color. Toxicity concerns historically occurred from the potential presence of chlorinated organic compounds such as dioxins, furans, and others (collectively referred to as adsorbable organic halides, or AOX) in wastewaters after the chlorination/extraction sequence. With the substitution of chlorine dioxide for chlorine, discharges of the chlorinated compounds have decreased dramatically.

Due to the large volumes of water used in pulp and paper processes, virtually all U.S. mills have primary and secondary wastewater treatment systems to remove particulates and BOD. These systems also provide significant removals (e.g., 30 to 70%) of other important parameters such as AOX and chemical oxygen demand (COD).

TABLE 21.7
Common Water Pollutants from Pulp and Paper Processes

Source	Effluent Characteristics
Water used in wood handling/debarking and chip washing	Solids, BOD, color
Chip digester and liquor evaporator condensate	Concentrated BOD; can contain reduced sulfur
"White waters" from pulp screening, thickening, and cleaning	Large volume of water with suspended solids; can have significant BOD
Bleach plant washer filtrates	BOD, color, chlorinated organic compounds
Paper machine-water flows	Solids, often precipitated for reuse
Fiber and liquor spills	Solids, BOD, color

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

BOD, biochemical oxygen demand.

The major sources of pollutants from pulp and paper mills[12] are presented in Table 21.7.

Wood processing operations in pulp mills use water for a variety of purposes. The resulting wastewaters contain BOD, suspended solids, and some color. The condensates from chip digesters and chemical recovery evaporators are sources of BOD and reduced sulfur compounds. Wastewaters containing BOD, color, and suspended solids may be generated from pulp screening operations in mills using "atmospheric" systems, although most mills have modern pressure screens that virtually eliminate such wastewaters. Kraft bleaching generates large volumes of wastewater containing BOD, suspended solids, color, and chlorinated organic compounds. From paper machines, excess white water (named for its characteristic color) contains suspended solids and BOD. Fiber and liquor spills can also be a source of mill effluent. Typically, spills are captured and pumped to holding areas to reduce chemical usage through spill reuse and to avoid loadings on facility wastewater treatment systems.

Wastewater treatment systems can be a significant source of cross-media pollutant transfer. For example, waterborne particulates and some chlorinated compounds settle or absorb onto treatment sludge and other compounds may volatilize during the wastewater treatment process.

21.2.2.2 Air Pollutants

Table 21.8 is an overview of the major types and sources of air pollutant releases from various pulp and paper processes.[12]

Water vapors are the most visible air emission from a pulp and paper mill, but are not usually regulated unless they form a significant obscurement or are a climate modifier.

Pulp and paper mill power boilers and chip digesters are generic pulp and paper mill sources of air pollutants such as particulates and nitrogen oxides. Chip digesters and chemical recovery evaporators are the most concentrated sources of volatile organic compounds. The chemical recovery furnace is a source of fine particulate emissions and sulfur oxides. In the kraft process, sulfur oxides are a minor issue in comparison to the odor problems created by four reduced sulfur gases, known collectively as total reduced sulfur (TRS): hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The TRS emissions are primarily released from wood chip digestion, black liquor evaporation, and chemical recovery boiler processes. TRS compounds create odor nuisance problems at lower concentrations than sulfur oxides; odor thresholds for TRS compounds are approximately 1000 times lower than that for sulfur dioxide. Humans can detect some TRS compounds in the air as a "rotten egg" odor at a level as low as 1 μg/L.

TABLE 21.8
Common Air Pollutants from Pulp and Paper Processes

Source	Type
Kraft recovery furnace	Fine particulates
Fly ash from hog fuel and coal-fired burners	Coarse particulates
Sulfite mill operations	Sulfur oxides
Kraft pulping and recovery processes	Reduced sulfur gases
Chip digesters and liquor evaporation	Volatile organic compounds
All combustion processes	Nitrogen oxides

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

Pulp and paper mills have made significant investments in pollution control technologies and processes. According to industry sources, the pulp and paper industry spent more than USD 1 billion/yr from 1991 to 1997 on environmental capital expenditures. In 1991 and 1992, this represented 20% of their total capital expenditures.[22] Chemical recovery and recycling systems in the chemical pulping process significantly reduce pollutant outputs while providing substantial economic return due to recovery of process chemicals. Chemical recovery is necessary for the basic economic viability of the kraft process. According to U.S. EPA sources, all kraft pulp mills worldwide have chemical recovery systems in place. Some sulfite mills, however, still do not have recovery systems in place. Scrubber system particulate "baghouses" or electrostatic precipitators (ESPs) are often mill air pollution control components.

21.2.2.3 Residual Wastes

The significant residual wastestreams from pulp and paper mills include bark, wastewater treatment sludges, lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, scrubber sludges, and wood processing residuals. Because of the tendency for chlorinated organic compounds (including dioxins) to partition from effluent to solids, wastewater treatment sludge has generated the most significant environmental concerns for the pulp and paper industry.

Wastewater treatment sludge is the largest volume residual wastestream generated by the pulp and paper industry. Sludge generation rates vary widely among mills. For example, bleached kraft mills surveyed as part of U.S. EPA's "104-mill study" reported sludge generation that ranged from 14 to 140 kg sludge/T pulp.[23] Total sludge generation for these 104 mills was 2.5 million dry T/yr, or an average ca. 26,000 dry T/yr/plant. Pulp making operations are responsible for the bulk of sludge wastes, although treatment of paper-making effluents also generates significant sludge volumes. For the majority of pulp and integrated mills that operate their own wastewater treatment systems, sludges are generated on site. A small number of pulp mills, and a much larger proportion of paper-making establishments, discharge effluents to publicly owned treatment works (POTWs).

Potential environmental hazards from wastewater sludges are associated with trace constituents (e.g., chlorinated organic compounds) that partition from the effluent into the sludge. It should be noted, however, that recent trends away from elemental chlorine bleaching have reduced these hazards. A continuing concern is the very high pH (>12.5) of most residual wastes. When these wastes are disposed of in an aqueous form, they may meet the RCRA definition of a corrosive hazardous waste.[24]

Landfill and surface impoundment disposal are most often used for wastewater treatment sludge, but a significant number of mills dispose of sludge through land application, conversion to sludge-derived products (e.g., compost and animal bedding), or combustion for energy recovery.[25]

21.2.2.4 Process Inputs and Pollutant Outputs

Kraft chemical pulping and traditional chlorine-based bleaching are both commonly used and may generate significant pollutant outputs. Kraft pulping processes produced ca. 83% of the total U.S. pulp tonnage during 1998 according to the American Forest and Paper Association.[11] Roughly 60% of this amount is bleached in some manner.

Pollutant outputs from mechanical, semichemical, and secondary fiber pulping are small compared to kraft chemical pulping. In the pulp and paper industry, the kraft pulping process is the most significant source of air pollutants. Table 21.9 and Figure 21.7 illustrate the process inputs and pollutant outputs for a pulp and paper mill using kraft chemical pulping and chlorine-based bleaching. Table 21.9 presents the process steps, material inputs, and major pollutant outputs (by media) of a kraft pulp mill practicing traditional chlorine bleaching. U.S. EPA resources[3,26,27] are recommended for pollutant production data (e.g., pounds of BOD per ton of pulp produced) for those pollutants presented in Table 21.9. Figure 21.7 is a process flow diagram of the kraft process, illustrating chemical pulping, power recovery, and chemical recovery process inputs and outputs.[12]

21.2.3 MANAGEMENT OF CHEMICALS IN WASTESTREAMS

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of TRI chemicals in wastes and efforts made to eliminate or reduce their quantities. These data on TRI have been collected annually from 1991. The data were meant to provide a basic understanding of the quantities of toxic waste handled by the industry, the methods typically used to manage them, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

21.3 POLLUTION PREVENTION OPPORTUNITIES

The best way to reduce pollution is to prevent it in the first place. Industries have creatively implemented pollution prevention techniques that improve efficiency and increase profits while at the same time minimizing environmental impacts. This can be done in many ways, for example, by reducing material inputs, reengineering processes to reuse byproducts, improving management practices, and substituting for toxic chemicals. Some smaller facilities are able to get below regulatory thresholds just by reducing pollutant releases through aggressive pollution prevention policies.[1,2]

The chemical recovery systems used in chemical pulping processes are an example of pollution prevention technologies that have evolved alongside process technologies. An efficient chemical recovery system is a crucial component of chemical pulping mill operation. Recovery regenerates process chemicals, reducing natural resource usage and associated costs, as well as discharges to the environment, and may be used for producing energy. Many recent pollution prevention efforts have focused on reducing the releases of toxics, in particular chlorinated compounds. Pollution prevention techniques have proven to be more effective in controlling these pollutants than conventional control and treatment technologies. Most conventional, end-of-pipe treatment technologies are not effective in destroying many chlorinated compounds and often merely transfer the pollutants to another environmental medium. Efforts to prevent chlorinated releases have, therefore, focused on source reduction and material substitution techniques such as defoamers, bleaching chemical or wood chip substitution. Such source reduction efforts and material substitutions usually require substantial changes in the production process. In addition to process changes, the industry is implementing a number of techniques to reduce water use and pollutant releases (BOD, COD, and TSS); these include dry debarking, recycling of log flume water, improved spill control, bleach

TABLE 21.9
Kraft Chemical Pulped Bleached Paper Production

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs[a]	Pollutant Media
Fiber furnish preparation	Wood logs Chips Sawdust	Furnish chips	Dirt, grit, fiber, bark	Solid
			BOD TSS	Water
Chemical pulping kraft process	Furnish chips	Black liquor (to chemical recovery system), pulp (to bleaching/processing)	Resins, fatty acids	Solid
			Color BOD COD AOX VOCs [terpenes, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone (MEK)]	Water
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK) reduced sulfur compounds (TRS)	Air
	Cooking chemicals: sodium sulfide (Na_2S), NaOH, white liquor (from chemical recovery)		Organo-chlorine compounds (e.g., 3,4,5-trichloroguaiacol)	
Bleaching[b]	Chemical pulp	Bleached pulp	Dissolved lignin and carbohydrates Color COD AOX Inorganic chlorine compounds (e.g., chlorate (ClO_3^-))[c]	Water
	Hypochlorite (HClO, NaOCl, $Ca(OCl)_2$) Chlorine dioxide (ClO_2)		VOCs (acetone, methylene chloride, chloroform, MEK, chloromethane, trichloroethane)	Air/water
Papermaking	Additives, Bleached/unbleached pulp	Paper/paperboard product	Particulate wastes Organic compounds Inorganic dyes COD Acetone	Water
Wastewater treatment facilities	Process wastewaters	Treated effluent	Sludge	Solid
			VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Air
			BOD TSS COD Color Chlorophenolics VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)	Water
Power boiler	Coal, wood, unused furnish	Energy	Bottom ash: incombustible fibers	Solid
			SO_2, NO_x, fly ash, coarse particulates	Air

continued

TABLE 21.9 (continued)

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs[a]	Pollutant Media
Chemical recovery system				
Evaporators	Black liquor	Strong black liquor	Evaporator noncondensibles (TRS, volatile organic compounds: alcohols, terpenes, phenols)	Air
			Evaporator condensates (BOD, suspended solids)	Water
Recovery furnace	Strong black liquor	Smelt energy	Fine particulates, TRS, SO_2, NO_x	Air
Recausticizing	Smelt	Regenerated white liquor	Dregs	Solids
		Lime mud	Waste mud solids	Water, solid
		Slaker grits	Solids	Solid
Calcining (lime kiln)	Lime mud	Lime	Fine and coarse particulates	Air

Source: U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids; AOX, adsorbable organic halides; VOC, volatile organic compound; MEK, methyl ethyl ketone; TRS, total reduced sulfur compounds.

[a] Pollutant outputs may differ significantly based on mill processes and material inputs (e.g., wood chip resin content).

[b] Pollutant list based on elemental chlorine-free (ECF) bleaching technologies.

[c] Chlorate only significantly produced in mills with high rates of chlorine dioxide use.

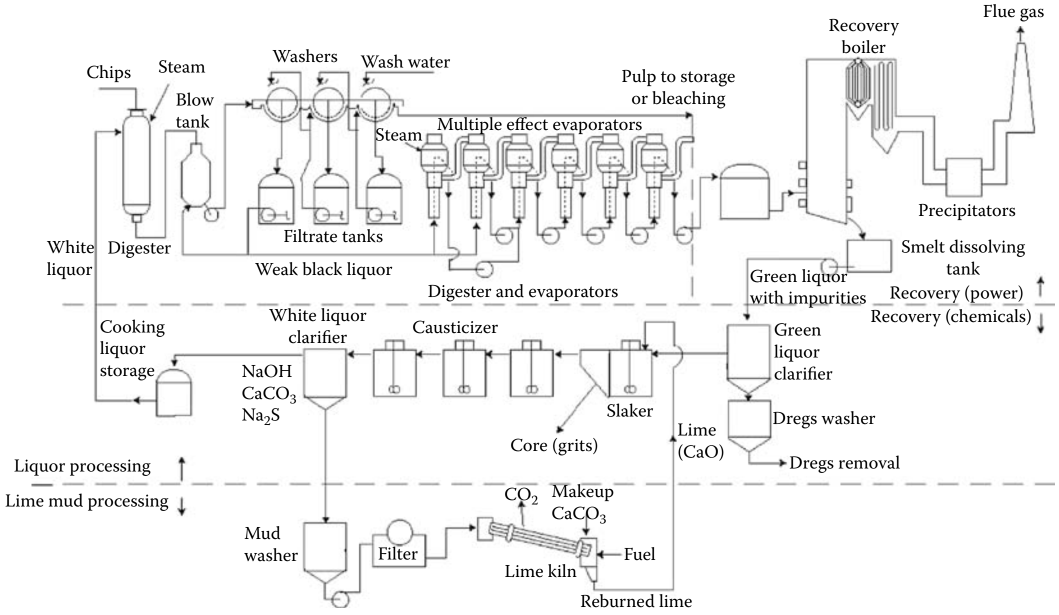

FIGURE 21.7 Kraft process flow diagram. (Taken from U.S. EPA, Profile of the Pulp and Paper Industry, 2nd ed., report EPA/310-R-02-002, U.S. EPA, Washington, November 2002.)

filtrate recycle, closed screen rooms, and improved stormwater management. The industry has also worked to increase the amount of secondary and recycled fibers used for the pulping process. According to industry sources, the pulp and paper industry set and met a 1995 goal of 40% recycling and reuse of all paper consumed in the U.S., and recovering 50% of all paper consumed in the U.S. for recycle and reuse. These figures should be compared with the utilization rate of secondary fibers (secondary fibers as a percentage of the total fibers used to make pulp), which is ca. 37% and is climbing slowly.[11] Current secondary fiber utilization rates in resource-deficient countries such as Japan are above 50%.

Because the pulp and paper industry is highly capital intensive and uses long-established technologies with long equipment lifetimes, major process-changing pollution prevention opportunities are expensive and require long time periods to implement. The pulp and paper industry is a dynamic one, however, that constantly makes process changes and material substitutions to increase productivity and cut costs. The trend towards materials substitutions is reflected in an increasing demand for alternative pulping and bleaching chemicals and in the participation of many facilities in voluntary environmental programs.

One of the factors that drove the industry towards pollution prevention much more rapidly is the integrated NESHAP (National Effluent Standards and Hazardous Air Pollutant) effluent limitation guidelines for the pulp and paper industry. These regulations were developed together in part to reduce the costs of compliance, to emphasize the multimedia nature of pollution control, and to promote pollution prevention. Many of the technology-based effluent limitation guidelines for the control of toxic releases consisted of process changes that substitute chlorine dioxide for elemental chlorine and that completely eliminate elemental chlorine in bleaching processes. The NESHAP standards also allowed hazardous air pollutant (HAP) reductions through recycling of wastewater streams to a process unit and routing pulping emissions to a boiler, lime kiln, or recovery furnace.

Brief descriptions of some pollution prevention techniques found to be effective at pulp and paper facilities are provided below. For more details on the pollution prevention options listed below and for descriptions of additional alternative pulping and bleaching processes see references 1, 2, 26, and 29–32. It should be noted that although many of the pollution prevention opportunities listed below are primarily aimed at reducing toxics releases, the process changes can often lead to reductions in conventional pollutants such as BOD_5 and TSS as well as COD and AOX, and contribute to reduced water use, a reduction in the sludge volumes and air emissions generated.

21.3.1 EXTENDED DELIGNIFICATION

Extended delignification further reduces the lignin content of the pulp before it moves to the bleach plant. Because the amount of bleaching chemicals required for achieving certain paper brightness is proportional to the amount of lignin remaining in the pulp after the pulping process, extended delignification can reduce the amounts of bleaching chemicals needed. Several different extended delignification processes have been developed. These processes include the following:

1. Increasing the cooking time
2. Adding the cooking chemicals at several points throughout the cooking process
3. Regulating the cooking temperatures
4. Carefully controlling the concentration of hydrogen sulfide ions and dissolved lignin

Most importantly, the process changes do not degrade the cellulose that would normally accompany increased cooking times. Extended delignification processes have been developed for both batch and continuous pulping processes. The lignin content of the brownstock pulp has been reduced by between 20 and 50% with no losses in pulp yield or strength using such processes. As a consequence, chlorinated compounds generated during bleaching are reduced in approximate proportion to reductions in the brownstock lignin content. In addition, the same changes have resulted in significant reductions in BOD_5, COD, and color. One study demonstrated a 29% decrease in BOD_5 resulting from an extended delignification process. Facility energy requirements have been shown to increase slightly with extended delignification. However, off-site power requirements (associated with decreased chemical use) have been estimated to more than offset the on-site increases.

21.3.2 Oxygen Delignification

Oxygen delignification also reduces the lignin content in the pulp. The process involves the addition of an oxygen reactor between the kraft pulping stages and the bleach plant.[32] The brownstock pulp from the digester is first washed and then mixed with sodium hydroxide or oxidized cooking liquor. The pulp is fluffed, deposited in the oxygen reactor, steam heated, and injected with gaseous oxygen, at which point it undergoes oxidative delignification. The pulp is then washed again to remove the dissolved lignin before moving to the bleaching plant. Oxygen delignification can reduce the lignin content in the pulp by as much as 50%, resulting in a potentially similar reduction in the use of chlorinated bleaching chemicals and chlorinated compound pollutants. The process can be used in combination with other process modifications that can completely eliminate the need for chlorine-based bleaching agents. In addition, unlike bleach plant filtrate, the effluent from the oxygen reactor can be recycled through the pulp mill recovery cycle, further reducing the nonpulp solids going to the bleaching plant and the effluent load from the bleach plant. The net effect is reduced effluent flows and lower sludge generation. Facility energy requirements have been shown to increase with oxygen delignification, however, the decrease in off-site power requirements (associated with decreased chemical use) has been estimated to exceed the on-site increases, resulting in a decrease in overall energy requirements. Also, the recovered energy and reduced chemical use offset the increased cost.

21.3.3 Ozone Delignification

As a result of a considerable research effort, ozone delignification (ozone bleaching) is now being used in the pulp and paper industry.[32] The technology has the potential to eliminate the need for chlorine in the bleaching process. Ozone delignification is performed using processes and equipment similar to that of oxygen delignification. The ozone process, however, must take place at a very low pH (1.0 to 2.0), requiring the addition of sulfuric acid to the pulp prior to ozonation. In addition to low pH, several process conditions are critical for ozone delignification: organic materials must be almost completely washed out of the brownstock pulp; temperatures must stay at about 20 °C; and ozone-reactive metals must be removed prior to the ozonation stage. Oxygen delignification or extended delignification processes are considered a prerequisite for successful ozone bleaching. When used in combination, the two processes can result in a high-quality bright pulp that requires little or no chlorine or chlorine dioxide bleaching. Overall emissions from the combination of the oxygen and ozone processes are substantially lower than conventional processes because effluents from each stage can be recycled. Systems consisting of ozone delignification in combination with oxygen delignification and oxygen extraction have shown reductions in BOD_5 of 62%, COD of 53%, color of 88%, and organic chlorine compounds of 98%. However, ozone is unstable and will decompose to molecular oxygen, so ozone must be generated on site and fed immediately to the pulp reactor. Ozone generation systems are complex and the initial equipment is expensive. Facility energy use will increase due to the on-site production of ozone; however, this energy will be offset by the energy that would normally be used to produce chlorine and chlorine dioxide.

21.3.4 Anthraquinone Catalysis

The addition of anthraquinone (a chemical catalyst produced from coal tar) to the pulping liquor has been shown to speed up the kraft pulping reaction and increase yield by protecting cellulose fibers from degradation. The anthraquinone accelerates the fragmentation of lignin, allowing it to be broken down more quickly by the pulping chemicals. This lowers the amount of lignin in the prechlorination pulp, thus reducing the amount of bleaching chemicals needed. Anthraquinone catalysts are increasingly used in combination with oxygen delignification and extended delignification to overcome boiler capacity bottlenecks arising from these delignification processes.

21.3.5 Black Liquor Spill Control and Prevention

The mixture of dissolved lignin and cooking liquor effluent from the pulping reactor and washed pulp is known as black liquor. Raw black liquor contains high levels of BOD, COD, and organic compounds. Spills of black liquor can result from overflows, leaks from process equipment, or from deliberate dumping by operators to avoid a more serious accident. Spills of black liquor can have impacts on receiving waters, are a source of air emissions, and can shock the microbial action of wastewater treatment systems. Black liquor losses also result in the loss of the chemical and heat value of the material. Systems needed to control black liquor spills are a combination of good design, engineering, and, most importantly, operator training. The following are a few elements of an effective spill control system:

1. Physical isolation of pieces of equipment
2. Floor drainage systems that allow spills to be collected
3. Backup black liquor storage capacity
4. Sensors that provide immediate warning of potential or actual spills
5. Enclosed washing and screening equipment

21.3.6 Enzyme Treatment of Pulp

Biotechnology research has resulted in the identification of a number of microorganisms that produce enzymes capable of breaking down lignin in pulp. Although the technology is new, it is believed that some mills are currently using enzyme treatment. The microorganisms capable of producing the necessary enzymes are called xylanases. Xylanases for pulp bleaching trials are available from several biotechnology and chemical companies. Because enzymes are used as a substitute for chemicals in bleaching pulp, their use will result in a decrease in the chlorinated compounds released, which is somewhat proportional to the reduction in bleaching chemicals used. Enzymes are also being used to assist in the deinking of secondary fiber. Research at the Oak Ridge National Laboratories has identified cellulase enzymes that will bind ink to smaller fiber particles, facilitating recovery of the ink sludge. Use of enzymes may also reduce the energy costs and chemical use in retrieving ink sludge from deinking effluent.

21.3.7 Improved Brownstock and Bleaching Stage Washing

Liquor solids remaining in the brownstock pulp are carried over to the bleach plant and then compete with the remaining lignin in the pulp for reaction with the bleaching chemicals. Improved washing, therefore, can reduce the required amount of bleaching chemicals and lead to subsequent reductions in chlorinated compounds as well as conventional pollutants. Modern washing systems with improved solids removal and energy efficiency are beginning to replace the conventional rotary vacuum washers. State-of-the-art washing systems include the following:

1. Atmospheric or pressure diffusion washers
2. Belt washers
3. Pulp presses

Opportunities for reducing effluent flows and water use are also present in the bleaching plant. Acid filtrates from hypochlorite or chlorine dioxide stages can be used as dilution and wash water for the first bleaching stage. Similarly, second extraction stage filtrates can be used as dilution and wash water in the first extraction stage. Most new mills are designed with these countercurrent washing systems, and some mills are retrofitting their existing wash systems.

21.3.8 IMPROVED CHIPPING AND SCREENING

The size and thickness of wood chips is critical for proper circulation and penetration of the pulping chemicals. Chip uniformity is controlled by the chipper and screens that remove under- and oversized pieces. Standard equipment does not normally sort chips by thickness, although it has been demonstrated that chip thickness is extremely important in determining the lignin content of pulp. Improper chip thicknesses can result in increased use of bleaching chemicals and the associated chlorinated compounds and conventional pollutants. Some mills have begun to incorporate equipment that will separate chips according to their thickness as well as by length and width.

21.3.9 OXYGEN-REINFORCED/PEROXIDE EXTRACTION

Oxygen-reinforced extraction (or oxidative extraction) and peroxide-reinforced extraction processes used separately or together have been shown to reduce the amount of elemental chlorine and chlorine dioxide needed in the bleaching process while increasing the pulp brightness. Gaseous elemental oxygen and aqueous hydrogen peroxide are used as a part of the first alkaline extraction stage to facilitate the solubilization and removal of chlorinated and oxidized lignin molecules. Oxygen-reinforced extraction has seen widespread adoption by the industry. It is estimated that up to 80% of mills in the U.S. are using oxygen-reinforced extraction, and that 25% of domestic mills are using peroxide extraction.[1]

21.3.10 IMPROVED CHEMICAL CONTROLS AND MIXING

The formation of chlorinated organics can be minimized by avoiding excess concentrations of chlorine-based bleaching chemicals within reactor vessels. This can be accomplished by carefully controlling the chemical application rates and by ensuring proper mixing of chemicals within the reactor. Modern chemical application control and monitoring systems and high-shear mixers have been developed that decrease the formation of chlorinated organic compounds.

21.4 APPLICABLE FEDERAL STATUTES AND REGULATIONS

The purpose of this section is to highlight and briefly describe the applicable federal requirements. For further information, readers should consult the Code of Federal Regulations and other state or local regulatory agencies.[1,2,33–36]

21.4.1 CLEAN AIR ACT (CAA)

21.4.1.1 National Ambient Air Quality Standards

At pulp and paper mills, air emissions from both process and combustion units are regulated under the National Ambient Air Quality Standards (NAAQS) and the State Implementation Plans (SIP) that enforce the standards. States may implement controls to limit emissions of particulate matter (PM), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and sulfur dioxide (SO_2).

Although many limits are implemented at the state level, there are national guidelines that serve as a basis for more specific limits. Sources that are considered "major" under the CAA are subject to prevention of significant deterioration (PSD) or new source review (NSR). Both PSD and NSR are permit programs for facilities that were constructed or modified after a certain date.

Facilities in NAAQS attainment areas must follow PSD requirements by demonstrating that the construction/modification project will not cause a violation of air quality limits and will implement the best available control technology (BACT).

New or modified facilities in nonattainment areas must follow NSR requirements, which require the source to meet the lowest achievable emission rate (LAER) and to obtain emission offsets to ensure that the nonattainment problem is not made worse by the new/modified source.

In addition to the PSD/NSR preconstruction obligations, there are process-specific operational standards: New Source Performance Standards (NSPS). 40 CFR 60 lists these standards, which serve as minimum requirements in states SIPs. Individual states may impose requirements that are stricter. The following NSPSs are particularly relevant to the pulp and paper industry.

Air toxics regulations apply to several parts of the pulp and paper milling process. National Emission Standards for Hazardous Air Pollutants (NESHAP) have been developed expressly for two processes of the pulp and paper industry. These standards establish process-based maximum achievable control technologies (MACT) for "major sources," which are defined as facilities that emit or have the potential to emit 10 t per year or more of any hazardous air pollutant (HAP) or 25 t per year or more of any combination of HAPs.

21.4.1.2 Risk Management Program

Pulp and paper mills are subject to a section of the CAA that states that stationary sources using extremely hazardous substances have a "general duty" to initiate specific activities to prevent and mitigate accidental releases. The general duty requirements apply to stationary sources that produce, process, handle, or store these substances, regardless of the quantity. The general duty clause requires facilities to identify hazards that may result from accidental releases, to design and maintain a safe facility, and to minimize the consequences of releases when they occur.

Most pulp and paper mills are subject to additional, more explicit risk management requirements. Facilities that have more than a threshold quantity of any of the 140 regulated substances in a single process are required to develop a risk management program and to summarize their program in a risk management plan (RMP). All facilities meeting the RMP threshold requirements must follow Program 1 requirements:

1. An off-site consequence analysis that evaluates specific potential release scenarios, including worst-case and alternative scenarios
2. A five-year history of certain accidental releases of regulated substances from covered processes
3. An RMP, revised at least once every five years that describes and documents these activities for all covered processes

In addition, most pulp and paper facilities may be subject to the requirements of Program 2 or 3. These additional requirements include the following:

1. An integrated prevention program to manage risk. The prevention program will include identification of hazards, written operating procedures, training, maintenance, and accident investigation
2. An emergency response program
3. An overall management system to put these program elements into

21.4.1.3 Title V Permits

Title V requires that all "major sources" (and certain minor sources) obtain an operating permit. Many pulp and paper mills are required to have a Title V permit, and may be required to submit information about emissions control devices and the general process at the facility in the permit application. Permits may limit pollutant emissions and impose monitoring record keeping and reporting requirements.

21.4.1.4 Title VI Stratospheric Ozone Protection

Many pulp and paper facilities operate industrial process refrigeration units such as chillers for chlorine dioxide plants. For those units that utilize ozone-depleting chemicals, such as chlorofluorocarbons (CFCs), facilities are required under Title VI to follow leak repair requirements.

21.4.2 Resource Conservation and Recovery Act (RCRA)

The pulp and paper industry generates hazardous wastes, but most are associated with wastewater, which is rendered nonhazardous in wastewater treatment or neutralization units within the manufacturing facilities and therefore is not subject to RCRA requirements. Also, black liquor is exempt as a solid waste if it is reclaimed in a recovery furnace and reused in the pulping process.

21.4.3 Emergency Planning and Community Right-to-Know Act (EPCRA)

Three of the components of EPCRA are directly relevant to the pulp and paper industry:

1. *Emergency planning.* Businesses that produce, use, or store "hazardous substances" must (a) submit material safety data sheets or the equivalent and (b) file annual inventory report forms to the appropriate local emergency planning commission. Those handling "extremely hazardous substances" are also required to submit a one-time notice to the state emergency response commission.
2. *Emergency notification of extremely hazardous substance release.* A business that unintentionally releases a reportable quantity of an extremely hazardous substance must report that release to the state emergency planning commission and the local emergency planning commission.
3. *Release reporting.* Manufacturing businesses with ten or more employees that manufactured, processed, or otherwise used a listed toxic chemical in excess of the "established threshold" must file annually a Toxic Chemical Release form with U.S. EPA and the state. Documentation supporting release estimates must be kept for three years.

21.4.4 Clean Water Act (CWA)

There are two industry-specific components of the CWA requirements: the NPDES (National Pollutant Discharge Elimination System) permitting and pretreatment programs. Other general CWA requirements, such as those for wetlands and stormwater, may also apply to pulp and paper mills.

21.4.4.1 National Pollutant Discharge Elimination System (NPDES) Permitting

Individual NPDES requirements have been developed for several subcategories of the industry. For each of these subcategories, the regulations outline some or all of the following for facilities that discharge wastewater directly to the environment:

1. Best practicable control technology currently available (BPT) and best conventional control technology (BCT) guidelines for the control of conventional pollutants (biological oxygen demand, total suspended solids, and pH)
2. Best available technology economically achievable (BAT) guidelines for the control of nonconventional and toxic pollutants (trichlorophenol and pentachlorophenol, which are chemicals used as biocides)
3. New source performance standards (NSPS) for the control of conventional, nonconventional, and toxic pollutants from new facilities that discharge directly to the environment

21.4.4.2 Pretreatment Standards

For facilities that discharge their wastewater to a POTW, pretreatment standards may apply. In addition to general standards established by U.S. EPA that address all industries, there are Pretreatment Standards for New Sources (PSNS) and Pretreatment Standards for Existing Sources (PSES) that are specific to the pulp and paper industry. These regulate the biocides trichlorophenol and pentachlorophenol, with limits that are specified for each subcategory of the industry. In 1998, in conjunction with the development of the pulp and paper cluster rule, U.S. EPA reorganized the regulations in order to group processes that are similar.

The Cluster Rule is an integrated, multimedia regulation to control the release of pollutants to two media (air and water) from one industry. The intent of the rule is to allow individual mills in particular segments of the industry to consider all regulatory requirements at one time. This combined rule allows mills to select the best combination of pollution prevention and control technologies that provide the greatest protection to human health and the environment. Because some air requirements that reduce toxic air pollutants also reduce mill wastewater toxic pollutant loadings (and water treatment requirements can reduce air impacts), the combined rules have a synergistic effect.

Some of the features of the coordinated rule include the following:

1. Alternative emission limits
2. Varying compliance periods (3 to 8 years)
3. New and existing source controls
4. Flexibility for evolving technologies
5. Compliance dates coordinated with effluent limitations guidelines and standards

The rule sets new baseline limits for the releases of toxics and nonconventional pollutants to the air and water. There are three significant components:

1. *Air emissions standards.* New and existing pulp and paper mills must meet air standards to reduce emissions of toxic air pollutants occurring at various points throughout the mills. Specifically, U.S. EPA requires mills to capture and treat toxic air pollutant emissions that occur during the cooking, washing, and bleaching stages of the pulp manufacturing process.
2. *Water effluent limitations guidelines and standards.* New and existing standards in the bleached papergrade kraft and soda subcategory and the bleached papergrade sulfite subcategory must meet standards to reduce discharges of toxic and nonconventional pollutants. Specifically, U.S. EPA has set effluent limitations for toxic pollutants in the wastewater discharged directly from the bleaching process and in the final discharge from the mills.
3. *Analytical methods for 12 chlorinated phenolics and adsorbable organic halides (AOXs).* Samples of air emissions and water discharges from each mill must be tested using the laboratory methods included in the rule. The new methods will enable more timely and accurate measurements of releases of these pollutants to the environment and will be used to ensure compliance with air emission and water discharge permit limits.

The Cluster Rules require that mills existing as of April 15, 1998, that discharge directly to receiving streams control toxic and nonconventional pollutants at the best available technology (BAT) economically achievable level of performance. U.S. EPA established Pretreatment Standards for Existing Sources (PSES) that are based on control technologies similar to BAT for indirect dischargers.[35] As shown in Table 21.10, except for the monitoring location for AOX, the BAT

TABLE 21.10
BAT Effluent Limitations Guidelines and Pretreatment Standards for Existing Bleached Papergrade Kraft and Soda Plants

Pollutants	**1-Day Maximum**[a]
Bleach Plant Effluent	
TCDD, dioxin	<ML[c]
TCDF, furan	31.9 pg/L[d]
Chloroform[b]	1-Day maximum: 6.92 g/T[e] Monthly average: 4.14 g/T[e]
Trichlorosyringol	<ML
3,4,5-Trichlorocatechol	<ML
3,4,6-Trichlorocatechol	<ML
3,4,5-Trichloroguaiacol	<ML
3,4,6-Trichloroguaiacol	<ML
4,5,6-Trichloroguaiacol	<ML
2,4,5-Trichlorophenol	<ML
2,4,6-Trichlorophenol	<ML
Tetrachlorocatechol	<ML
Tetrachloroguaiacol	<ML
2,3,4,6-Tetrachlorophenol	<ML
Pentachlorophenol	<ML
Final Effluent (for BAT) or Bleach Plant Effluent (for PSES)	
AOX (adsorbable organic halides)	1-Day maximum: 0.951 kg/T[e] Monthly average: 0.623 kg/T[e]

Source: U.S. EPA, Guidance Manual for Pulp, Paper, and Paperboard and Builders' Paper and Board Mills Pretreatment Standards, U.S. EPA, Effluent Guidelines Division, WH-562, Washington, September 1984.

BAT, best available technology economically achievable; TCDD, 2,3,7,8-tetrachlorodibenzo-p-dioxin; TCDF, 2,3,7,8-tetrachlorodibenzofuran.

[a] U.S. EPA established monthly average limitations guidelines for only chloroform and AOX.

[b] For mills that are certified to use TCF, refer to 40 CFR 430.

[c] <ML means less than the minimum level at which the analytical system gives recognizable signals and an acceptable calibration point. The MLs for each pollutant are specified in 40 CFR 430.

[d] pg = pictogram = 10–12 g.

[e] T = metric ton = 1000 kg.

limitations guidelines and PSES for indirect dischargers are the same. U.S. EPA promulgated regulations for new sources (New Source Performance Standards for direct dischargers, and Pretreatment Standards for New Sources for indirect dischargers). However no new bleached kraft or papergrade sulfite mills have been constructed since 1998. Table 21.11 presents the BAT limitations guidelines and PSES for papergrade sulfite mills.

Mills in the Bleached Papergrade Kraft and Soda subcategory have additional flexibility under the Cluster Rule. Mills may comply either with the baseline regulations or with more stringent wastewater regulations under a more forgiving timetable. This latter arrangement, called the Voluntary Advanced Technology Incentives Program (VATIP), allows mills to undertake customized compliance and pollution reduction plans that further reduce environmental impacts.

Under the VATIP, each participating mill develops "Milestones Plans" for each fiber line that it enrolls in the program. Permit writers will use the Milestones Plan to incorporate enforceable

TABLE 21.11
BAT Effluent Limitations Guidelines and Pretreatment Standards for Papergrade Sulfite Existing Plants

Pollutants	Segment A Calcium, Magnesium, and Sodium Sulfite	Segment B Ammonium Sulfite[a]
Bleach Plant Effluent		
TCDD, dioxin	Not regulated	<ML
TCDF, furan	Not regulated	<ML
Chloroform	Not regulated	Reserved
Trichlorosyringol	Not regulated	<ML
3,4,5-Trichlorocatechol	Not regulated	<ML
3,4,6-Trichlorocatechol	Not regulated	<ML
3,4,5-Trichloroguaiacol	Not regulated	<ML
3,4,6-Trichloroguaiacol	Not regulated	<ML
4,5,6-Trichloroguaiacol	Not regulated	<ML
2,4,5-Trichlorophenol	Not regulated	<ML
2,4,6-Trichlorophenol	Not regulated	<ML
Tetrachlorocatechol	Not regulated	<ML
Tetrachloroguaiacol	Not regulated	<ML
2,3,4,6-Tetrachlorophenol	Not regulated	<ML
Pentachlorophenol	Not regulated	<ML
Final Effluent (for BAT) or Bleach Plant Effluent (for PSES)		
AOX	1-Day maximum: 2.64 kg/T[b]	Reserved
	Monthly average: 1.41 kg/T[b]	Reserved

Source: U.S. EPA, Guidance Manual for Pulp, Paper, and Paperboard and Builders' Paper and Board Mills Pretreatment Standards, U.S. EPA, Effluent Guidelines Division, WH-562, Washington, September 1984.

TCDD, 2,3,7,8-tetrachlorodibenzo-p-dioxin, TCDF, 2,3,7,8-tetrachlorodibenzofuran.

[a] <ML means less than the minimum level at which the analytical system gives recognizable signals and an acceptable calibration point. The MLs for each pollutant are specified in 40 CFR 430.

[b] T = metric ton = 1000 kg.

interim requirements into the mill's discharge permit. The three basic components of a Milestones Plan are the following:

1. A description of each technology component or process modification the mill intends to implement
2. A master schedule showing the sequence of implementing new technologies and process modifications
3. Descriptions of the anticipated improvements in effluent quality

21.4.5 STATE STATUTES

In 1986, six states (California, Kentucky, Louisianan, Maryland, North Carolina, and South Carolina) had fully U.S. EPA-approved plans to control TRS at kraft pulp mills, two states had approved TRS standards but their compliance schedules had not yet been approved (Arkansas and Georgia), and

Tennessee's and Florida's plans had been submitted for approval. Since that time, additional states have received approval of their plans. The number of states grew to 18 in 1999 (36) (Alabama, California, Florida, Georgia, Indiana, Kentucky, Maine, Michigan, Mississippi, New Hampshire, North Carolina, Ohio, Oregon, Tennessee, Texas, Virginia, Washington, and Wisconsin).

In general, PM emissions limits are established on a per ton of pulp produced basis or for specific processes (e.g., lime kilns, smelt tanks, and recovery furnaces). Certain states have also established opacity limits and performance standards for specific processes. Investigations related to the integrated rulemaking identified 17 states with regulations specific to the pulp and paper industry.

21.4.6 Summary of National Regulatory Requirements

This section describes the applicable national regulatory requirements for bleached, unbleached, and dissolving kraft mills. Potential pollutants of concern for kraft pulp mills as reflected in the effluent limitations guidelines and standards promulgated by U.S. EPA and in a sampling of NPDES permits are summarized in Table 21.12.

The reader, however, should note that permit requirements will be specifically tailored for each discharging facility. Table 21.13 summarizes the discussion of regulatory requirements presented below.

Prior to the Cluster Rules, direct discharge kraft mills were regulated as shown in §11.4.4.1.

Indirect discharge kraft mills were subject to performance standards for existing sources or new sources (PSES or PSNS, as applicable) for the control of pentachlorophenol and trichlorophenol.

For kraft pulp mills, the Cluster Rules add toxic and nonconventional pollutants to the list of regulated pollutants only for bleached papergrade kraft mills. Effluent limitations guidelines and standards were added for the following BAT and PSES pollutants (and NSPS/PSNS for new sources): chloroform, 2,3,7,8-TCDD, 2,3,7,8-TCDF, 12 chlorinated phenolic compounds, and AOX. All of the

TABLE 21.12
Regulated Pollutant Parameters for Kraft Pulp Facilities

Effluent Guidelines/Standards	Other Potential Permit-Specific Parameters
BOD_5	Total cadmium
TSS	Total mercury
pH	Total silver
Pentachlorophenol	Total zinc
Trichlorophenol	Total copper
AOX	Lead
Chloroform	Mercury
TCDD	Temperature and thermal load
TCDF	Dissolved oxygen
Chlorinated phenols (12 pollutants)	Total phosphorous
	Ammonia
	Aluminum
	Color
	COD

Source: U.S. EPA, Guidance Manual for Pulp, Paper, and Paperboard and Builders' Paper and Board Mills Pretreatment Standards, U.S. EPA, Effluent Guidelines Division, WH-562, Washington, September 1984.

AOX, adsorbable organic compounds; COD, chemical oxygen demand; TCDD, 2,3,7,8-tetrachlorodibenzo-p-dioxin; TCDF, 2,3,7,8-tetrachlorodibenzofuran.

TABLE 21.13
Wastewater Regulations for Kraft Pulp Mills

Type of Kraft Mill	Direct or Indirect Discharger	BPT	Precluster Rules BAT	Cluster Rules BAT	Precluster Rules PSES	Cluster Rules PSES
Bleached kraft mills	Direct discharger	T	T	T		
	Indirect discharger				T	T
Unbleached kraft mills	Direct discharger	T	T			
	Indirect discharger				T	
Dissolving kraft mills	Direct discharger	T	T			
	Indirect discharger				T	

Source: U.S. EPA, Guidance Manual for Pulp, Paper, and Paperboard and Builders' Paper and Board Mills Pretreatment Standards, U.S. EPA, Effluent Guidelines Division, WH-562, Washington, September 1984.

BPT, best practicable control technology; PSES, Pretreatment Standards for Existing Sources; BAT, best available technology economically achievable.

preCluster Rules effluent limitation guidelines and standards applicable to kraft pulp mills remain in effect, although the Cluster Rules have reorganized these limits into new subcategories.

The Cluster Rules reorganized the subcategorization scheme to simplify the categories. Previously, mills were grouped by the types of products manufactured. The Cluster Rules reduced the number of subcategories by grouping mills by similar processes.

In the previous regulations, bleached kraft mills were divided into four subparts and unbleached kraft mills were divided into three subparts. As a result, the remaining preCluster Rules limits (i.e., BPT for BOD_5, TSS, and pH, and BAT and PSES for pentachlorophenol and trichlorophenol) for the four previous bleached kraft mill subparts now exist as four segments. Likewise, the remaining preCluster Rules limits for the three previous unbleached kraft subparts now exist as three segments.

21.4.7 SUMMARY OF WORLD BANK LIQUID EFFLUENTS GUIDELINES

Emissions levels for the design and operation of each pulp and paper mill project must be established through the environmental assessment (EA) process on the basis of national legislation and handbooks[1,2,36,37] as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The following guidelines present emissions levels normally acceptable to the World Bank Group[37] in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. These emissions levels can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems. The guidelines are expressed as concentrations to facilitate monitoring. Dilution of effluents to achieve these guidelines is unacceptable. All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

Liquid effluent requirements for direct discharge to surface waters from pulp and paper manufacturing should achieve the following maximum levels[37]:

pH: 6–9
COD: 300 mg/L and 15 kg/T for kraft pulp mills; 700 mg/L and 40 kg/T for sulfite pulp mills; 10 mg/L and 5 kg/T for mechanical and recycled fiber pulp; 250 mg/L for paper mills.
AOX: 40 mg/L and 2 kg/T (aim for 8 mg/L); 0.4 kg/L for retrofits; 4 mg/L and 0.2 kg/T for new mills; 4 mg/L for paper mills.

Total phosphorus: 0.05 kg/T
Total nitrogen: 0.4 kg/T

Molecular chlorine should not be used in the process. The effluent should not result in a temperature increase of more than 3 °C at the edge of the zone where initial mixing and dilution take place. Where the zone is not defined, 100 m from the point of discharge should be used. Solid wastes should be sent to combustion devices or disposed of in a manner that avoids odor generation and the release of toxic organics to the environment.

Solid waste treatment steps include dewatering of sludge and combustion in an incinerator, bark boiler, or fossil-fuel-fired boiler. Sludges from a clarifier are dewatered and may be incinerated; otherwise, they are landfilled.

21.5 TREATMENT OF WASTEWATER FROM PULP AND PAPER FACILITIES

According to the European Commission (EC) the best available techniques for kraft pulp mills are the following[38]:

1. Dry debarking of wood
2. Increased delignification before the bleach plant by extended or modified cooking and additional oxygen stages
3. Highly efficient brown stock washing and closed-cycle brown stock screening
4. Elemental chlorine free (ECF) bleaching with low AOX or totally chlorine free (TCF) bleaching
5. Recycling of some, mainly alkaline process water from the bleach plant
6. Effective spill monitoring, containment, and recovery system
7. Stripping and reuse of the condensates from the evaporation plant
8. Sufficient capacity of the black liquor evaporation plant and the recovery boiler to cope with the additional liquor and dry solids load
9. Collection and reuse of clean cooling waters
10. Provision of sufficiently large buffer tanks for storage of spilled cooking and recovery liquors and dirty condensates to prevent sudden peaks of loading and occasional upsets in the external effluent treatment plant
11. In addition to process-integrated measures, consider primary treatment and biological treatment as BAT for kraft pulp mills

The BAT for sulfite pulp mills, also according to the EC, are considered to be the following[38]:

1. Dry debarking of wood
2. Increased delignification before the bleach plant by extended or modified cooking
3. Highly efficient brown stock washing and closed-cycle brown stock screening
4. Effective spill monitoring containment and recovery system
5. Closure of the bleach plant when sodium-based cooking processes is being used
6. Total chlorine free (TCF) bleaching
7. Neutralizing of weak liquor before evaporation followed by reuse of most condensate in the process or anaerobic treatment
8. For prevention of unnecessary loading and occasionally upsets in the external effluent treatment due to process cooking and recovery liquors and dirty condensates, sufficiently large buffer tanks for storage are considered as necessary
9. In addition to process-integrated measures, primary and biological treatment are considered BAT for sulfite pulp mills

The BAT for recovered paper processing mills according to EC are the following[38]:

1. Separation of less contaminated water from more contaminated water and recycling of process water.
2. Optimal water management (water loop arrangement), water clarification by sedimentation, flotation or filtration techniques, and recycling of process water for different purposes.
3. Strict separation of water loops and countercurrent flow of process water.
4. Generation of clarified water for deinking plants (air flotation).
5. Installation of an equalization basin and primary treatment.
6. Biological effluent treatment—an effective option for deinked grades and, depending on the conditions, also for nondeinked grades is aerobic biological treatment and in some cases also flocculation and chemical precipitation. Mechanical treatment with subsequent anaerobic–aerobic biological treatment is the preferable option for nondeinked grades. These mills usually have to treat more concentrated wastewater because of the higher degree of water circuit closure.
7. Partial recycling of treated water after biological treatment; the possible degree of water recycling is dependent on the specific paper grades produced. For nondeinked paper grades this technique is BAT. However, the advantages and drawbacks need to be carefully investigated and will usually require additional polishing (tertiary treatment).
8. Treating internal water circuits.

Kraft pulp mills treat wastewater using primary (physical) and secondary (biological) treatment to reduce pollutant discharges to receiving waters. Kraft mills typically collect and treat the following wastewaters[36]:

1. Water used in wood handling and debarking
2. Digester, turpentine recovery, and evaporator condensates
3. Wastewater from brown stock screening
4. Bleach plant effluent
5. Paper machine white water
6. Spent pulping liquor spills from pulp processing areas

Wastewater treatment typically includes (a) neutralization, screening, sedimentation, and flotation/hydrocycloning to remove suspended solids and (b) biological/secondary treatment to reduce the organic content in the wastewater and to destroy toxic organics. Chemical precipitation is also used to remove certain cations. Fibers collected in primary treatment should be recovered and recycled. A mechanical clarifier or a settling pond may be used as primary treatment. Flocculation to assist in the removal of suspended solids is also sometimes necessary. Biological treatment systems, such as activated sludge, trickling filter, aerated lagoons, and anaerobic fermentation, can reduce BOD by over 99% and achieve a COD reduction of between 50 and 90%. Tertiary treatment may be performed to reduce toxicity, suspended solids, and color.[37]

21.5.1 PRETREATMENT

The recommended treatment option for control of toxic pollutants regulated under PSES categorical standards is chemical substitution. Although chemical substitution of sodium hydrosulfite for zinc hydrosulfite is recommended for control of zinc at groundwood mills, PSES for zinc were calculated using treatment performance data for lime precipitation.[39]

21.5.1.1 Lime Precipitation

The removal of zinc from wastewaters using zinc hydrosulfite as a bleaching agent can be achieved through both chemical coagulation and clarification or by changing to another chemical bleaching agent such as sodium hydrosulfite.

The lime application and settling process treatment consists of adding a milk of lime slurry to the wastewater to precipitate the hydroxide of the heavy metals and reduce dissolved sulfate concentrations through the formation of gypsum. Sufficient lime is needed to adjust the pH to between 10 and 11.5. Also, settling may have to be aided by adding small quantities of organic polyelectrolytes.

21.5.1.2 Chemical Substitution

It is often possible to use different process chemicals to accomplish the same goal. For example, both zinc hydrosulfite and sodium hydrosulfite can be used to bleach mechanical pulps. The substitution of the use of sodium hydrosulfite for zinc hydrosulfite was prompted, at least in part, by the establishment of effluent limitations controlling the discharge of zinc. Other opportunities exist to minimize the discharge of toxic and nonconventional pollutants through chemical substitution.

Slimicide and biocide toxic pollutants containing pentachlorophenol are used at mills in the pulp, paper, and paperboard industry. Initially, pentachlorophenol was used as a replacement for heavy metal salts, particularly mercuric types. Trichlorophenols are also used because of their availability as a byproduct from the manufacture of certain herbicides. Formulations containing organo-bromides and organo-sulfur compounds are also being used. Substitution of alternative slimicide and biocide formulations can lead to the virtual elimination of pentachlorophenol and trichlorophenol from these sources.

Ammonia is used as a cooking chemical at mills in the semichemical, dissolving sulfite pulp, and both papergrade sulfite subcategories. One method for reducing ammonia (NH_3) discharges is the substitution of a different chemical, such as sodium hydroxide, for ammonia in the cooking liquor. The equipment changes necessary to receive and feed a 50% solution of NaOH are not likely to be significant.

After conversion to the use of sodium-based chemicals, spent liquor could be incinerated, and sulfur dioxide, sodium sulfate, carbonate, or sulfide could be recovered. These compounds could be sold for use at nearby kraft mills or for other industrial uses.

Reducing smelting furnaces that produce a high-sulfidity, kraft-like green liquor are now employed at sodium-based sulfite mills. U.S. EPA anticipates that it would be necessary to replace the existing recovery boilers at ammonia-based mills if chemical substitution to a sodium base were employed. Additionally, it is likely that, because the heat value of sodium spent liquor is lower than ammonia spent liquor, evaporator modification may he required if excess capacity does not already exist.

21.5.2 PRIMARY TREATMENT

Figure 21.8 shows a typical sequence of the major equipment systems in a wastewater treatment plant.[36] The function of primary treatment is to remove suspended solids from the wastewater, and then to remove organic materials by biological secondary treatment. Primary treatment processes used by kraft mills typically involve screening followed by either sedimentation or flotation.[40]

21.5.2.1 Sedimentation

Kraft mills use mechanical clarifiers[41] or, occasionally, settling ponds that provide sufficient holding time to enable suspended solids to settle. After settling occurs in the mechanical clarifier, the resulting sludge (which contains up to 6% solids) is pumped from the clarifier to sludge-handling facilities where it is dewatered prior to disposal. Mechanical clarifiers can remove as much as 80 to 90% of suspended solids.[40,42]

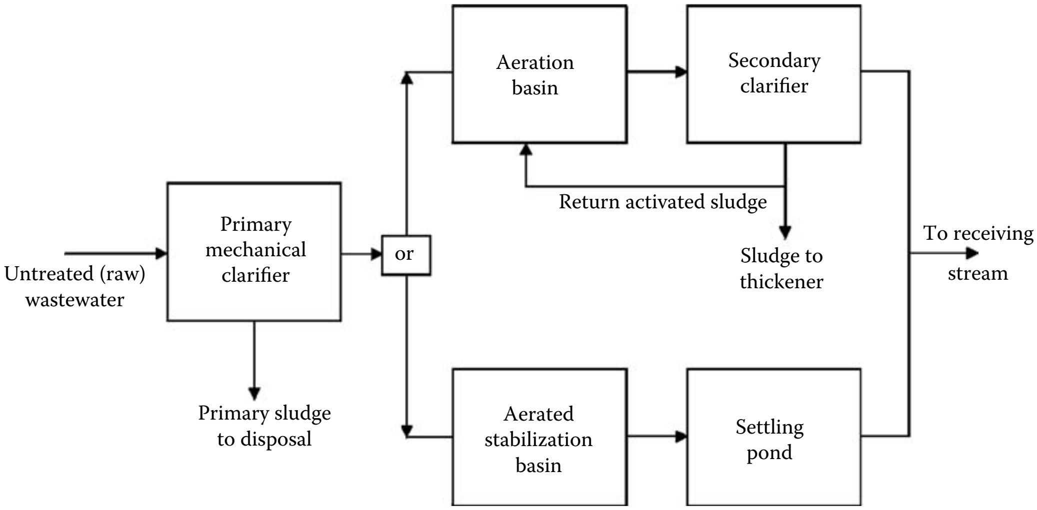

FIGURE 21.8 Typical wastewater treatment plant. (Taken from U.S. EPA, Kraft Pulp Mill Compliance Assessment Guide (CAA, CWA, RCRA and EPCRA), U.S. EPA, EPA/310-B-99-001, Washington, May 1999.)

Settling ponds, a less sophisticated alternative to mechanical clarifiers, also remove suspended solids by sedimentation. Settling ponds may be clay-lined, synthetic-lined, or unlined and earthen, and have longer retention times than clarifiers. Settling ponds produce less constant solids loadings than mechanical clarifiers, but still provide sufficient solids removal prior to secondary treatment.[40,42]

21.5.2.2 Flotation

Flotation is a solids removal process that introduces a gas, usually air, into the wastewater stream. The gas adheres to the suspended solids, reducing their density and causing them to rise to the surface of the water, where they are skimmed off. The advantage of flotation clarification over sedimentation is that lighter particles that require very long retention times to settle are removed more quickly.

A common modification of this process is dissolved air flotation (DAF), in which air under pressure is injected into the wastewater. DAF units are more efficient than conventional flotation clarifiers because more air is introduced into the wastewater, thereby removing more solids.[43–45,59]

21.5.3 SECONDARY TREATMENT

Kraft mills employ secondary treatment to reduce BOD_5 and toxicity in wastewaters. This process makes use of microorganisms (mostly bacteria and fungi) under aerobic conditions to digest the organic matter in the wastewater. The organic matter is removed as biosolids and the treated wastewater is discharged into receiving waters.[46,47] Because pulp mill wastewater is deficient in nitrogen and phosphorus relative to its high carbon load, these nutrients are usually added to the process to enhance microbial activity. Detailed information on bacterial species and biological treatment can be found in the literature.[48–52,59,87]

21.5.3.1 Aerated and Nonaerated Stabilization Basins

About 75% of U.S. kraft mills use aerated stabilization basins.[36] These basins are equipped with continuous mechanical aerators or diffusers to introduce air into the wastewater. By aerating the wastewater, an increased amount of oxygen is introduced into the wastewater stream, thereby maintaining an aerobic environment. This action significantly speeds up the biological activity compared to a nonaerated basin, so that a retention time of 5 d may achieve 90% BOD removal. The continuous aeration also provides thorough mixing, which allows mills to operate effective aeration lagoons at depths up to 7.5 m (25 ft). These basins are typically lined with clay or a combination of synthetics and clay.

Some kraft mills use basins without mechanical aerators. Known as stabilization basins, this is the simplest form of aerobic treatment. This process uses shallow basins that cover very large areas and relies on natural diffusion of air into the wastewater and algae to create aerobic conditions. At depths greater than 1.2 m (4 ft), anaerobic microorganisms will become active in lower depths; thus, stabilization basins are shallow. Typically, the basin is earthen although some are lined with compacted clay. Wastewater retention time may last up to 30 d to achieve up to 90% BOD_5 removal.

Some kraft mills use both aerated and nonaerated basins. The stabilization basin, which may precede or follow the aerated stabilization basin, serves as a "polishing" or "holding" pond to remove additional organic materials, including biological solids, or to reduce final effluent discharges to receiving waters.

21.5.3.2 Activated Sludge System Including Deep Shaft Process

This system features a microbial floc held in suspension in an aeration chamber. Soluble organic matter in the wastewater is metabolized by the microbial floc, which changes it into biosolids, thereby increasing the suspended solids load. After aeration, treated wastewater is routed to a clarifier where the biosolids are removed as sludge. A significant fraction of this sludge biosolids is recycled back to the aeration chamber to maintain the high level of microbial biomass (this is the "activated sludge").[46,83] Retention times for this system can range from 6 h to >12 h. The biosolids[53] that are removed may be further treated and dewatered before disposal or beneficial reuse.

The deep shaft biological treatment process,[87] which is one of the activated sludge systems, has been successfully applied to a paper mill wastewater treatment in Japan (see Case Study III, Section 21.6.3).

21.5.3.3 Anaerobic and Aerobic Biological Treatment

This process, according to the manufacturer,[54] has been developed in such a way that space requirements are kept to a minimum. A BIOPAQ® IC reactor is used as the initial step in the treatment process. The name of this anaerobic reactor is derived from the "gas-lift" driven internal circulation that is generated within a tall, cylindrical vessel. These reactors have been operational in the paper industry since 1996. The second step in the purification process is a mechanically mixed and aerated tank. The aerating injectors can be cleaned in a simple way without the need to empty the aeration tank. Potential scaling materials are combined into removable fine particles. At the same time, the materials that may cause an odor nuisance are oxidized into odorless components. The process can be completed by a third and a fourth step. The third step focuses on suspended solids recovery and removal. The fourth step is an additional water-softening step with lamella separation and continuous sand filters in order to produce fresh water substitute. The benefits claimed by the manufacturer are as follows[54]:

1. Reduction in fresh water costs
2. Savings in energy costs; biogas production makes positive energy balance
3. No water discharge permit needed
4. Minimized space requirement
5. Few chemicals needed
6. Very few waste products
7. Emissions of volatile organics drastically reduced

21.5.4 TERTIARY TREATMENT

Partial recycling of treated water after biological treatment will usually require additional polishing (tertiary treatment). This may include chemical addition, flocculation, and DAF. This is BAT according to the EC.[38]

21.5.5 BIOSOLIDS MANAGEMENT PROCESSES

Some mills may perform biosolids grinding, gravity, or flotation thickening or chemical preconditioning to achieve up to 10% biosolids concentration.[53]

21.5.5.1 Gravity Thickening

Gravity thickening is a common process for dewatering and for the concentration of sludge. Gravity thickening is essentially a sedimentation process similar to what occurs in all settling tanks. The process is simple and is the least expensive of the available thickening processes.[55,56]

Gravity thickening may be classified as plain settling and mechanical thickening. Plain settling usually results in the formation of scum at the surface and stratification of sludges near the bottom. Gentle agitation is usually employed to stir the sludge, thereby opening channels for water to escape and promoting densification. A common mechanical thickener consists of a circular tank equipped with a slowly revolving sludge collector. Organic polyelectrolytes (anionic, nonionic, and cationic) have been used successfully to increase the sludge settling rates, the overflow clarity, and the allowable tank loadings.[57]

21.5.5.2 Flotation Thickening

In a DAF thickening process, air is added at pressures in excess of atmospheric pressure (2.1 to 4.9 kg/cm^2; 30 to 70 psig) either to the incoming sludge stream or to a separate liquid stream. When the pressure is reduced and turbulence is created, air in excess of that required for saturation at atmospheric pressure leaves the solution as very small bubbles of 50 to 100 μm in diameter. The bubbles adhere to the suspended particles or become enmeshed in the solids matrix. As the average density of the solids–air aggregate is less than that of water, the agglomerate floats to the surface. The floated solids build to a depth of several inches at the water surface. Skimmers continuously remove the float.[58]

Polyelectrolytes are frequently used as flotation aids, to enhance performance and create a thicker sludge blanket.[59] The advantages of a DAF thickener are as follows:

1. It provides better solids–liquid separation than a gravity thickener.
2. For many sludges, it yields higher solids concentration than gravity thickener.
3. It requires less area than a gravity thickener.
4. It has less chance of odor problems than a gravity thickener.

21.5.5.3 Belt Filter Press

Biosolids are squeezed between two porous cloth belts. The dewatered cake is scraped from the belts by blades.[60] This operation results in a typical biosolids concentration of 50% for the primary and 20% for secondary biosolids.

21.5.5.4 Vacuum Filters

Vacuum filter systems consist of a horizontal cylinder partially submerged in a tank of biosolids. A layer of porous filter media fabric or tightly wound coils covers the outer surface of the cylinder. As the cylinder surface passes through the tank, a layer of biosolids adheres to the cylinder and vacuum is applied.[61] The dewatered biosolids cake is then scraped off the fabric at up to 30% solids.

21.5.5.5 Screw Presses

Many kraft mills use screw presses that can achieve up to 55% biosolids concentration when dewatering primary biosolids. This operation does not require preconditioning to achieve high concentrations.

21.5.6 BIOSOLIDS DISPOSAL PROCESSES

Subsequent to biosolids handling processes, kraft mills dispose of biosolids by land application, landfill, or combustion.

21.5.6.1 Land Application

Biosolids from kraft mills are classified as a soil amendment because it is too low in nutrients to be of any value as a fertilizer. Owing to concerns regarding dioxin- and furan-contaminated biosolids, in 1994 U.S. EPA and AF&PA (American Forest & Paper Association) entered into an agreement governing the land disposal of biosolids.[62] In this agreement, AF&PA agreed to compile annual monitoring reports for those mills that land-apply materials with a dioxin/furan concentration equal to or greater than 0.01 μg/L. Individual mills also entered in separate agreements with U.S. EPA governing the land application of their biosolids.

21.5.6.2 Landfill

This is the most common disposal method. Kraft mills may use on-site landfills or off-site commercial landfills.[63]

21.5.6.3 Combustion

Some mills will combust the biosolids for heat recovery in a specialized biosolids incinerator, or a hogged or fossil fuel power boiler. Currently, this disposal method is less common than landfilling.[64]

21.5.7 AIR POLLUTANT EMISSIONS FROM TREATMENT PLANTS

The two main sources of air pollutants that may be emitted from basic wastewater treatment plant operations are pulping condensates and bleach plant effluent. The pulping condensates may include total reduced sulfur (TRS) compounds as well as volatile organic compounds (VOCs) such as methanol. The primary pollutants of concern for the bleach plant effluent are chloroform and methanol. Any volatile compounds that could be released as air emissions from basic wastewater treatment plant operations are relatively minor and are generally not subject to specific regulation.[65,66]

In addition, if a mill operates a sludge incinerator, there will be emissions from the incinerator. Inorganic gases (such as CO, NO_x, SO_x, and HCl) may be present, as well as particulate matter (including ash and heavy metals) and organic gases. The only compound subject to specific federal regulations for industrial wastewater sludge incinerators is mercury. In most cases, compliance with the incinerator requirements involves only an initial test to document mercury levels, with a follow-up estimate of the impact on mercury emissions if operating conditions are changed.

21.5.8 WATER POLLUTANT DISCHARGES FROM TREATMENT PLANTS

Kraft mills treat wastewater in order to minimize effluent impacts on receiving waters. Generally, treated effluent is discharged from the wastewater treatment system at a single discharge point. The following pollutants of concern exist at all kraft mills: BOD_5, total suspended solids (TSS), color, and chemical oxygen demand (COD). At kraft mills that bleach pulp with chlorine-containing compounds, additional pollutants of concern include chloroform, 2,3,7,8-TCDD (dioxin), 2,3,7,8-TCDF (furan), chlorinated phenolic compounds, and adsorbable organic halides (AOX). Each of these pollutants is discussed below[67–75]:

1. *BOD_5 and TSS*. The high concentrations of organic matter found in kraft mill wastewater result in high levels of BOD_5. Treatment of this BOD_5 results in the generation of large quantities of TSS. In general, kraft mills achieve 90% (or greater) removal of these pollutants when primary and secondary treatments are well operated.
2. *Color*. Kraft pulp mill effluents contain highly colored lignin and lignin derivatives that have been solubilized and removed from wood during pulping and subsequent bleaching operations. For kraft mill wastewaters, color is determined by spectrophotometric comparison of the sample with a 1 mg/L solution of platinum, in the form of chloroplatinate ion. The color of kraft mill wastewaters is considered to be the color of the water from which turbidity has been removed ("true" color). Further, wastewater color is highly pH dependent, so the pH of color samples is adjusted to pH 7.6. The U.S. EPA has not promulgated national regulations for color because the potential for significant aesthetic or aquatic impacts from color discharges is driven by highly site-specific conditions, such as the color of the receiving stream and the relative contribution of the mill discharge to the stream flow. However, many individual NPDES permits contain water quality-based effluent limitations on the discharge of color, developed to address local conditions.
3. *COD*. COD is a measure of the quantity of chemically oxidizable material present in wastewater. Sources of COD include the pulping area, chemical recovery area, bleaching area, and papermaking area. A portion of COD is readily biodegradable, and the rest is resistant to biodegradation (i.e., "refractory"). Although the amount and sources of refractory COD will vary from mill to mill, some portion of it is derived from black liquor; thus, COD biodegradability indicates the degree to which black liquor is recovered from brownstock pulp and kept out of the wastewater stream. Wastewater COD loads also relate to discharges of toxic organic pollutants that are not readily biodegraded. Although U.S. EPA has not established COD effluent limitations guidelines at this time, U.S. EPA is planning to do so in a future rulemaking.[36]
4. *Chloroform*. Chloroform is an extremely volatile compound that is generated during the bleaching of pulp with hypochlorite, chlorine, or chlorine dioxide. Hypochlorite bleaching results in the greatest amount of chloroform generation, and chlorine dioxide bleaching results in the least amount of chloroform generation. As chloroform is generated, it partitions to air and to bleach plant effluent (with a small fraction remaining with the pulp). Any chloroform found in bleach plant effluent that is not emitted to the air prior to reaching the wastewater treatment plant may be volatilized or degraded during secondary treatment or discharged in the effluent.
5. *Dioxin and furan*. During the late 1980s, bleaching with chlorine and hypochlorite were discovered to be a source of dioxin and furan. Although the use of chlorine dioxide (ClO_2) bleaching minimizes the formation of chlorinated pollutants, measurable quantities of 2,3,7,8-TCDF and possibly 2,3,7,8-TCDD may still be formed. Dioxin and furan are not effectively degraded during wastewater treatment; they partition to the sludge (and may be discharged with TSS into receiving waters untreated).
6. *Chlorinated phenolic compounds*. Chlorinated phenolic compounds include phenols, guaiacols, catechols, and vanillins substituted with from one to five chlorine atoms per molecule. Typically, bleaching processes that result in the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF also generate the higher substituted tri-, tetra-, and penta-chlorinated compounds. U.S. EPA has established effluent limitations guidelines and pretreatment standards for the following 12 chlorinated phenolic compounds: trichlorosyringol, 3,4,5-trichlorocatechol, 3,4,6-trichlorocatechol, 3,4,5-trichloroguaiacol, 3,4,6-trichloroguaiacol,

4,5,6-trichloroguaiacol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, tetrachlorocatechol, tetrachloroguaiacol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol.

7. *Adsorbable organic halides (AOX).* AOX is a measure of the total amount of halogens (chlorine, bromine, and iodine) bound to dissolved or suspended organic matter in a wastewater sample. In bleached kraft mill effluent, essentially all of the AOX comprises chlorinated compounds formed during bleaching with chlorine and other chlorinated bleaching agents. Inefficient application of chlorine-containing bleaching chemicals can generate increased levels of AOX. Minimizing AOX will usually have the effect of reducing the generation of chloroform, 2,3,7,8-TCDD, 2,3,7,8-TCDF, and chlorinated phenolic compounds. Some AOX is biodegraded during secondary treatment.

In addition to retaining the existing effluent limitations guidelines and standards for BOD_5, TSS, and pH, the Cluster Rules establish new effluent limitation guidelines and standards for bleached papergrade kraft mills for the other parameters described above, with the exception of color and COD. The Cluster Rules regulations require bleached kraft mills to meet limits on in-process streams and treated effluent, depending on the pollutant. See references for further sources of information on the applicable discharges and control strategies.[59,76–87]

21.5.9 BIOSOLIDS/HAZARDOUS WASTE DISCHARGES FROM TREATMENT PLANTS

Kraft pulp mills generate both primary and secondary biosolids (sludges). The collected solids may be thickened in gravity or flotation thickeners or chemically conditioned prior to dewatering. Primary solids are usually generated in greater quantities than secondary biosolids. Although the biosolids potentially can be used for alternative beneficial uses, generally dewatered biosolids are disposed of through land application, landfilling, or combustion. Because of concerns about potential contamination with dioxin, U.S. EPA was required to make a hazardous waste listing determination for solids from bleached kraft mill effluents unless the final effluent guidelines were based on the use of at least one of certain specified technologies. These technologies enable the mill to use less chlorine in bleaching pulp and thus to generate less dioxin contamination. After the promulgation of the Cluster Rules, U.S. EPA determined that the final guideline was based on the specified technologies, and thus U.S. EPA determined that it was not required to make a hazardous waste listing determination for pulp mill solids. If the solids at a particular mill exhibit a hazardous waste characteristic, the solids would be hazardous wastes even without a U.S. EPA listing determination.[36]

21.5.10 RECOVERY OF FIBERS AND TITANIUM DIOXIDE

The principal material in paper is the cellulose fiber—from wood, or less frequently from cotton—and particulate mineral filler is incorporated to enhance certain properties, especially opacity. Operations to recover the papermaking materials from wastewaters must deal with both the fiber and the filler. The most common fillers, clay and precipitated calcium carbonate, are less expensive than fiber, and so efficiency of recovery of them is of secondary importance. However, in some special types of paper, where extreme opacity is required, the much more expensive filler titanium dioxide is employed. Titanium dioxide (TiO_2) is a fine, white crystalline powder having an extremely small particle size of 0.1 to 0.4 μm that forms a negatively charged colloid in aqueous media. Because of its colloidal properties and high refractive index (ca. 2.52 for anatase and 2.76 for rutile), titanium dioxide suspensions are very stable in dilute concentrations and have an intense white to blue color. This substance is used as a filler and brightener in high-quality paper and as a white pigment for paints. As a consequence of the manufacturing process, both fibers and titanium dioxide are present in the waste effluents of paper, pulp, and other related industries. The effective and economic recovery of titanium dioxide and fibers offers both the possibility of savings in process costs and the solving of a significant pollution problem.

The case histories presented in Section 21.6.4 to 21.6.6 demonstrate that fibers and titanium dioxide can be recovered from a whitewater by DAF under full flow pressurization mode or recycle pressurization mode with or without chemical addition.[59]

21.6 CASE STUDIES

21.6.1 Case I: International Paper Company, Jay, Maine

This case study was a U.S. EPA initiative to evaluate the extent to which regulatory flexibility and other innovative environmental approaches could be used to achieve superior environmental performance at reduced economic and administrative burdens.

The primary goals of the project were to provide leadership in environmental stewardship and flexibility in regulation as an alternative to the command and control approach enumerated in the Cluster Rules (promulgated in 1998). The project, designated International Paper Effluent Improvements Project, was conducted at the International Paper (IP) Androscoggin Paper Mill in Jay, Maine (Figure 21.9) between the project start date of July 29, 2000, and its formal conclusion on December 29, 2004.[81]

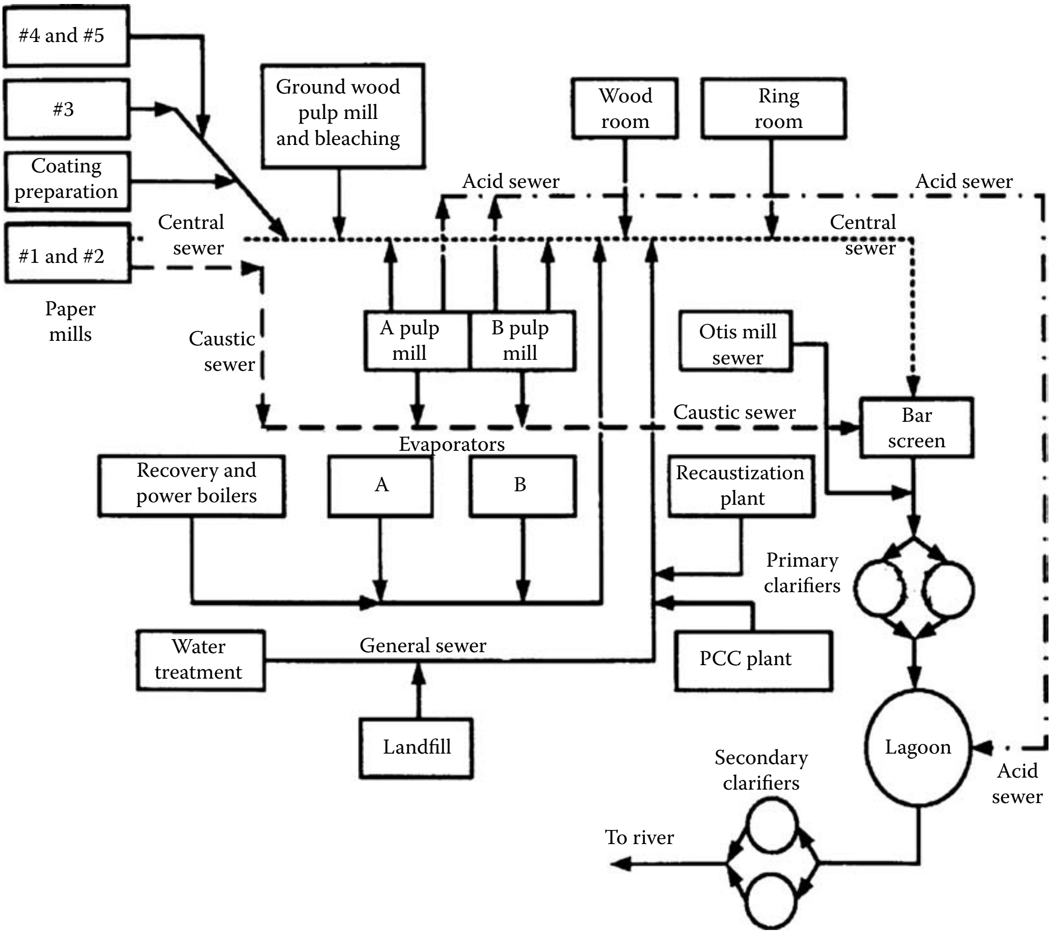

FIGURE 21.9 Schematic diagram of the IP Jay Paper Mill showing points of discharge to wastewater treatment plant. (Taken from U.S. EPA, International Paper XL-2 Effluent Improvements Project, Final Report, U.S. EPA, Maine Department of Environmental Protection, Jay, Maine, September 6, 2005.)

21.6.1.1 Description of Wastewater Collection and Treatment Plant

The wastewater treatment facility (Figure 21.10) provides primary treatment, biological treatment, and secondary clarification. The components of the facility include two coarse mechanical bar screens, two 58-m (190-ft) diameter primary clarifiers with skimmers, four influent pumps with provisions for chemical addition for pH adjustment and nutrient addition, a 265,000 m^3 (70 MG) aerated lagoon, two 77.8-m (255-ft) diameter secondary clarifiers with polymer addition to enhance settling, four return sludge pumps, a 24.4-m (80-ft) diameter thickener and eight screw presses and two belt filter presses, a foam dissolving tank, an emergency spill basin with pumps (not shown), a heat exchanger, and a diffuser.

Stormwater, cooling water, water treatment backwash water, landfill leachate, and wastewater generated in the pulp and papermaking process are discharged into the mill's general sewer (caustic/neutral pH wastewater) by way of a series of collection pipes and sewers. The general sewer flows through the mechanically raked bar screens to remove large objects. The screened objects are then sent to the landfill. Process wastewater from the Otis Mill (see Figure 21.10) is combined with the general sewer after the bar screens. The combined wastewater then flows by gravity through a splitter box and into the two primary clarifiers.

Acid process wastewater is collected separately from the caustic and neutral pH range wastewater. The sanitary wastewater from the mill discharges into the process wastewater acid sewer. The sanitary waste is disinfected by reaction with the oxidants in the acid sewer coming from the bleach plant. Disinfection can also be done by using sodium hypochlorite, calcium chlorite, or other suitable oxidants when the acid sewer is unavailable for treatment. The acid wastewater, including sanitary wastewater, has few suspended solids that can be removed by screening or conventional primary clarification. Therefore, the acid sewer combines with the general wastewater effluent from the primary clarifies just downstream from the primary clarifier (Figure 21.9).

pH adjustments using lime, caustic, or sulfuric acid on the combined wastewater occur in the collection box prior to flowing to the wastewater treatment plant's influent pump station. Four

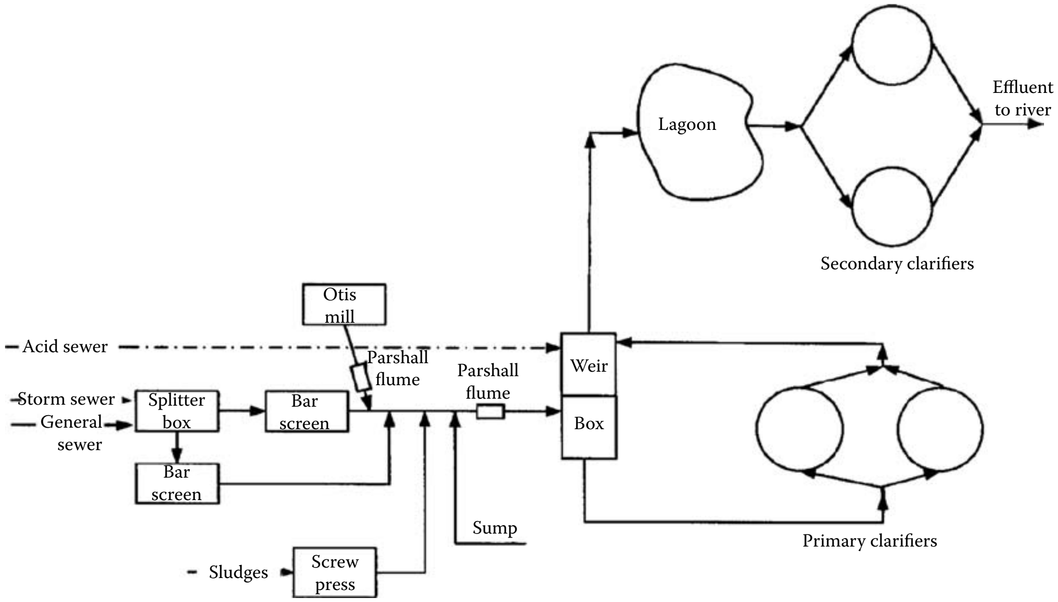

FIGURE 21.10 Schematic diagram of wastewater treatment plant, IP Company at Jay, Maine. (Taken from U.S. EPA, International Paper XL-2 Effluent Improvements Project, Final Report, U.S. EPA, Maine Department of Environmental Protection, Jay, Maine, September 6, 2005.)

centrifugal pumps lift the combined wastewater from a wet well to the aerated lagoon through a 1100-mm (42-in) force main. Before the wastewater enters the lagoon, nutrients such as phosphoric acid, urea, and other suitable nutrients are injected into the force main, as needed, to provide phosphorous and nitrogen to enhance growth of biological solids.

The lagoon at IP Jay is an irregular shaped earth-berm structure with a volume of approximately 265,000 m^3 (70 MG) and an effective process volume of 90,840 m^3 (24 MG). Fifty-five aerators are used to entrain air and mix the solids and liquid in the aeration lagoon to promote biological treatment of wastewater. The aerators consume about 3133 kW (4200 hp) of mechanical power.

Wastewater exits the lagoon and flows over a weir and into a splitter box where the flow is split to the two secondary clarifiers. Cationic polymer is added, as needed, before the secondary clarifiers, to enhance settling of the suspended solids. The settled solids consist of active biological matter and are returned via return sludge pumps to the lagoon through a return line that discharges from two pipes within 7.6 m (25 ft) of the influent from the lift pumps.

The waste sludge pumps also convey excess solids from the secondary clarifiers to the gravity thickener. This waste sludge is then pumped to a sludge dewatering system consisting of screw and belt filter presses. Polymer is added to the sludge prior to dewatering to increase floc size and aid in dewatering. After dewatering by the presses, the dewatered sludge is incinerated in the multifuel boiler waste fuel incinerator (WFI), or temporarily stockpiled and trucked to the mill landfill site for disposal.

Defoamer is added at the overflow from the secondary clarifiers, as necessary, as it flows to a collection box for discharge to the Androscoggin River. The effluent is monitored at the collection box for compliance with permit requirements. Before being discharged to the river, the effluent passes through a heat exchanger, which is operated during the winter months to recapture waste heat. The effluent then passes into a foam dissolving tank that allows for the physical separation of any foam from the effluent and then through a diffuser for discharge into the Androscoggin River.

21.6.1.2 Performance of the Wastewater Treatment Plant

Efficiencies for removal in the wastewater treatment plant were estimated for total and soluble BOD, total COD, soluble COD, color, total suspended and dissolved solids, and total solids. The removal efficiencies summarized in Table 21.14 are high for total BOD, soluble BOD, and suspended solids, at 96%, 96%, and 95%, respectively. The removal efficiencies for total and soluble COD were significantly lower at 76% and 66%, respectively. The removal efficiency for color was only about 38%. This value is typical for biological treatment of pulp and paper wastewater, and may be due, at least partially, to the formation of new colored groups when the bleach effluents are oxidized in the treatment system.

21.6.2 CASE II: UPGRADED TREATMENT PLANT AT A PAPER MILL IN LUFKIN, TEXAS, USING A DAF CELL

The activated sludge treatment plant at a paper mill in Lufkin, TX, treats 68,200 m^3/d (18 MGD) of wastewater. The plant was designed to produce a final effluent with BOD and TSS that would not exceed 20 mg/L. However, several expansions resulted in poor effluent quality and borderline permit compliance, particularly during the periods of peak BOD loading. The first alternative to solve the plant's problems, namely increasing the aeration time by adding another aeration basin of the same size, was not a viable option. The company did not have enough land space and the capital expenditure for this conventional option is high. The alternative decision was the use of a 16.8 m (55 ft) dissolved air flotation (DAF) cell (see Figure 21.11) as a secondary clarifier that would be installed in front of the final sedimentation tanks and has a capacity to handle 30,000 m^3/d (8 MGD) of flow.[45,82–84] This was accomplished at only 12% of the cost of the conventional expansion project estimate. A top view of the DAF cell is shown in Figure 21.12.

TABLE 21.14
Removal Efficiencies in Wastewater Treatment Plant

Variable	Influent T/d	Effluent T/d	Removal Efficiency %
Total BOD_5	43	1.7	96
Soluble BOD_5[a]	24	0.9	96
Total COD	153	33	78
Soluble COD[a]	75	25	66
Color	65	40	38
Total suspended solids (TSS)	97	5.2	95
Soluble solids (SS)	171	167	2.9
Estimated total solids	268	172	36
Flow			
MGD[b]	40.8	42.5	
ML/d[c]	154.4	160.9	
M^3/d	154,400	160,900	

Source: U.S. EPA, International Paper XL-2 Effluent Improvements Project, Final Report, U.S. EPA, Maine Department of Environmental Protection, Jay, Maine, September 6, 2005.

BOD, biochemical oxygen demand; COD, chemical oxygen demand.

[a] Samples were filtered through a 0.8 μm filter.

[b] MGD = million gallons per day.

[c] ML/d = million liters per day.

The sludge return to the aeration basin from the flotation cell at 2% concentration is five times thicker than the 0.4% sludge return from the final settling tanks. The resulting reduction in the volume of recycle to the aeration basin by 9500 m^3/d (2.5 MGD) provides an extra 10% hydraulic capacity for aeration. The solids removed from the 30,000 m^3/d flow processed by the flotation cell reduced the solids flowing to the final clarifiers by at least 30% so that no violations of the discharge limits have occurred since installation. The net results were reduced solids loading to the final clarifiers, increased hydraulic capacity and retention time of the aeration basin, threefold increase in overall concentration of biosolids, more active recycled sludge, better effluent quality, and no biosolids bulking problems. More case histories of waste treatment in the pulp and paper industry using flotation technology can be found from the literature.[85,86]

21.6.3 CASE III: DEEP SHAFT PLANT AT OHTSU PAPER COMPANY IN OHTSU, JAPAN

The deep shaft plant at Ohtsu Paper Co. came on line in 1980. It treats the wastewater generated by a cardboard recycling facility located within 18.3 m (60 ft) of a residential area inside the city of Ohtsu. The plant discharges treated wastewater to a beautiful recreational body of water named Lake Biwa.

21.6.3.1 Plant Description

Flow to the deep shaft biological wastewater treatment plant is screened and goes through a DAF unit for fiber removal prior to entry into the deep shaft. The Ohtsu plant consists of one shaft 2.79 m (110 in.) in diameter by 100 m (330 ft) deep. The shaft design incorporates one downcomer and one riser where the downcomer is located concentrically within the shaft with the resultant annular volume serving as the riser. Mixed liquor in the shaft is maintained at approximately 5000 mg/L and the hydraulic detention time in the shaft is 1 h. Mixed liquor enters the head tank at the top of the shaft where gas disengagement occurs. The head tank is 6 m × 12 m × 3 m

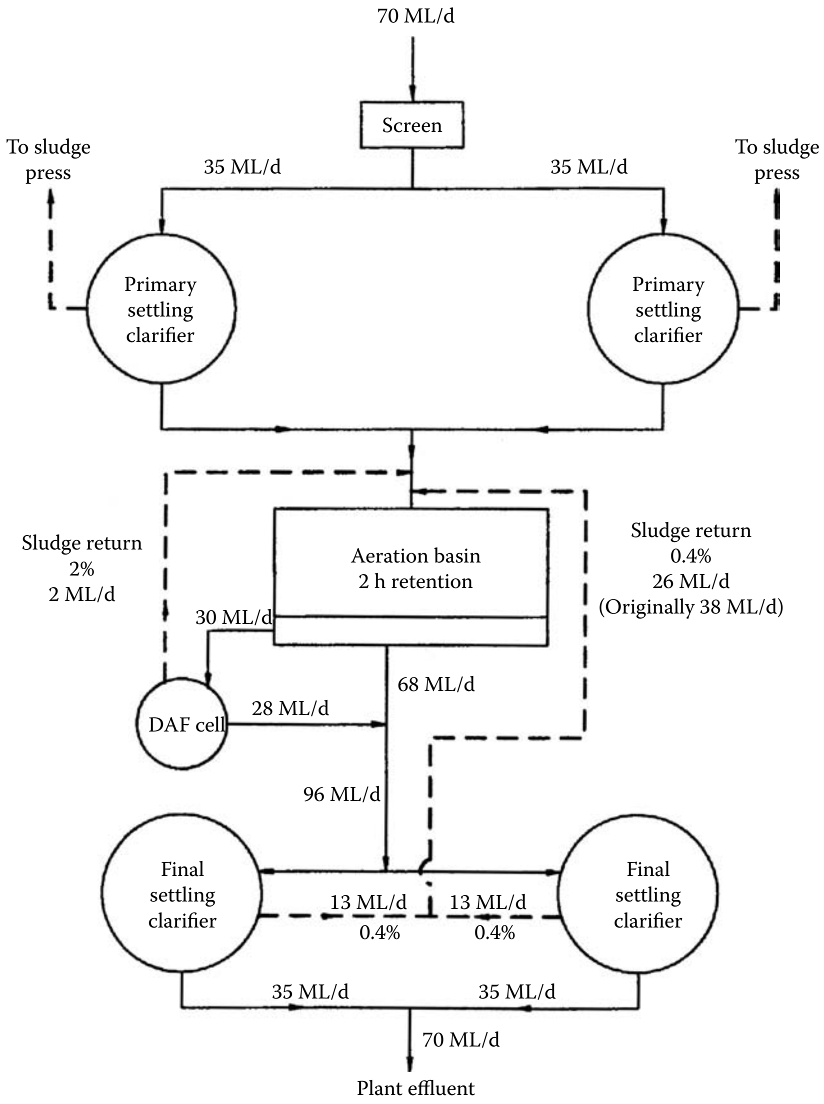

FIGURE 21.11 Process flow diagram of upgrade activated sludge plant at a paper mill using a DAF cell.

(20 ft × 40 ft × 10 ft). A portion of the mixed liquor overflows the head tank to a vacuum degasser, which is 3.8 m (12.5 ft) diameter by 10.1 m (33 ft) high equipped with one operating vacuum pump of 14.9 kW (20 hp) capacity. The degasser overflows by gravity into a holding tank that splits the flow equally to two sedimentation clarifiers, both of which are 25 m (82 ft) in diameter and have 2.7 m (9 ft) sidewater depth. Sludge is wasted at 1% concentration to a sludge holding tank. Waste sludge is subsequently pumped to a belt filter press and dewatered to a 40% by weight solids content prior to disposal.[87]

The aeration requirements of the deep shaft (vertical shaft bioreactor using flotation technology) are provided by two, 100 hp rotary screw compressors rated at a pressure of 7 kg/m^2 (100 psig). Dissolved oxygen (DO) levels of 4 mg/L are maintained in the head tank, and during the startup phase of the plant a DO meter measured a dissolved oxygen concentration of 25 mg/L at the shaft bottom.

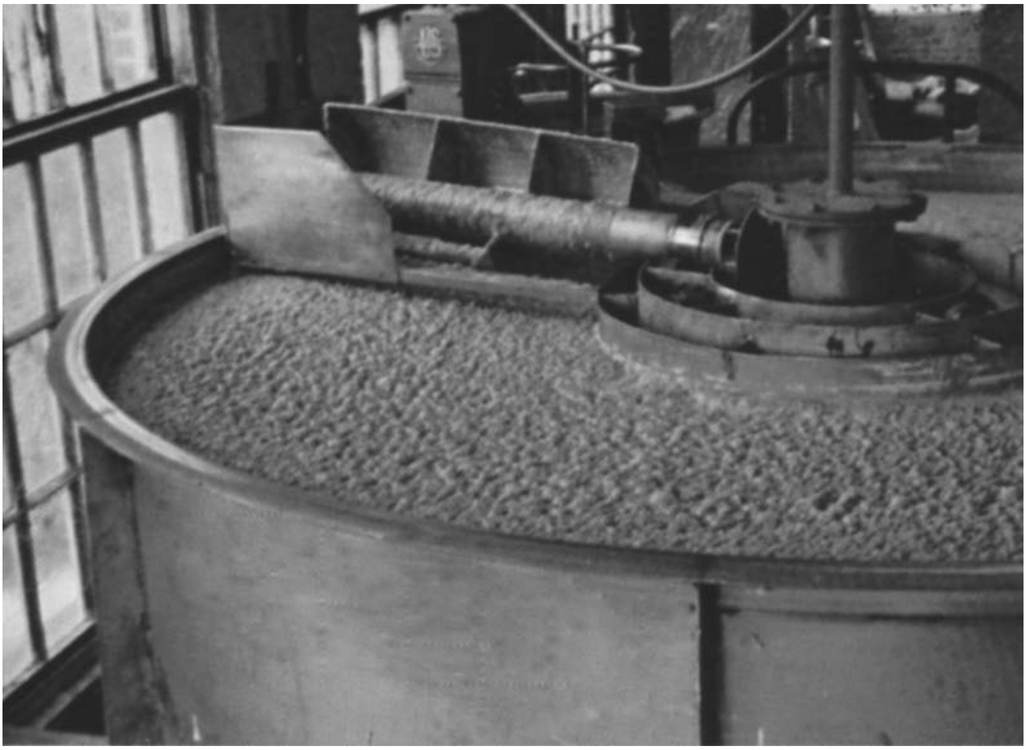

FIGURE 21.12 Top view of DAF cell.

Operating staff at the plant consist of two operators per shift plus one maintenance person on dayshift. The wastewater is nutrient deficient and a ratio of 100 : 8 : 1 of BOD : N : P is maintained by the addition of diammonium phosphate and phosphoric acid for nitrogen and phosphorous requirements, respectively.

21.6.3.2 Performance

The plant has performed very well over its operating lifetime since 1980. Problems experienced have been a transmittance problem on one occasion, which was resolved by the addition of bentonite clay to the mixed liquor suspended solids (MLSS). This provided an inexpensive solution and the problem has never reoccured. Bentonite addition is still being practiced as an added insurance. Septage collecting in the degasser caused an odor problem during low flow periods and it was corrected by the installation of an air line in the base of the degasser.

Table 21.15 illustrates the mean operating performance of the plant. The regulatory standard for the plant is based on effluent COD, which is monitored three times per day. A BOD_5 test is done once per month. The BOD/COD correlation for the plant effluent is BOD = COD – 25.[87]

21.6.4 Case IV: Cotton Fiber Recovery Flotation Cell of Krofta Engineering Corporation, Lenox, Massachusetts

Cotton paper (100%) obtained from Mead Corporation in South Lee, Massachusetts, was pulped at Krofta Engineering Corporation (KEC), Lenox, MA.[59] A known amount of pulp was suspended in tap water to determine the percent recovery by a circular DAF cell (Model Supracell Type 3; diameter = 0.91 m [3 ft]; depth = 55.88 cm [22 in.]; flow = 45 L/min [12 gal/min]). The initial total

TABLE 21.15
Performance of Ohtsu Paper Company's Deep Shaft Biological Treatment Plant in Japan

Parameter	Influent[a] (mg/L)		Effluent (mg/L)	
	Design	Operation Range	Design	Operation Range
BOD_5	200	100–215	<10	<10
COD	30	120–260	34	21–30
TSS	22	10–60	20	10–18

Source: Adapted from Daly, P.G. and Shen, C.C., The deep shaft biological treatment process, in *Proceedings of the 43rd Purdue Industrial Waste Conference*, May 1988. With permission.

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids.

[a] Flow range = 18,000–23,000 m3/d; temperature range = 10–29°C.

suspended solids concentration (TSS) of raw pulp was 1260 mg/L. In two separate continuous full flow pressurization operations, 95.5% fiber was recovered without any chemical addition, and 98% fiber was recovered with the addition of 1 mg/L polymer Betz 1260. It was concluded that recovery of cotton fiber by a DAF clarifier can be successfully achieved even without chemical addition. It is also important to note that rectangular DAF cell should be equally effective for fiber recovery although the exact fiber recovery efficiency must be demonstrated by a pilot plant testing.

21.6.5 Case V: Fiber and Titanium Dioxide Recovery Facility at Mead Corporation, South Lee, Massachusetts

Almost all fiber and partial titanium dioxide can be recovered from white water by DAF under full flow pressurization mode[43] with chemical addition. On June 10, 1982, at Mead Corporation, pulp was prepared with 40% cotton fiber and 60% wood fiber. The loading of titanium dioxide was about 50% (i.e., 273 kg TiO_2 per 600 kg total pulp). The white water from No. 2 machine was fed to a DAF cell (diameter = 3 m) at 15.8 L/s (250 gal/min) under full flow pressurization mode. Turkey red oil (TRO) was dosed as a flotation aid at 80 mL/min. The influent white water (before TRO addition), DAF effluent, and floated scum were sampled for analysis. The DAF influent had 98 mg/L of TSS, and 650 NTU of turbidity at pH 9.27. The DAF effluent had 15 mg/L TSS and 550 NTU of turbidity at pH 9.25. Although TSS (fiber and titanium dioxide) recovery rate was 85%, the ash content (titanium dioxide) of the recovered TSS was very low. Therefore, using a DAF clarifier under full flow pressurization mode and TREO, the majority of fibers in white water but only about half of titanium dioxide can be recovered.

21.6.6 Case VI: Resource Recovery Facility of Lenox Institute of Water Technology (LIWT), Lenox, Massachusetts

Both fibers and titanium dioxide can be almost totally recovered by DAF under recycle flow pressurization mode[59] when using adequate coagulant. Various operational modes of DAF can be found in the literature.[43] White water containing 500 mg/L titanium dioxide and 1000 mg/L cotton fiber was continuously fed to a LIWT research facility (circular high rate DAF cell; diameter = 0.9 m) at 45 L/min (12 gal/min) under 33.3% recycle flow pressurization mode. After one hour of continuous operation and at steady state, the influent, effluent and floated scum were sampled for analysis. It was found that over 99% of titanium dioxide and fibers was recovered when 100 mg/L of magnesium carbonate, 120 mg/L of calcium hydroxide, and 0.3 mg/L of polymer Magnifloc 1563 C were dosed at pH 11. Initial DAF influent feed was milky. The DAF effluent became crystal clear having a turbidity of 2 NTU. The floated scum was 3.9% in consistency. Titanium dioxide concentrations were measured by both atomic absorption spectrometry and ash content.

A separate continuous DAF operation conducted by Krofta and Wang[59] under 33.3% recycle flow pressurization mode demonstrated that aluminum sulfate, sodium aluminate, and polyelectrolyte combination at pH 6.2 also effectively recovered both fibers and titanium dioxide from the same white water containing 500 mg/L of titanium dioxide and 1000 mg/L of cotton fibers.

In practical applications, adequate coagulants should be chosen based on the quality of the floated scum (i.e., recovered titanium dioxide and fiber mixture), which is intended to be reused in the paper manufacturing process. The reused titanium dioxide and fibers should not adversely affect the quality of the paper.

Additional research conducted by LIWT[88–91] has shown that the wastestreams, such as those shown in Figure 21.11, can be effectively treated by the two-stage biological-physicochemical process system or two-stage DAF-DAFF (dissolved air flotation-filtration) process system. The readers are referred to the literature[88–91] for details.

NOMENCLATURE

AF&PA	American Forest & Paper Association
AOX	Adsorbable organic halides
BAT	Best available technology economically achievable
BCT	Best conventional pollutant control technology
BOD	Biochemical oxygen demand
BPT	Best practicable control technology
CAA	Clean Air Act
CAAA	Clean Air Act Amendments of 1990
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFCs	Chlorofluorocarbons
CFR	Code of Federal Regulations
COD	Chemical oxygen demand
CWA	Clean Water Act
ELGs	Effluent Limitations Guidelines and Standards
EPCRA	Emergency Planning and Community Right-to-Know Act
F/M	Food/microorganisms ratio
HAPs	Hazardous Air Pollutants (CAA)
LDR	Land Disposal Restrictions (RCRA)
LEPCs	Local Emergency Planning Committees
MACT	Maximum achievable control technology (CAA)
MCLGs	Maximum contaminant level goals
MCLs	Maximum contaminant levels
ML	Minimum level
NAAQS	National Ambient Air Quality Standards (CAA)
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NESHAP	National Emission Standards for Hazardous Air Pollutants
NOX	Nitrogen oxides
NPDES	National Pollutant Discharge Elimination System (CWA)
NPL	National Priorities List
NSPS	New Source Performance Standards (CAA)
OPA	Oil Pollution Act
OSHA	Occupational Safety and Health Administration
PAC	Polycyclic aromatic compounds
POTW	Publicly owned treatment works

PSES	Pretreatment Standards for Existing Sources
PSNS	Pretreatment Standards for New Sources
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SIC	Standard Industrial Classification
SOX	Sulfur oxides
T	Metric ton = 1000 kg
t	English ton = 2000 lb
TRI	Toxic release inventory
TSCA	Toxic Substances Control Act
TSS	Total suspended solids
U.S. EPA	U.S. Environmental Protection Agency
UST	Underground storage tanks (RCRA)

APPENDIX

U.S. Army Corps of Engineers Civil Works Construction Yearly Average Cost Index for Utilities (for conversion of USD costs in terms of 2008 USD).

TABLE A21.1
U.S. Army Corps of Engineers Civil Works Construction Yearly Average Cost Index for Utilities

Year	Index	Year	Index
1967	100	1988	369.45
1968	104.83	1989	383.14
1969	112.17	1990	386.75
1970	119.75	1991	392.35
1971	131.73	1992	399.07
1972	141.94	1993	410.63
1973	149.36	1994	424.91
1974	170.45	1995	439.72
1975	190.49	1996	445.58
1976	202.61	1997	454.99
1977	215.84	1998	
	459.40		
1978	235.78	1999	460.16
1979	257.20	2000	468.05
1980	277.60	2001	472.18
1981	302.25	2002	484.41
1982	320.13	2003	495.72
1983	330.82	2004	506.13
1984	341.06	2005	516.75
1985	346.12	2006	528.12
1986	347.33	2008	552.16
1987	353.35		

Source: U.S. ACE. Yearly average Cost Index for Utilities, in *Civil Works Construction Cost Index System Manual*, 110-2-1304, U.S. Army Corps of Engineers, Washington, p. 44, 2008. Available at http://www.nww.usace.army.mil/cost.

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22 Waste Treatment in the Inorganic Chemical Industry

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CONTENTS

22.1 INTRODUCTION

22.1.1 INDUSTRIAL WASTEWATER

All the water that is sent to the drain or is pooled together after being subjected to one process or the other in an industry is known as wastewater. It is usually classified into municipal wastewater and industrial wastewater. Industrial wastewaters are primarily from both small- and large-scale industries, which predominantly include manufacturing industries. The type of industry greatly influences the characteristics of industrial wastewater both in type and in varying amount; depending on contaminants concentrations, industrial wastewater can be classified further into strong, medium, or weak.[1] The discharge of industrial wastewater into the environment has manifold adverse effects on humans and aquatic species.

22.1.2 PROCESS WASTES

All manufacturing industries produce peculiar wastes from their production processes. The bulk of the wastes is conveyed to the wash waters that end up as wastewaters. The washing operations include washing of raw materials, the intermediate and final products, the plant (before and after production batch), and unsolicited rain storm that washes the exposed plant parts.

22.1.2.1 Inorganic Process Wastes

Inorganic chemical industries, metallurgical industries, and petroleum industries are major processing industries that generate volumes of inorganic process wastes. The inorganic process wastes are characteristically toxic and may be acidic or basic in nature, but do not pose the biological problems often associated with wastewaters. It, however, poses a high problem of disposal when it combines with organic wastes because of the likely reactions that may lead to the formation of more complex hazardous compounds.

22.1.2.2 Organic Process Wastes

The organic chemical industry, the food processing industry, the pulp and paper industry, the textile industry, and the petroleum industry are important industries that produce organic process wastes. Unlike inorganic process wastes, they contain dissolved and insoluble matter in the main wastewater stream; thus, they are more difficult to handle for disposal. They have its characteristic biological problems and spontaneous interaction with the surrounding environment, particularly, under high solar radiation.

22.1.3 GENERAL WASTEWATER TREATMENTS

Treatment of wastewater generated in most industries is often achieved in many steps depending on the volume, shape, and nature of constituents of the wastewater. A typical wastewater treatment plant combines water treatment unit operations and processes to achieve different levels of treatment. They include the following.

22.1.3.1 Preliminary Treatment

The objective of this treatment level is to reduce or eliminate nonfavorable wastewater characteristics that are likely to adversely affect the operation and efficiency of the processes and equipment of the wastewater plant. These processes include screening, comminution, flotation, flow equalization, septage handling, and odor control methods.[2] The targeted wastewater characteristics include large solids, rags, abrasive grit, odor, and organic loadings.[2]

22.1.3.2 Primary Treatment

This treatment process employs the use of physical operations such as screening and sedimentation to partially remove suspended solids and organic matter from the wastewater. This process provides the secondary treatment with wastewater that is partially free of solids, in order to facilitate further treatment. The effluent from the primary treatment contains primarily organic matter and is characterized by a relatively high biochemical oxygen demand (BOD).[2]

22.1.3.3 Secondary Treatment

The secondary treatment is linked to the primary treatment in a typical wastewater treatment plant. It is designed to remove soluble and colloidal organics as well as suspended solids that are not trapped in the primary treatment. The treatment processes employed in this section of the wastewater treatment plant include activated sludge, lagoon systems, and sedimentation.[2] The sludge generated as waste in this system is digested by microorganisms, mainly bacteria and protozoa.[3] In general, the system involves biological processes.

22.1.3.4 Advanced Treatment

In this treatment process, unit operations such as chemical coagulation, flocculation, and sedimentation followed by filtration, activated carbon, ion exchange, and reverse osmosis are employed to remove significant amounts of nitrogen, phosphorus, heavy metals, organic matters, bacteria, and viruses present in wastewater.[2] It is always the last process step in the wastewater treatment plant that finally renders the treated wastewater reusable and disposable into the environment without any adverse effect (Figure 22.1).

22.1.4 COMMON WASTEWATER TREATMENT PROCESSES

To meet the specified standard,[4] wastewaters are often subjected to a series of treatment processes before they are discharged into the environment, particularly, water bodies. The treatment processes include physical, chemical, and biological processes that may be applied singly or collectively. The collective application of the processes can be employed in a variety of systems classified as primary, secondary, and tertiary wastewater treatment, to achieve different levels of contaminants removal.[2]

22.1.4.1 Physical Treatment Processes

These are age-long processes that involve the application of physical forces to remove contaminants in wastewater. It includes the following.

22.1.4.1.1 Screening

The process involves the use of a screen to remove gross pollutants in the form of particles from a wastewater stream in order to prevent damages to downstream equipment and plant operation units. Common screening devices consist of parallel bars, rods, grating, wire mesh, and perforated plates with either circular or rectangular opening.[4] The screens are further categorized according to their size of openings; these include coarse (≥6 mm), fine (1.5–6 mm), very fine (0.2–1.5 mm), and microscreens (0.001–0.3 mm).[5]

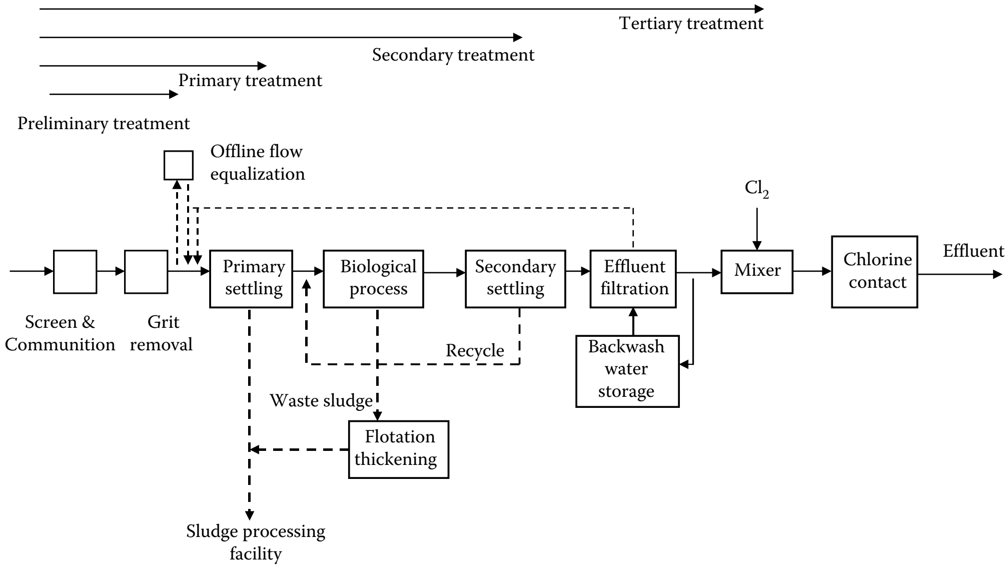

FIGURE 22.1 Flow diagram showing treatment levels in a wastewater treatment plant.

22.1.4.1.2 Sedimentation

This is another widely used process in the physical treatment process of wastewater; it simply involves gravitational settling of heavy particles that are suspended in a mixture; it has wide application within the treatment plant, particularly, in the primary settling basin, where grits, particulate matter, and biological and chemical flocs are removed, in the activated sludge settling basin. Three main designs of the sedimentation or settling tank are horizontal flow, solid contacts, and inclined surface.[3]

22.1.4.1.3 Communition

The communitors are generally placed between the grit chamber and the primary settling tank in the wastewater treatment plant; they are used to pulverize large floating materials in the wastewater. This process helps reduce odors and flies. A communitor may have rotating or oscillating cutters, a barminutor (a special type of communitor), and a bar screen.[5]

22.1.4.1.4 Flotation

This is a unit operation process where air bubbles, as gas, are used to remove solid or liquid particles from the liquid wastewater. The air bubbles are often trapped in the morphology of the suspended particles and as a result of buoyant forces, the particles move up and float on the surface where they are skimmed out. The common flotation methods include dissolved air, air flotation, vacuum flotation, and chemical additives.[3]

22.1.4.2 Chemical Treatment Process

This treatment process involves the use of chemical compounds to initiate a chemical reaction in the wastewater stream, which ends up neutralizing negatively charged colloids and thus, causing changes that would alter the nature of the wastewater, particularly to conform to the standard of wastewater discharge.[4] The treatment process possesses an inherent disadvantage, especially net increase in the dissolved constituents of the wastewater, which can hinder reuse of the wastewater.[2] Common chemical treatment processes are discussed below.

22.1.4.2.1 Chemical Precipitation

Chemical precipitation precedes the sedimentation process in a wastewater treatment plant and involves flocculation of finely divided solids into more readily settleable flocs that can be easily removed. The quantity of chemical as well as the dosing processes determines the degree of clarification. The coagulants commonly used include alum, $Al_2(SO_4)_3 \cdot 14H_2O$; ferric chloride, $FeCl_3 \cdot 6H_2O$; ferric sulfate, $Fe_2(SO_4)_3$; ferrous sulfate, $FeSO_4 \cdot 7H_2O$; lime, $Ca(OH)_2$; and sometimes organic polyelectrolytes.[6] This process facilitates greater removal efficiency but results in a larger mass of primary sludge, which is often more difficult to thicken and dewater; also, it requires high operation cost expertise.[5,7–11]

22.1.4.2.2 Adsorption

This process involves the use of a solid interface like activated carbon to remove a portion of the dissolved organic matter and heavy metals in wastewater. The activated carbons are produced by heating organic matter such as bone, wood, and agricultural wastes such as coconut shell[12,13] and *Chrysophyllum albidum* seed shell[14] to a high temperature followed by activation using oxidation process at a high temperature. They contain pores that provide large internal surface areas on which dissolved organic matter is adsorbed. The common types of activated carbon are granular activated carbon (GAC) and powdered activated carbon (PAC) with a diameter of 0.1 m and 2 mm, respectively.[3] Wastewater is passed through a fixed-bed column packed with GAC from the top and withdrawn from the bottom as treated water while the GAC remain in position. Backwashing and surface washing are applied to limit head loss buildup, a common problem associated with packed bed columns.[2] The GAC could be regenerated. PAC is usually added directly to the wastewater in a contacting basin for a certain length of time, the mixture is allowed to settle to the bottom of the tank, and the sludge formed is removed by filtration through filters or centrifugation. Inability to regenerate PAC is still a factor militating its usage.

22.1.4.2.3 Disinfection

Wastewater often harbors a number of human eccentric organisms that are associated with waterborne treatments; this must be given proper attention in wastewater treatment. Disinfection facilitates the selective destruction of disease-causing microorganisms. It involves the following mechanisms: damage of the cell wall of microorganisms, thus altering cells' permeability; alteration of the colloidal nature of the protoplasm, and inhibition of enzyme activity. Contact time, concentration and types of chemical agent, intensity and nature of physical agent, temperature, the number of microorganisms, and the nature of suspending liquid are some of the factors to be considered when applying a disinfectant.[15] Common means of disinfecting wastewater include the use of physical agents, chemical agents, mechanical means, and radiation.[16]

22.1.4.2.4 Dechlorination

Chemical treatment of wastewater leaves total, combined, or free chlorine in the "treated" wastewater, thus rendering it totally unsafe for reuse or even for discharge to receiving water bodies. Presence of these chlorine compounds in water is toxic in nature and can cause long-term adverse effect on humans and aquatic lives, hence the need to dechlorinate. This process can be achieved by the use of activated carbon or by the addition of reducing agents such as SO_2, Na_2SO_3, or $Na_2S_2O_5$.[3]

22.1.4.3 Biological Treatment Process

The biological treatment process involves the use of microorganisms such as bacteria and fungi to convert finely divided colloidal and dissolved carbonaceous organic matter in wastewater into various gases and into cell tissues that are then removed from sedimentation tanks as flocculent settleable organic and inorganic solids. This process often complements both physical and chemical processes and it is classified as follows.

22.1.4.3.1 Activated Sludge Process

This process is a continuous flow aerobic system involving the mixing of clarified wastewater with an active mass of microorganisms, mainly bacteria and fungi, which eventually aerobically degrade organic matter into CO_2, H_2O, and other by-products.[17–21] It is a system that requires series of tanks and efficient operation of the sludge plans.[3]

22.1.4.3.2 Aerated Lagoons Process

This process is similar to the activated sludge process; however, it requires a large surface area to cause more temperature effects than that experience in the activated sludge process. The aeration process in this system supplies oxygen to the influent wastewater and the turbulent generated keeps the contents of the basin in suspension. The suspended solids are then removed in a settling tank where the wastewater may further be treated before discharge.[2,3]

22.1.4.3.3 Others

Due to the focus of this work, other biological processes will also be mentioned. They include trickling filters, coating biological contactors, pond stabilization, anaerobic digestion, and biological nutrient removal.[2,3,5]

22.1.5 WASTEWATER CHARACTERIZATION

Wastewaters generated from manufacturing plants that produce or use inorganic chemicals vary considerably, depending on raw materials, type of process, and the end product, among others. A screening program is often conducted to determine the presence, concentration, and toxicity of metal ions in such wastewaters. The minimum detection limits for the toxic metals are presented in Table 22.1.

TABLE 22.1
Minimum Detection Limits for Some Toxic Metals

Pollutant	Concentration (μg/L)
Antimony	10
Arsenic	10
Beryllium	15
Cadmium	1
Chromium	25
Copper	20
Lead	10
Mercury	0.5
Nickel	25
Selenium	10
Silver	15
Thallium	2
Zinc	1

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

22.1.6 EFFLUENT DISPOSAL

Treated wastewater effluents are often discharged into the biosphere where water bodies are the largest receivers. This practice requires sound engineering practices in order not to cause any adverse effect on the receiving environment; hence, many scientific and engineering factors are considered to facilitate proper mixing and disposal of the effluent.[15] Environmental standards, developed by various environmental agencies, are designed to ensure that the impacts of treated wastewater discharged into receiving water bodies are acceptable. Table 22.2 lists the limitations set by some environmental agencies.

22.2 INORGANIC CHEMICAL INDUSTRIES

Most inorganic chemical industries are aggregates of small facilities where over 300 different chemicals are being produced.[22] These chemicals are often of mineral origin, mainly employed at some stages in the manufacture of varieties of chemical and nonchemical products; they are not present in the final products.[22] Products such as acids, alkalis, salts, oxidizing agents, industrial gases, and halogens are used as basic chemicals for industrial processes, whereas pigments, dry colors, and alkali metals are mostly employed in manufacturing products.

22.2.1 CLASSIFICATION OF INORGANIC CHEMICAL INDUSTRIES

The inorganic chemical industries classification is based on the Standard Industrial Classification (SIC) that assigns the code 281 to industrial inorganic chemicals.[23] SIC is a statistical classification standard used for all U.S.-based establishments of Federal economic statistics.

22.2.1.1 General Classification of Inorganic Chemical Industries

The SIC classified the chemicals with codes as stated in Table 22.3 having considered the effluent limitations and pretreatment standard within the inorganic chemicals manufacturing point source.

TABLE 22.2
U.S. EPA, NPDES, and ECEDR for Discharges from Wastewater Treatment Plants

Parameter	NPDES[a] 30-Day Average Concentration	NPDES[a] 7-Day Average Concentration	NPDES[a] Percentage of Removal[c]	ECEDRWD[b] Concentration (mg/L)	Percentage of Removal[c]
BOD_5	30 mg/L	45 mg/L	85	25	70–90
TSS	30 mg/L	45 mg/L	85	35–60	70–90
pH	6–9	—	—	—	—
COD	—	—	—	125	75
Total nitrogen[d]	—	—	—	10–15	70–80
Total phosphorus[d]	—	—	—	1–2	80

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] National Pollutant Discharge Elimination System for secondary wastewater treatment plants.

[b] European Community Environmental Directive Requirements for wastewater discharges.

[c] Removal in relation to influent load.

[d] Limited to sensitivity areas subject to eutrophication.

The SIC 281 category does not include some integrated firms that manufacture other types of chemicals within the same site. Other manufacturing facilities that produce and use inorganic chemicals in their process within the facilities used in producing the SIC 281 group are stated in Table 22.4.

Top U.S. companies with inorganic chemical manufacturing operations are listed in Table 22.5.

22.2.1.2 Subcategory Classification

As a result of variation shown in toxicity, the evaluation of technologies applicable for discharge control, and treatment by some compounds within the industrial chemicals, the SIC 281 groups are further subdivided into 11 subcategories.[23] They are aluminum fluoride, chlor-alkali, chrome pigments, copper sulfate, hydrofluoric acid, hydrogen cyanide, nickel sulfate, sodium bisulfate, sodium

TABLE 22.3
General Classification of SIC

Code	Name	Example
SIC 2812	Alkalis and chlorine	Chlorine, caustic soda, soda, ash, potassium, carbonate, hydrogen, helium, oxygen, nitrogen, chrome pigments
SIC 2813	Industrial gas	
SIC 2816	Inorganic pigments	
SIC 2819	Industrial inorganic chemicals not classified elsewhere	

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

TABLE 22.4
SIC Category of Manufacturing Plants within SIC 281 Facilities

Code	Name
SIC 286	Organic chemical facilities
SIC 287	Fertilizer plant
SIC 26	Paper and pulp mills
SIC 31	Iron and steel mills

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

dichromate, sodium hydrosulfite, and titanium dioxide. Although these subcategories are further subdivided into 44 subcategories,[23] this work will focus on the main 11 subdivisions stated above.

22.3 INDUSTRIAL PROCESSES, WASTEWATER GENERATION, AND TREATMENT IN INORGANIC CHEMICALS PRODUCTION

This section describes the major industrial processes of individual inorganic chemicals under the 11 subcategories and the related wastewater generated. It contains the sources of wastewater and typical treatment processes.

22.3.1 ALUMINUM FLUORIDE

22.3.1.1 Description and Production Process

Aluminum fluoride is produced when partially dehydrated alumina hydrate reacts with hydrofluoric acids gas. The solid aluminum fluoride produced is cooled with noncontact cooling water prior to further processing, while the gases from the reactor are scrubbed with water to remove unreacted hydrofluoric acid from the gas stream. Aluminum fluoride is mainly used in the production of

TABLE 22.5
Top U.S. Companies With Inorganic Chemical Manufacturing Operations

Rank	Company	City	State
1	Dow Chemical Co.	Midland	Michigan
2	Hanson Industrial Co.	Iselin	New Jersey
3	W.R. Grace and Co.	Boca Raton	Florida
4	Occidental Chemical	Dallas	Texas
5	BOC Group Inc.	Murray Hill	New Jersey
6	FMC Corp.	Chicago	Illinois
7	Eastman Kodak Co.	Kingsport	Tennessee
8	Air Products and Chemical Inc.	Allentown	Pennsylvania
9	ARCO Chemical Co.	Newtown Square	Pennsylvania
10	Ethyl Corp.	Richmond	Virginia

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

cryolite and as flux, particularly in the metallurgy, ceramic, and brazing industries for welding, glazing, and fabrication, respectively.

22.3.1.2 Wastewater Characterization

Generally, water used in the aluminum fluoride industry is employed as noncontact cooling water to cool the products coming out of the reactor. Water is equally used in the scrubber located in the plant to scrub the reacted gases before they are vented to the atmosphere. Wastewater resulting from the scrubbing process is often loaded with hydrofluoric acid, aluminum fluoride, aluminum oxide, and sulfuric acid. Wastewater is also generated in the plant housekeeping practices, which cover floor and equipment washings.

A typical plant production of aluminum fluoride indicating water use and wastewater generation is shown in the flow diagram (Figure 22.2).

Results of waste load found in verification sampling of unit product of aluminum fluoride are given in Table 22.6.

22.3.1.3 Wastewater Treatment Process

Copper, arsenic, chromium, and selenium are the major toxic pollutants associated with the production of aluminum fluoride. Selenium, on the other hand, is not regarded as process-related product because of its presence in the raw material. These pollutants are generally reduced by neutralization with lime followed by settling process in a series of settling ponds. The content of the last pond is given a final pH adjustment before being discharged into the environment or recycled to the plant as may be required (Figure 22.3).

Some innovating treatment technologies may be introduced in the treatment of wastewater generated in the aluminum fluoride industry to make its effluent safer. The ion exchange process can be applied to the clarified solution to remove copper and chromium. At a very low concentration, these two pollutants can be removed by xanthate precipitation.[24] A combination of lime and ferric sulfate coagulation will effectively reduce arsenic concentration in the wastewater.

22.3.2 CHLOR-ALKALI

22.3.2.1 Description and Production Process

Chlorine, hydrogen, caustic soda, and sometimes caustic potash are coproducts of the electrolysis of saturated aqueous solutions of sodium chloride called brine. The overall chemical reaction is given as

$$2\mathrm{NaCl} + 2\mathrm{H_2O} \rightarrow 2\mathrm{NaOH} + \mathrm{Cl_2} + \mathrm{H_2}. \tag{22.1}$$

The pulp and paper industry, the plastic industry, and water treatment plants are the major industries using chlorine in large quantity. Chlorine is also an essential raw material in the manufacture of vinyl chloride, chlorinated ethers, and other inorganic and organic chemicals. Chlorine is commonly produced in electrolytic cells where energy in the form of direct current is supplied to drive the reaction. The mercury cell process, the diaphragm cell process, and the membrane cell process are the three types of electrolytic process used for the manufacture of chlorine, caustic soda, and hydrogen from brine; however, mercury and diaphragm cells have large industrial application. Each electrolytic cell consists of two electrodes, anode and cathode, in contact with the electrolyte (brine solution). The method employed to separate and prevent the mixing of the chlorine gas and sodium hydroxide is what distinguishes one cell from another.[25]

22.3.2.1.1 Mercury Cell Process

The electrolyzer and the decomposer are the two main sections of a typical mercury cell. The electrolyzer is slightly inclined steel trough through which a thin layer of mercury flows over the

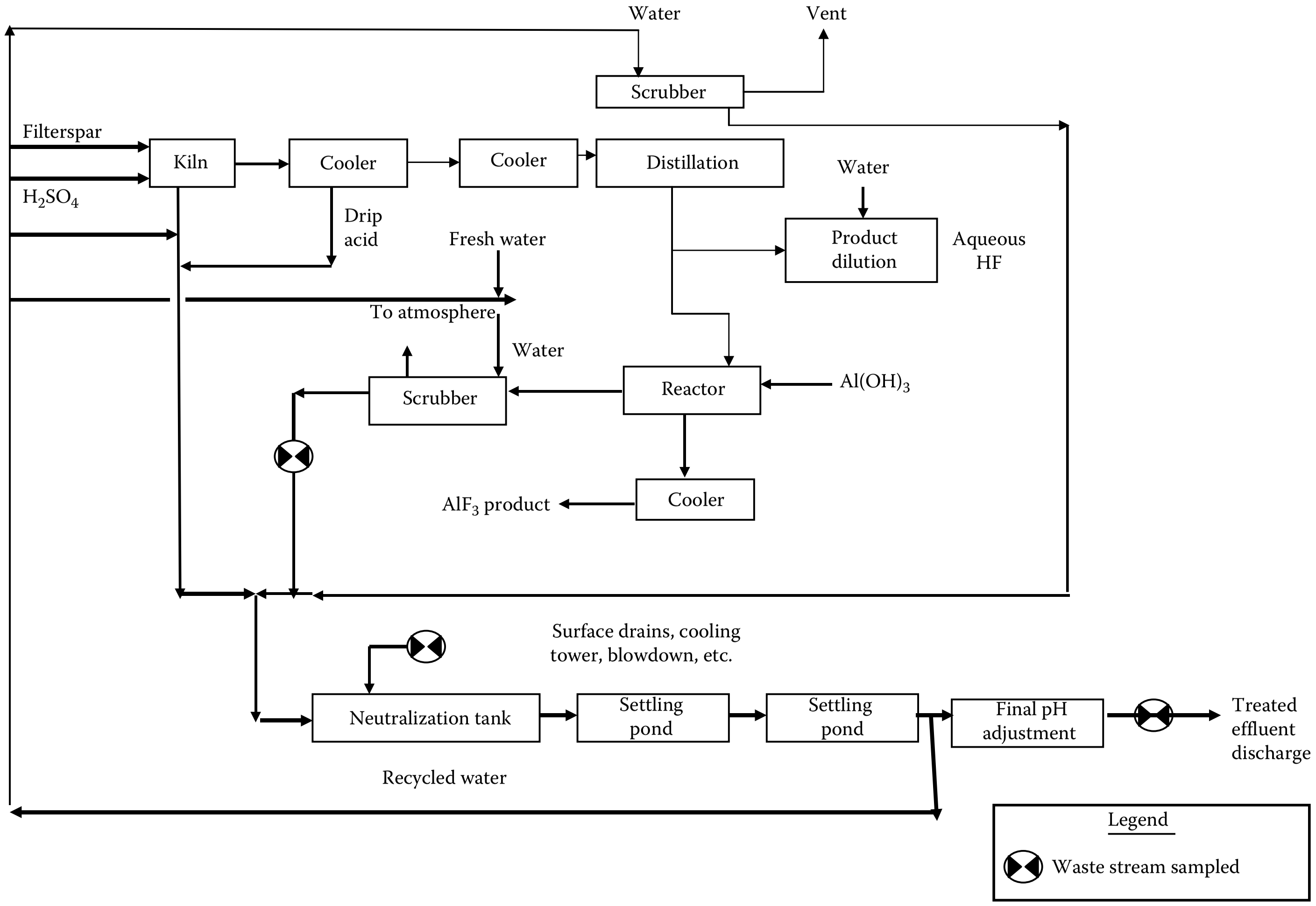

FIGURE 22.2 A typical plant production of aluminum fluoride indicating water use and wastewater generation.

TABLE 22.6
Summary of Waste Loadings Found in Aluminum Fluoride Verification Data

Pollutions	Maximum Waste Loadings (kg/Mg)
Antimony	0.000005
Arsenic	0.002
Beryllium	0.000002
Cadmium	0.0002
Chromium	0.005
Copper	0.001
Lead	0.0002
Nickel	0.003
Mercury	0.00005
Selenium	0.002
Zinc	0.002

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

Note: 1 kg/Mg = 1 kg/10^6 g.

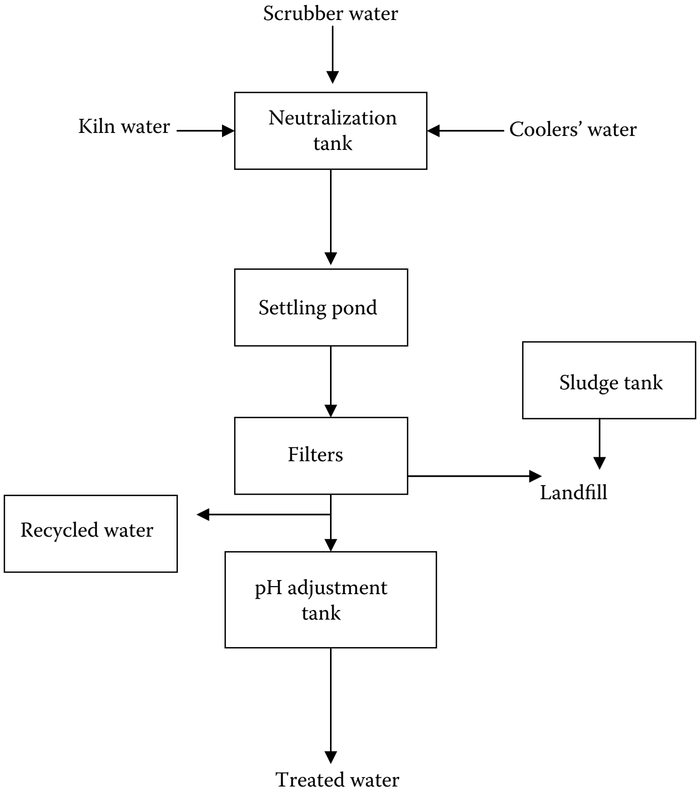

FIGURE 22.3 General wastewater treatment process flow diagram at an aluminum fluoride plant.

bottom to form the cathode of the cell. The saturated brine flows through the troughs above the mercury and parallel graphite or recently developed titanium-coated ruthenium. Titanium oxides form the anode on top of the brine.[25] Electric energy flowing through the cell decomposes the brine to chlorine at the anode where it moves upward through gas extraction slits in the cell covers. The sodium ions are absorbed by the cathode to form an amalgam, a mixture of sodium and mercury, which is processed in decomposer cells to generate sodium hydroxide, hydrogen, and reusable mercury.

$$2NaCl_{(aq)} + 2Hg \rightarrow Cl_{2(aq)} + 2Na(Hg), \qquad (22.2)$$

$$2Na(Hg) + 2H_2O \rightarrow 2NaOH + H_2 + 2Hg. \qquad (22.3)$$

In the decomposer, deionized water reacts with the amalgam, which becomes the anode to a short-circuited cathode. The caustic soda produced is stored or evaporated, if higher concentration is required. The hydrogen gas is cooled by refrigeration to remove water vapor and traces of mercury. Some of these techniques are employed in different facilities to maximize the production of chlorine, minimize the consumption of NaCl, and also to prevent the buildup of impurities such as sulfate in the brine.[26] The production of pure chlorine gas and pure 50% sodium hydroxide with no need for further concentration of the dilute solution is the advantage that the mercury cell possesses over other cells. However, the cell consumes more energy and requires a very pure brine solution with least metal contaminants and above all requires more concern about mercury releases into the environment.[4]

22.3.2.1.2 Diaphragm Cell Process

The diaphragm cell consists of multiple electrolytic cells having the anode plates and cathodes mounted vertically and parallel to each other. The cathodes, often flat hollow perforated steel structures that are covered with asbestos fibers, serve as the diaphragm that prevents the mixing of hydrogen and chlorine and back diffusion of hydroxide (OH^-) ions from the cathode to the anode. Brine fed into the cell is decomposed to approximately half of its original concentration to produce chlorine gas at the anode and hydrogen and sodium hydroxide at the cathode.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2. \qquad (22.4)$$

The chlorine gas is drawn off from above the anodes while the hydrogen from the top of the cathode is cooled to remove water and other impurities before being subjected to further use.[26] The concentrated sodium hydroxide is settled and stored. The diaphragm cell process does not require a brine purge to prevent sulfate buildup or treatment to remove entrained chlorine gas that is peculiar to the mercury cell.[26] Consumption of relatively low electricity and ability to process less pure brine are the advantages this process possesses over the mercury cell process. However, the chlorine gas from the diaphragm process is always contaminated with oxygen, water, salt, and sodium hydroxide, while the caustic soda, equally produced, contains chlorides and they must be processed further to bring them to a usable standard.[27]

22.3.2.1.3 Membrane Cell Process

This type of electrolytic cell consists of anodes and cathodes that are separated by a water impermeable ion-conducting membrane. Brine is fed through the anode where chlorine gas is generated and sodium hydroxide solution collects at the cathode. Chloride ions are prevented from migrating from the anode compartment to the cathode compartment by the membrane and this, consequently, leads to the production of sodium hydroxide, free of contaminants like salts. The condition of the membrane during operation requires more care. They must remain stable while being exposed to chlorine and strong caustic solution on either side; they must allow, also, the transport of sodium ions and not chloride ions.

The membrane cell produces a very pure caustic soda solution and consumes less energy unlike the mercury and diaphragm processes.[24] Also, it poses less pollution risk to the environment unlike

TABLE 22.7
Main Characteristics of the Different Electrolysis Processes

Component	Mercury Cell	Diaphragm Cell	Membrane Cell
Cathode	Mercury flouring over steel	Steel or steel coated with activated nickel	Steel or nickel with a nickel-based catalytic coating
Diaphragm/membrane	None	Asbestos or polymer modified asbestos	Ion exchange membrane
Anode	Titanium with RuO_2 or TiO_2 coating	Titanium with RuO_2 or TiO_2 coating	Titanium with RuO_2 or TiO_2 coating
Cathode product	Sodium amalgam	10–12% NaOH with 15–17% NaCl and H_2	30–33% NaOH and H_2
Decomposer/evaporator product	50% NaOH and H_2 from decomposer	50% NaOH with 1% NaCl and solid salt from evaporation	50% NaOH with very little salt
Electricity consumption	3300 kWh per ton Cl_2		

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

the presence of mercury and asbestos pollutions in the case of mercury and diaphragm cells, respectively. However, like the diaphragm cell process, the chlorine gas produced must be further processed to remove oxygen and water vapor, while the caustic soda produced must be evaporated to increase its concentration. The process also requires very high-purity brine that invariably makes this process very expensive[27] (Table 22.7).

22.3.2.2 Wastewater Characterization

General water use in this industry is for noncontact cooling, cell washings, tail gas scrubbing, equipment maintenance, and general area washdown. Wastewater streams from mercury cell facilities mainly come from the chlorine drying process, brine purge, floor sump, and cell. The tail gas is also water scrubbed; although often reused as brine, it contributes to the wastewater stream. The wastewater stream from the diaphragm cell facilities emanates from the borometric condenser during caustic soda evaporation, chlorine drying, and from purification of the salt recovered from the evaporators[28] (Table 22.8).

TABLE 22.8
Summary of Contents of Waste Contents of the Three Cells Used in Chlor-Alkali Industry

Waste	Source	Content
Brine mud	Cell	Mercury, other solids
Cell room waste	Leak, spill, cell wash water	Asbestos fibers, dissolved chlorine, dissolved hydrogen, sodium chloride lead, chlorinated organic compound
Chlorine condensate	Graphite anodes cooler	Lead, chlorinated organic compound, such as methylene chloride and hexachlorinated benzenes
Sulfuric acid	Scrubber	Mercury, asbestos fibers, chlorinated hydrocarbons
Tail gas scrubber liquid	Scrubber	Hypochlorite
Caustic filter washdown	Cell	Mercury or asbestos fibers, dissolved salts

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

This wastewater stream contains lead (Pb) salts and chlorinated hydrocarbons generated from corrosion of the anodes as well as asbestos particles generated as a result of degradation of the diaphragm with use. Wastewater is also generated from the scrubber where the chlorine is wet scrubbed and from the ion exchange resin used to purify the brine solution. These wash water often contains dilute hydrochloric acid with small amounts of dissolved calcium magnesium and aluminum chloride. Like in other cells, the scrubber water also contributes to the wastewater stream.

Flow diagrams of a typical plant production of chlor-alkali indicating water use and wastewater generation are given in Figure 22.4.

Results of raw waste load found in verification sampling of unit product of chlor-alkali are given in Table 22.9.

22.3.2.3 Wastewater Treatment Process

Toxic pollutants found in the mercury cell wastewater stream include mercury and some heavy metals like chromium and others stated in Table 22.8, some of them are corrosion products of reactions between chlorine and the plant materials of construction. Virtually, most of these pollutants are generally removed by sulfide precipitation followed by settling or filtration. Prior to treatment, sodium hydrosulfide is used to precipitate mercury sulfide, which is removed through filtration process in the wastewater stream. The tail gas scrubber water is often recycled as brine make-up water. Reduction, adsorption on activated carbon, ion exchange, and some chemical treatments are some of the processes employed in the treatment of wastewater in this cell. Sodium salts such as sodium bisulfite, sodium hydrosulfite, sodium sulfide, and sodium borohydride are also employed in the treatment of the wastewater in this cell[28] (Figure 22.5).

Prominent among toxic pollutants found in the diaphragm cell are arsenic, chromium, copper, lead, nickel, and zinc, as shown in a typical verification sampling in Table 22.8. Chlorinated hydrocarbons are generated from corrosion of the anodes and reaction of the chlorine with process-exposed rubber. Most of the metals are removed by sulfide or carbon precipitation, while the asbestos is treated with a chemical and the resulting flocs are removed by filtration. The spent caustic solution is also neutralized using a chemical before being discharged. The chlorinated hydrocarbons are removed by the use of vacuum or a steam stripper and sometimes carbon adsorption (Figure 22.6).

The wastewater generated in the membrane cell and other process wastewaters in the cell are generally treated by neutralization.[28] Other pollutants similar to those in mercury and diaphragm cells are treated in the same process stated above. Ion exchange and xanthate precipitation methods can be applied in this process to remove the metal pollutants, while incineration can be applied to eliminate some of the hydrocarbons. The use of modified diaphragms that resist corrosion and degradation will help in reducing the amount of lead, asbestos, and chlorinated hydrocarbon in the wastewater stream from the chlor-alkali industry.[28]

22.3.3 CHROME PIGMENTS

22.3.3.1 Description and Production Process

Pigments are commercially classified according to their colors, but they are scientifically classified according to the inorganic compounds coming together as the base elements. A variety of chrome pigments are available in commercial quantities and they include chrome yellow, chrome orange, molybdate chrome orange, anhydrous and hydrous chromium oxide, zinc yellow, and iron blues, which are manufactured in different plants or the same plant within a factory. Chromium forms the base element for these types of chrome pigments. They are widely used in the production of paints, printing ink, floor covering products, paper, ceramics, cements, and asphalt roofing.

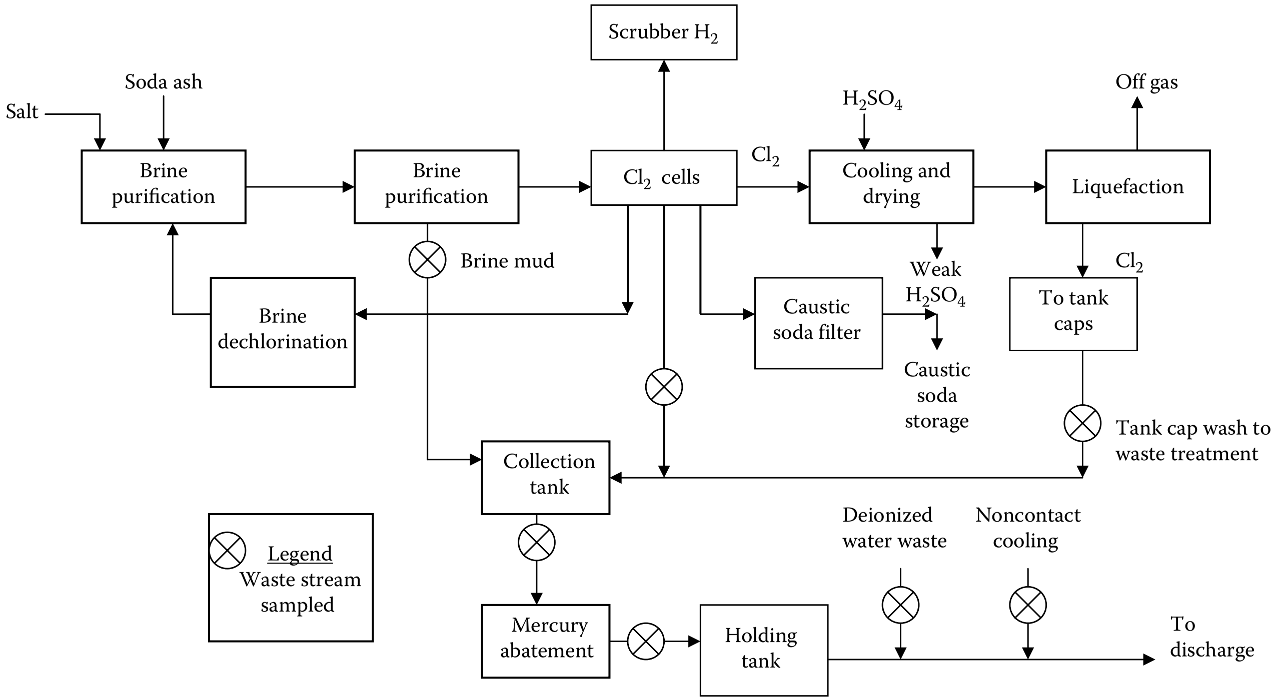

FIGURE 22.4 Flow diagram of a typical plant production of chlor-alkali indicating water use and wastewater generation.

TABLE 22.9

Summary of Raw Waste Loadings Found in Verification Sampling of Unit Product of Chlor-Alkali (Mercury Cell and Diaphragm Cell Processes)

	Maximum Raw Waste Loadings (10^{-3} kg/Mg)	
Pollutant	**Mercury Cell**	**Diaphragm Cell**
Antimony	0.77[a]	—
Arsenic	1.1	2.1
Cadmium	0.23	0.0061
Chromium	0.4	4.6
Copper	0.6	1.1
Lead	0.7	1.5
Nickel	0.7	1.8
Mercury	48	0.014
Thallium	5.4	BDL
Selenium	—	BDL
Beryllium	—	BDL
Silver	0.83	0.0007
Zinc	10	2.1

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 0.77 (10^{-3} kg/Mg) = 0.00077 Kg/10^6 g.

BDL, below detection limit.

22.3.3.1.1 Chrome Oxide

Chrome oxide is produced by mixing sodium dichromate and sulfur with water and the resultant mixture is heated in a kiln. The kiln products are slurred with water, filtered, washed, dried, ground, screened, and packaged.

22.3.3.1.2 Chrome Yellow

Chrome yellow pigment is made up of lead chromate, and it is formed as a precipitate of the reaction involving lead nitrate, caustic soda, and sodium dichromate. The precipitate is filtered, treated with

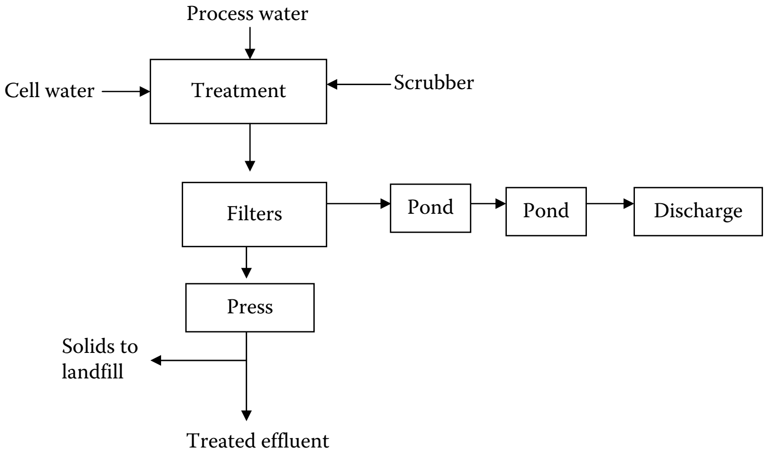

FIGURE 22.5 General wastewater treatment process flow diagram at a mercury cell plant for the production of chlor-alkali.

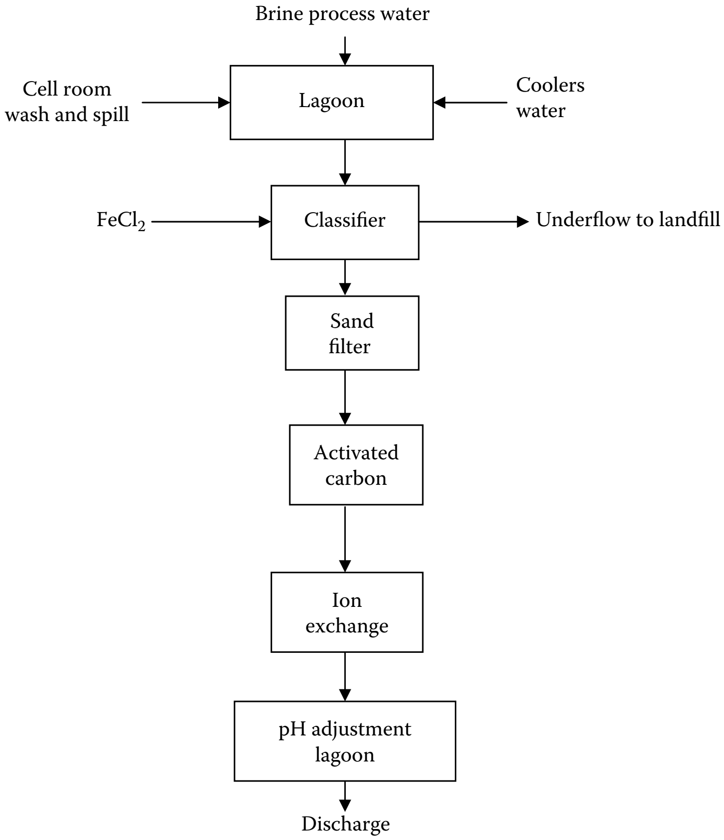

FIGURE 22.6 General wastewater treatment process flow diagram at a diaphragm cell plant for production of chlor-alkali.

chemicals to develop the desired pigment properties, dried, milled, and packaged. Chrome orange is produced in the same process and shares many characteristics with chrome yellow.

22.3.3.1.3 Chrome Green

Chrome green is produced by mechanically mixing chrome yellow and iron blue pigments in water. An iron blue, $[Fe(NH_4)\ (FeCN_6)]$, is an oxidized precipitate product of the reaction between an aqueous solution of iron sulfate and ammonium sulfate with sodium hexacyanoferrate.

22.3.3.1.4 Molybdenum Orange

This type of pigment is the precipitate formed when molybdic oxide is dissolved in aqueous sodium hydroxide with the addition of sodium chromate. The resulting mixture is reacted with a solution of lead nitrate. The precipitate formed is further processed through filtration, washing, drying, milling, and packaging.

22.3.3.1.5 Zinc Yellow

The reaction of zinc oxide, hydrochloric acid, sodium dichromate, and potassium chloride produced zinc yellow as a precipitate, which is a complex compound of zinc, potassium, and chromium. The complex compound is further subjected to filtration, washing, drying, milling, and packaging for use.

22.3.3.2 Wastewater Characterization

Water is used in the chrome pigment industry mainly to cool most of the equipment such as heat exchangers, generate steam in the boilers, make slurry of raw materials, scrub the reactor vent gases, and wash the precipitated products. Wastewater generated as a result of water use varies in quantity of pollutant, which is directly related to the raw materials use. Generally, these wastewaters contain dissolved chromium and pigment particles. Wastewaters emanating from the chrome yellow and chrome orange facilities often contain additional sodium and lead salts. A chrome oxide plant uses more volume of water because of the additional scrubber; the process water contains sodium sulfate and sometimes sodium borate and boric acid, particularly, when boric acid is one of the essential raw materials in the preparation of hydrated chromic oxide. Sodium salts and lead salts similar to those present in the chrome oxide plant wastewater are found in wastewater emanating from the molybdenum orange facility. In addition, the wastewater includes chromium hydroxide and silica. Wastewater from the zinc yellow plant contains soluble zinc salts, hydrochloric acid, sodium chloride, and potassium chloride. In the chrome green process plant, the wastewater generated contains sodium nitrate, sodium chloride, ammonium sulfate, ferrous sulfate, sulfuric acid, and iron blue pigment particulates, when iron blue is one of the essential raw materials.

Results of raw waste load found in verification sampling of a chrome pigment plant are given in Table 22.10.

22.3.3.3 Wastewater Treatment Process

In addition to the heavy metals stated in Table 22.10, ferro- and ferricyanide are also part of the pollutants in the wastewater generated in a chrome pigment plant. These wastes are generally combined and treated through reduction, precipitation, equalization, and neutralization to be followed by clarification and filtration processes. Most of the heavy metals are precipitated using lime or caustic soda at specific pH. Chromium is reduced by SO_2 to a trivalent form, wherein it is precipitated as chromium hydroxide at specific pH. Sodium bisulfide is also employed to precipitate some of the metals at a low pH. The treated water is recycled for plant use while the sludge is sent to landfills (Figure 22.7).

Some other types of treatment processes can be employed in the chrome pigment industry in order to achieve safer industrial practices in terms of pollution. Processes such as ion exchange, biological oxidation, and use of glass for filtration before settling have potential application in this industry.

TABLE 22.10
Summary of Raw Waste Loadings Found in Verification Sampling of Chrome Pigment

Pollutants	Maximum Raw Waste Loadings (kg/Mg)
Antimony	1.5
Cadmium	0.15
Chromium	24
Copper	1.4
Lead	6.8
Nickel	0.03
Zinc	13
Cyanide	0.84
Mercury	0.0072

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

Note: 1 kg/Mg = 1 kg/10^6 g.

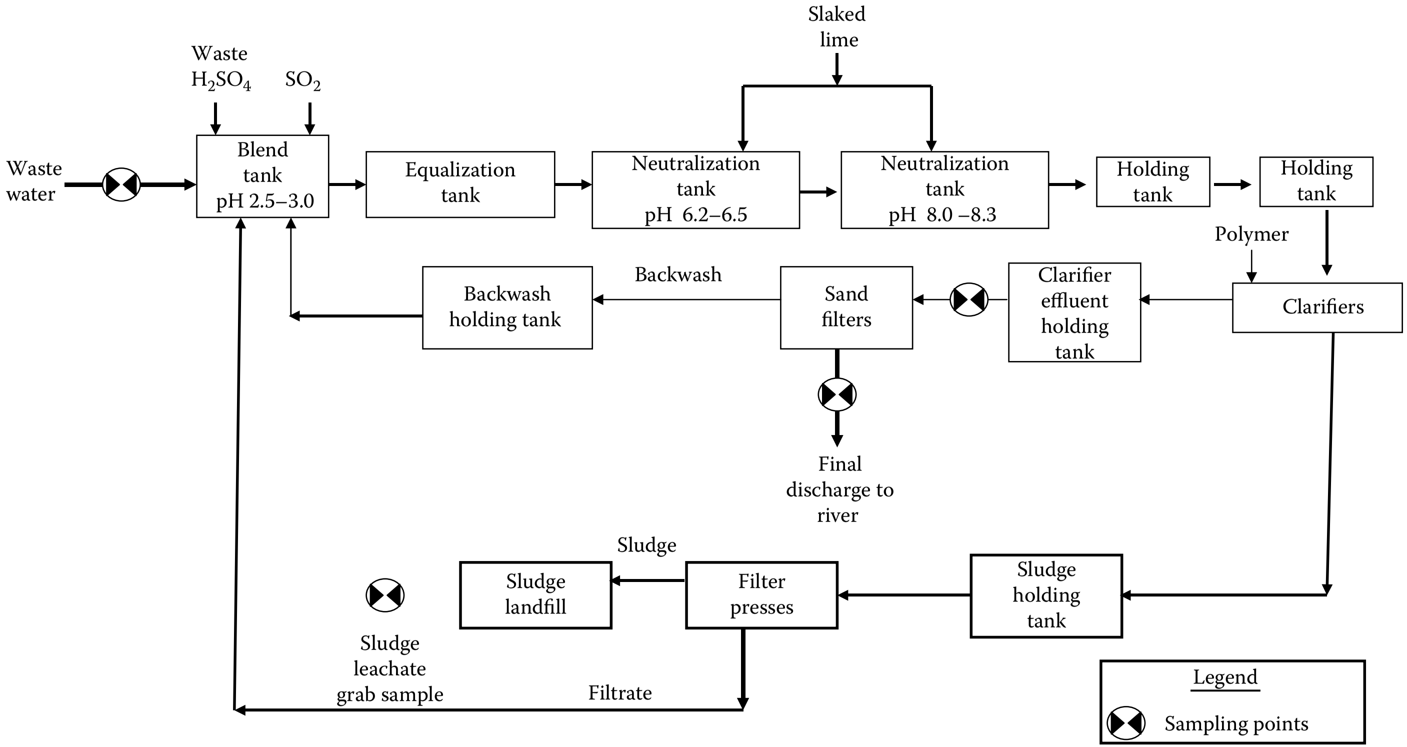

FIGURE 22.7 General wastewater treatment process flow diagram at a typical chrome pigment plant.

22.3.4 Copper Sulfate

22.3.4.1 Description and Production Process

Copper sulfate can be described as a by-product of copper refining that is obtained by crystallization of the weak liquor. The copper sulfate precipitate formed is centrifuged, dried, screened, and finally packaged in bags and drum. However, it is produced in some chemical industries by reacting copper shot with sulfuric acid, air, and water. It is widely used as an insecticide, additive nutrients (for soils that are deficient in copper), copper electroplating, wood preservation, and in petroleum refining.

22.3.4.2 Wastewater Characterization

Water use in copper sulfate plants is mainly used as contact water, noncontact cooling water, washdowns, and as wash water, where solid copper sulfate product is required. Noncontact water is generated as steam condensate from the evaporators and is used to cool the crystallizers. Contact wastewater comes mainly from washdowns, spills, and leaks. Both types of wastewater contain relatively small quantities of copper sulfides and other heavy metals.

A typical plant production of copper sulfate indicating water use and wastewater generation is shown in the flow diagram (Figure 22.8).

Results of raw waste load found in verification sampling for a copper sulfate plant are given in Table 22.11.

22.3.4.3 Wastewater Treatment Process

Prominent among the heavy metals found in the wastewater generated in the copper sulfate industry are copper, arsenic, cadmium, nickel, antimony, lead, chromium, and zinc (Table 22.11). They are traced to the copper and acids sources used as raw materials. These pollutants are generally removed by precipitation, clarification, gravity separation, centrifugation, and filtration. Alkaline precipitation at pH values between 7 and 10 can eradicate copper, nickel, cadmium, and zinc in the wastewater, while the quantity of arsenic can be reduced through the same process at a higher pH value.

Wastewater treatment in the copper sulfate industry can further be improved, particularly the removal of the toxic metals, through sulfide precipitation, ion exchange, and xanthate processes. Addition of ferric chloride alongside alkaline precipitation can improve the removal of arsenic in the wastewater.

22.3.5 Hydrofluoric Acid

22.3.5.1 Description and Production Process

Hydrofluoric acid is produced from fluorspar (CaF_2) and sulfuric acid. These raw materials are continuously fed in an externally fired kiln to produce calcium sulfate and hydrogen fluoride gas. The gas, which is a high boiling compound called drip acid, is precooled to a condensate consisting of primarily of fluorosulfonic and unreacted sulfuric acids. The hydrogen fluoride is further condensed in the refrigeration unit of the plant and may be further diluted to remove the residual impurities; the anhydrous form of the gas is stored in tanks. The hydrofluoric acid content of the waste gas is often scrubbed with water; at the refrigeration unit, it is scrubbed with sulfuric acid and then recycled to the plant.

Hydrofluoric acid is an important refrigerant and it is used as a bulking agent in foam industries. It is widely used in the aluminum production industry, nuclear fuel, steel, petroleum refining, and fluoride salt production.

22.3.5.2 Wastewater Characterization

Water is mainly used as noncontact cooling water, scrubbing water, and in the transportation of gypsum as slurry to the wastewater treatment facility. The water in the heat exchangers is used to

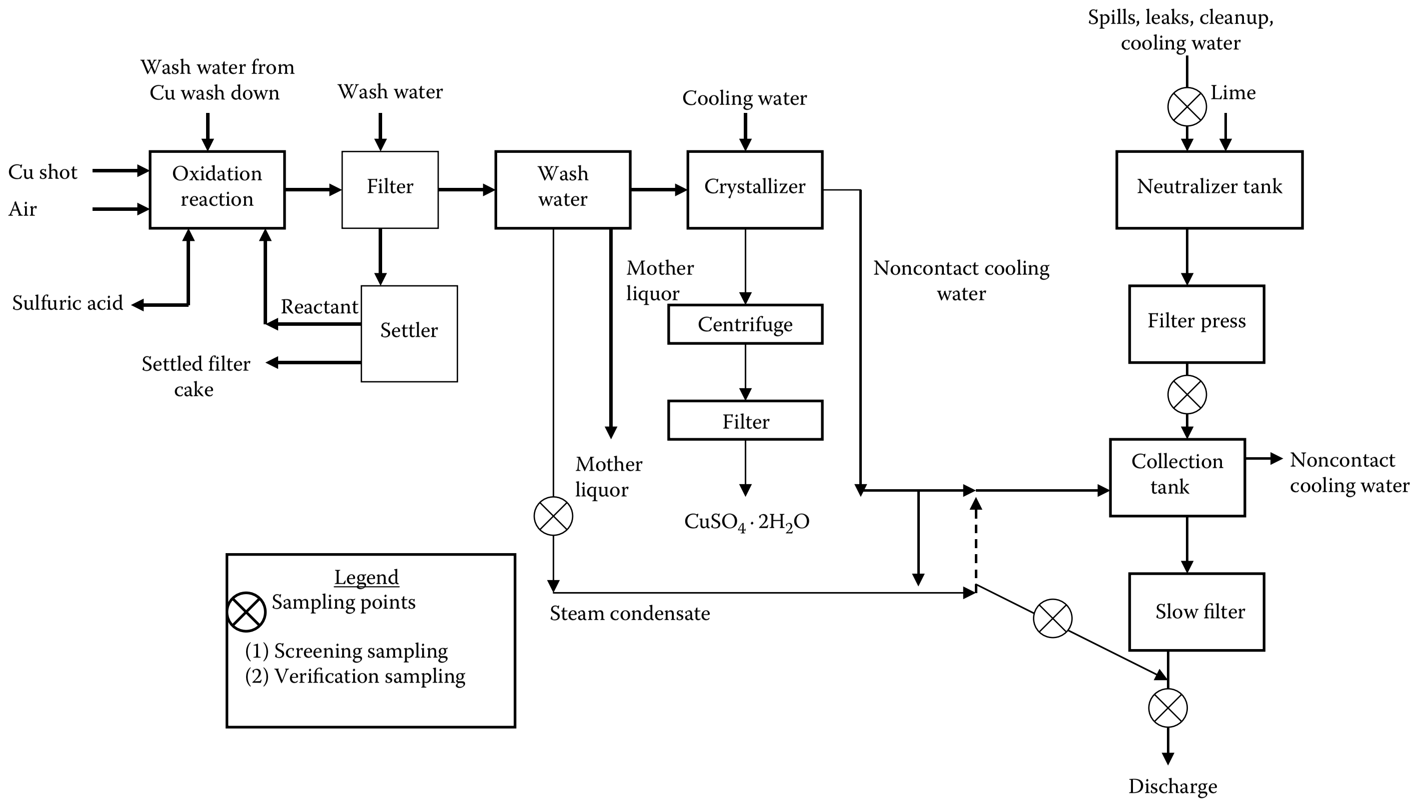

FIGURE 22.8 Flow diagram of a typical plant production of copper sulfate indicating water use and wastewater generation.

TABLE 22.11
Summary of Raw Waste Loadings Found in Screening and Verification Sampling of Copper Sulfate

Pollutants	Maximum Raw Waste Loadings (kg/Mg) × 10^{-3}
Antimony	1.2[a]
Arsenic	97
Cadmium	3.5
Copper	4600
Lead	1.8
Nickel	250
Zinc	27
Chromium	0.08
Selenium	<0.024

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 1.2 (kg/Mg) × 10^{-3} = 0.0012 kg/10^6 g.

cool the gas; it seldom contains pollutants and as such it is recycled. The scrubber water is the major source of wastewater in the plant and often contains hydrogen fluoride, silicon hexafluoride, and hexafluorosilicic acid. The scrubbing process in the distillation unit generates acidified wastewater and the slurry process contributes to solid wastes, of gypsum, in the wastewater.

A typical plant production of hydrofluoric acid indicating water use and wastewater generation is shown in the flow diagram (Figure 22.9).

Results of raw waste load found in verification sampling for a hydrofluoric acid plant are given in Table 22.12.

22.3.5.3 Wastewater Treatment Process

Heavy metal pollutants such as zinc, lead, nickel, mercury, chromium, arsenic, copper, and selenium are predominantly found in the raw wastewater generated in the hydrofluoric acid plant; these are traceable to the raw materials. These pollutants are also found in the scrubber and washdown wastewaters in the plant. The wastewater resulting from leaks and spills of the drip acid contains fluorosulfonate complex. These pollutants are generally treated by alkaline precipitation, settling, filtration, and clarification. Drip acid and hydrofluoric acid spill wastewaters are combined and treated with aluminum fluoride. The gypsum content of the wastewater is removed in the gypsum pond and the overflow from this pond is neutralized and linked to other waste stream lines for final pH adjustment before discharge. Some other wastewater treatment processes applicable to a hydrofluoric acid plant include sulfide precipitation for effective removal of zinc, nickel, lead, copper, and antimony. The xanthate process and ion exchange are also potent treatment processes in this industry.

22.3.6 HYDROGEN CYANIDE

22.3.6.1 Description and Production Process

Hydrogen cyanide is an important product of the Andrussaw process. In this process, air, ammonia, and methane are reacted over a platinum catalyst at a high temperature to produce hydrogen cyanide. The accompanying gases in the reaction process contain ammonia, nitrogen, carbon monoxide, carbon dioxide, hydrogen, and oxygen. These gases are precooled before being scrubbed with phosphate

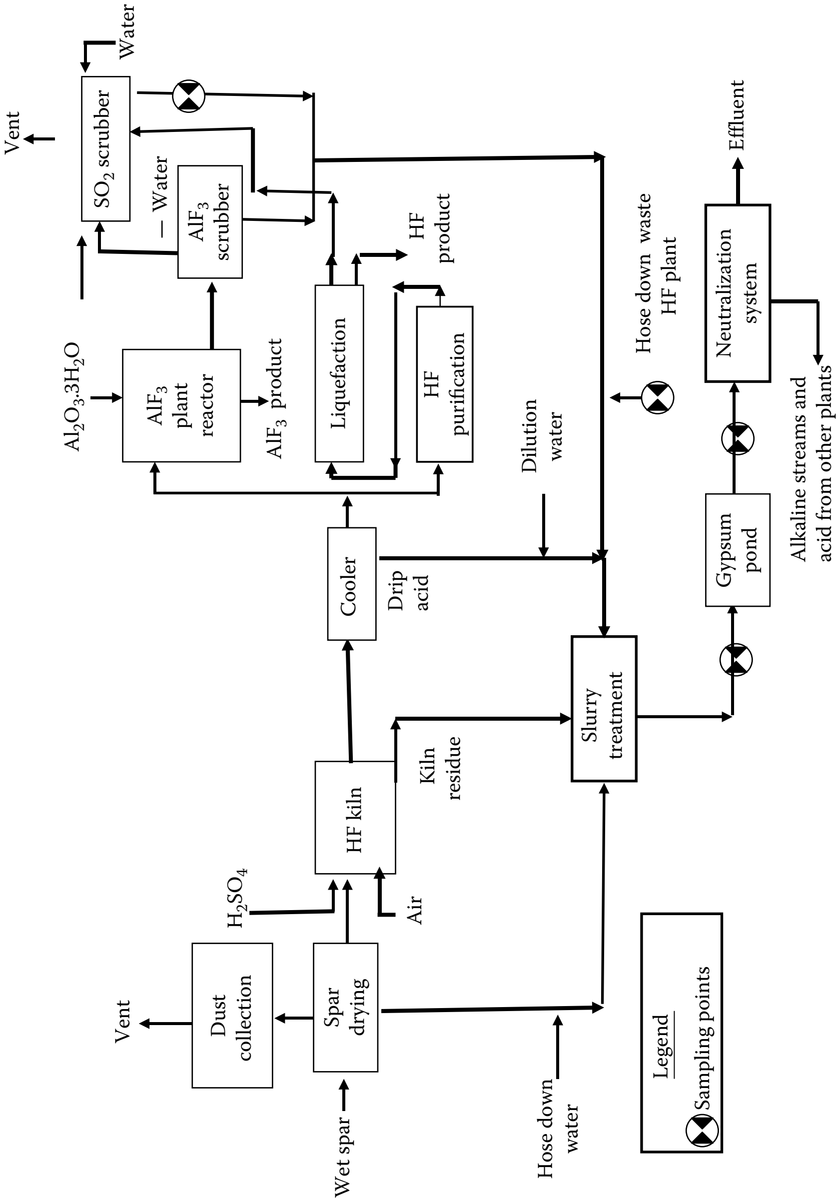

FIGURE 22.9 Flow diagram for production of hydrofluoric acid indicating water use and wastewater generation.

TABLE 22.12
Summary of Raw Waste Loadings Found in Verification Sampling of Hydrofluoric Acid

Pollutant	Maximum Raw Waste Loadings (kg/Mg) × 10^{-2}
Antimony	12[a]
Arsenic	0.91
Cadmium	0.047
Chromium	4
Copper	5.1
Lead	14
Mercury	0.15
Nickel	10
Selenium	0.14
Thallium	0.33
Zinc	130

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 12 (kg/Mg) × 10^{-2} = 0.12 kg/10^6 g.

solution to remove unreacted ammonia. The scrubbed liquor is decomposed to obtain the phosphate solution and ammonia that are recycled to the plant. Alternatively, sulfuric acid may be used instead of the phosphate solution. Hydrogen cyanide from the ammonia scrubber effluent gases is absorbed in cold water to vent off other gases and the absorbed solution that contains hydrogen cyanide, steam, and other contaminants are sent to the distillation unit to produce a high-purity hydrogen cyanide gas. This gas can also be obtained as a by-product of the production process of acrylonitrile.

Hydrogen cyanide is an important raw material used in the production of methyl methacrylate and is widely used for Lucite, Plexiglas molding, and extrusion powders as well as coating resins. It is used widely in the agricultural sector to fumigate orchards and tree crops.

22.3.6.2 Wastewater Characterization

Water is mainly used in heat exchanger segments of units and as wash water for the equipment. Leaks and spills water is also used in the scrubber and the distillation unit; the resulting wastewater contains ammonia, hydrogen cyanide, and small amounts of organic nitriles. Scrubber purging is employed in order to avoid the buildup of impurities in other sources of wastewater in the plant. General plant wash water and rainfall runoff collectively contribute to the volume and characteristics of the wastewater in this plant.

Results of raw waste load found in verification sampling for a hydrogen cyanide plant are given in Table 22.13.

22.3.6.3 Wastewater Treatment Process

Both oxidizable cyanides and metallic complexes of ferro- and ferrycynides are the main pollutants found in a hydrogen cyanide process plant. Treatment processes generally employed in this industry include alkaline precipitation, settling, filtration, clarification, and recycling. The cyanide is oxidized to produce carbon dioxide and nitrogen. When ammonia is present in the waste stream, chlorine is used as oxidizing agents and the choice of hydrogen peroxide is hampered by high operating costs. The combined wastewater in the plant is sent to an alkaline chlorination treatment unit where sodium hypochlorite is added and the pH is adjusted to 10 with dilute caustic soda in succeeding

TABLE 22.13
Summary of Raw Waste Loadings Found in Screening and Verification Sampling of Hydrogen Cyanide

Pollutant	Maximum Raw Waste Loadings (kg/Mg)
Cyanide, total	6.1
Cyanide, free	0.82

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.
Note: 1 kg/Mg = 1 kg/10^6 g.

ponds. Sufficient chlorine and caustic soda are further added in the last pond to meet the discharged standard. Chlorine concentration resulting from excessive usage in the treatment process is removed through biological treatments, particularly aeration and trickling filtration (Figure 22.10).

Some other types of treatment processes that can be employed in the hydrogen cyanide industry include ozonation, to oxidize the wastewater chlorine. Potency of sulfur oxide is also high in the oxidation process.

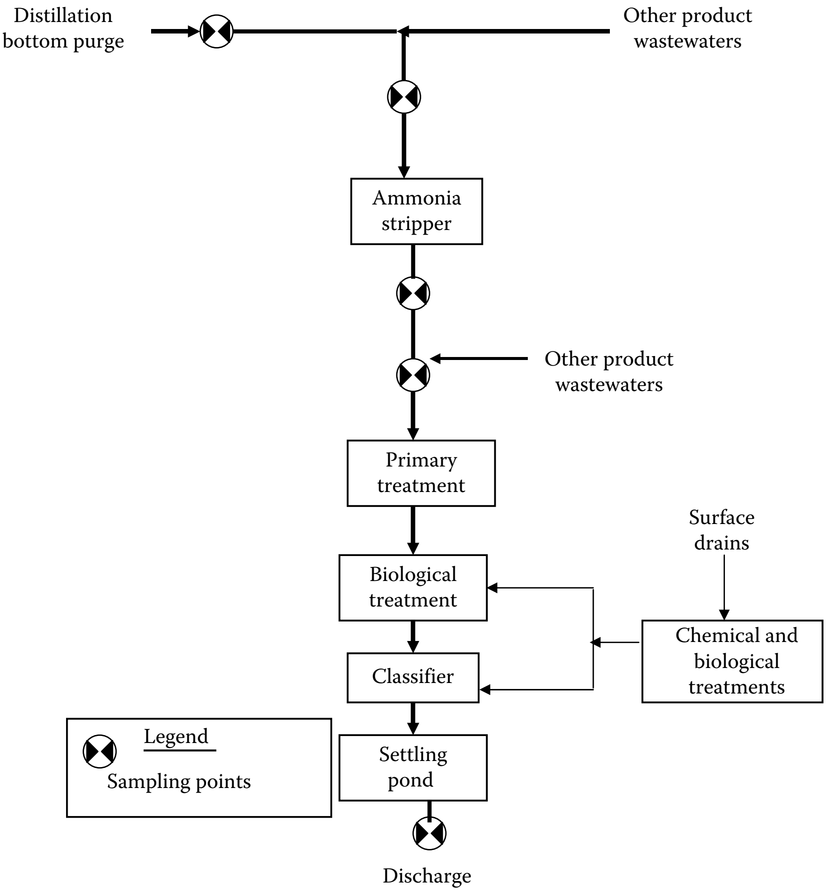

FIGURE 22.10 General wastewater treatment process flow diagram at a typical hydrogen cyanide plant.

22.3.7 Nickel Sulfate

22.3.7.1 Description and Production Process

Nickel sulfate can be produced from either pure or impure sources. The pure source involves the reaction of pure nickel or nickel oxide powder (combined or separately) with sulfuric acid to produce nickel sulfate that is filtered and crystallized to produce a solid product. The impure raw material may be spent industrial liquor that contains a high percentage of nickel sulfate. The impurities in the liquor are precipitated by sequential treatment with oxidizers; lime and sulfides can later be filtered out. The treated liquor, which is a pure solution of nickel sulfate, can be packaged in a drum or further crystallized and dried to produce solid nickel sulfate. Nickel sulfate is used mainly in the metal plating industries. Other uses include dyeing and printing of fabrics and production of patina, an alloy of zinc and brass.

22.3.7.2 Wastewater Characterization

Generally water is used, in a nickel sulfate plant for process reaction, cooling of reactor, crystallization, plant washdown of spills, pump leaks and general cleanup. The water used in the process reaction is for preliminary preparation of the spent plating solution. In other units, especially where impure nickel raw material is used, the wastewater is often recycled. Wastewaters from this plant contain contact and noncontact water, which predominantly contain nickel as a major impurity.

A typical plant production of nickel sulfate is shown in the flow diagram (Figure 22.11).

Results of raw waste load found in verification sampling for a nickel sulfate plant are given in Table 22.14.

22.3.7.3 Wastewater Treatment Process

The source and nature of raw materials employed in the production process of nickel sulfate determine the type and quantity of pollutants generated in a typical nickel sulfate production plant. However, nickel is the significant pollutant in some plants (Table 22.14), while copper shows prominence in others. As stated in the production process, most heavy metals in the spent liquor, an impure source of raw material, are precipitated as sludge before using the pure liquor for the production of nickel sulfate. Generally, wastewater generated in the production process is treated through alkaline precipitation at pH between 9 and 10, followed by filtration and settling before discharge into the environment. The sludge generated in the plant is disposed of or used in a landfill.

General wastewater treatment process flow diagram at a typical nickel sulfate plant is shown in Figure 22.12.

Precipitation of nickel and other heavy metals, besides chromium, as metallic sulfide, followed by separation by settling and filtration of the wastewater containing the metals, is an improved treatment process of wastewater in the nickel sulfide industry.

22.3.8 Sodium Bisulfite

22.3.8.1 Description and Production Process

Sodium bisulfite is the product of a reaction between sodium carbonate, sulfur dioxide, and water. The slurry product contains crystals of sodium bisulfite that can be packaged in its liquid form or processed further through thickening, centrifuging, and drying to form anhydrous sodium metabisulfite. Sodium bisulfite is an important photographic chemical. It is also widely used in organic chemicals, textiles, food processing, tanning, and paper production industries.

22.3.8.2 Wastewater Characterization

Wastewater generated in most sodium bisulfite plants is mainly the process water that is used in making slurry of sodium carbonate. Washdowns and general cleanup water are other sources. The

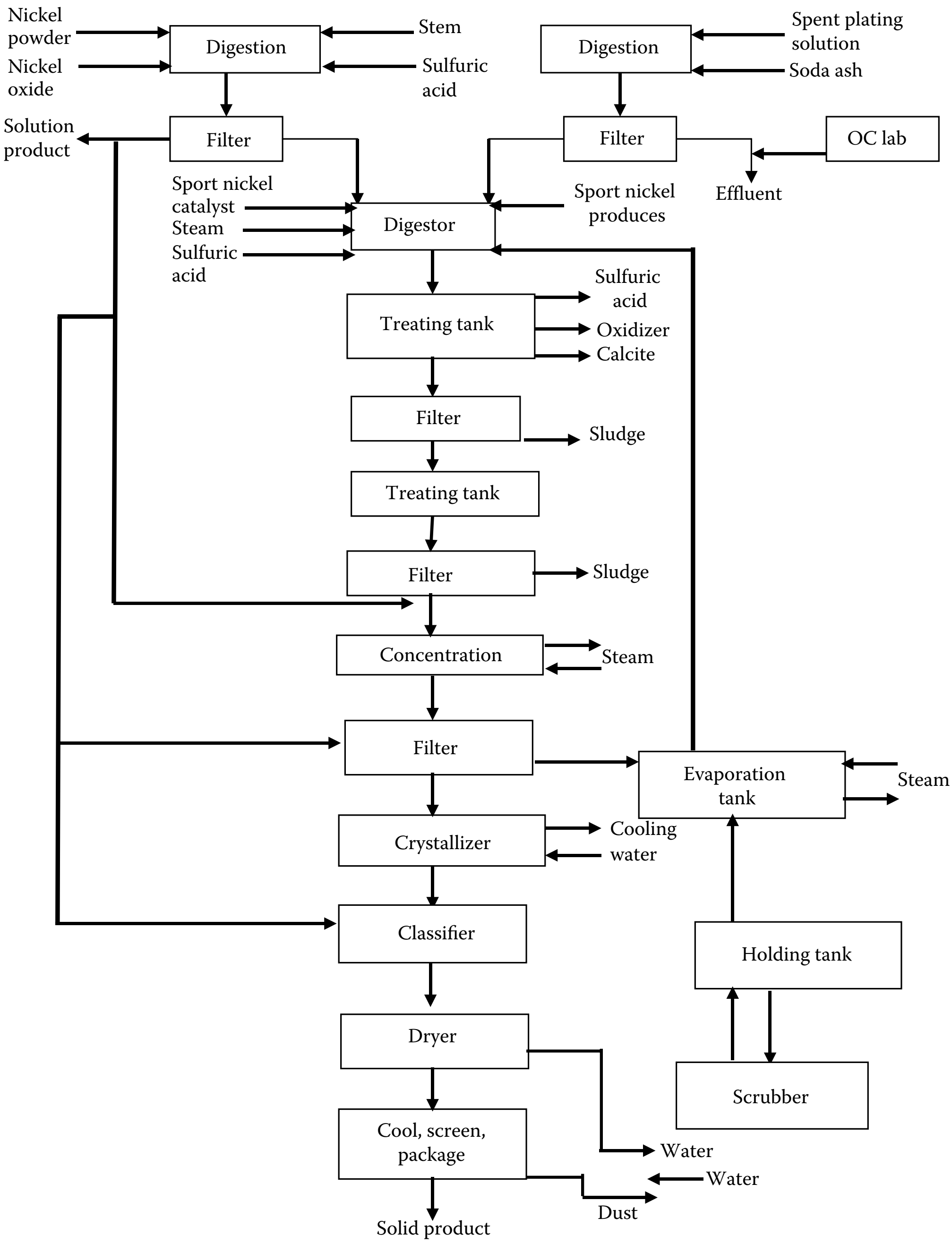

FIGURE 22.11 Flow diagram of a typical plant production of nickel sulfate.

filter wash, wastewaters from other units of the plant, and wash water are combined and neutralized with caustic soda (50%) to a high pH of 9–10. The mixture is then passed through an aeration tank between 8 and 17 retention times to facilitate the conversion of bisulfate waste to sulfite, which are eventually oxidized to sulfate with air. The treated wastewater passes through the primary and secondary settling ponds before being discharged. The noncontact water is mainly used in cooling the centrifuge. The wastewater from this plant is relatively very low.

TABLE 22.14
Summary of Raw Waste Loading Found in Screening and Verification Sampling of Nickel Sulfate

Pollutant	Maximum Raw Waste Loading (kg/Mg) × 10^{-4}
Antinomy	2[a]
Arsenic	0.35
Cadmium	0.038
Chromium	5.4
Copper	0.03
Lead	0.38
Mercury	BDL
Nickel	0.073
Selenium	0.5
Thallium	0.088
Zinc	1.1

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 2 (kg/Mg) × 10^{-4} = 0.0002 kg/10^6 g.

BDL, below detection limit.

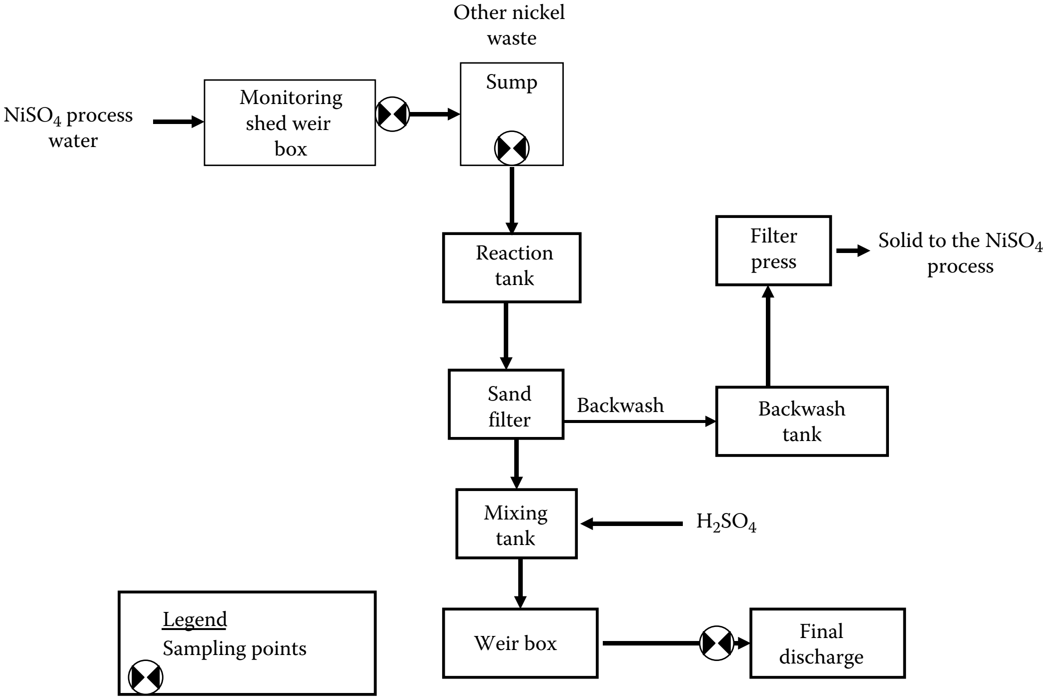

FIGURE 22.12 General wastewater treatment process flow diagram at a typical nickel sulfate plant.

A typical plant production of sodium bisulfite indicating water use and wastewater generation is shown in the flow diagram (Figure 22.13).

Results of raw waste load found in verification sampling for a sodium bisulfite plant are given in Table 22.15.

22.3.8.3 Wastewater Treatment Pollutant

Presence of heavy metals in the wastewater coming from a sodium bisulfite plant is least expected since the raw materials used in its production do not bear traces of these pollutants. Table 22.15 clearly shows that raw wastewater from this plant contains low concentration of the heavy metals. Of all the investigated pollutants, dissolved zinc, which is suspected to be from corrosion of galvanized metal or zinc compounds used in the industry, has the highest concentration. Generally, the toxic metal pollutants in this plant are precipitated by treating the wastewater with lime, sodium carbonate, and caustic soda, followed by settling and filtration processes before discharging the treated wastewater. Other treatments applicable to the wastewater from this plant include sulfide precipitation that effectively precipitates zinc from the solution, the ion exchange process that removes other ions, and the xanthate process.

22.3.9 SODIUM DICHROMATE

The chemical reactions involving chromites, limestone, and soda ash produce sodium chromate, which when reacted with sulfuric acid produces sodium dichromate. Chromites ore, which primarily consists of ferrous chromite and small amounts of aluminum, silica, and magnesia, is finely powdered in the plant and mixed with soda ash before being calcined in rotary kilns. The kiln product is dissolved using hot water and the solution formed is filtered through the filtration process; the filtrate is then evaporated to produce a concentrated solution of sodium chromate. Sulfuric acid is then reacted with the concentrated solution of sodium chromate to produce sodium dichromate and sodium sulfate. The latter is crystallized and the former is filtered out of the boiling solution. The filtrate is sent to the multiple-effect evaporators for further concentration and later to the water cooling crystallizer where sodium dichromate is crystallized; this is followed by centrifugation, drying, and packaging. The aluminum found in the thickener overflow is hydrolyzed before being precipitated out as aluminum hydrate slurry, which is finally sent out of the plant. Sodium dichromate is an important raw material used in the production of chromic acid and chrome pigments. It is also used in the tannery and metal plating industries as a corrosion inhibitor.

22.3.9.1 Wastewater Characterization

Generally, water is used in this plant to cool, leach, filter wash, scrub, heat, and washdown. The unreacted ore is slurred and sent, along with chromium and other impurities originally present in the ore, to the treatment plant. The boiler blowdown, which is sometimes contaminated with chromium escaping from the process area, adds to the volume of wastewater coming from the plant. The noncontact cooling water from the plant contains dissolved sulfate, chloride, and chromate; thus it is sent to a wastewater treatment plant. The scrubber water may be used to slurry the ore or discharged.

Results of raw waste load found in verification sampling for a sodium dichromate plant are given in Table 22.16.

22.3.9.2 Wastewater Treatment Process

Hexavalent chromium and metals such as zinc and nickel that are present as impurities in the chromites ore are predominant pollutants associated with the sodium dichromate plant. They are generally removed through alkaline precipitation, clarification, filtration, and settling processes. The wastewater is treated with sodium sulfide to reduce hexavalent chromium to trivalent chromium,

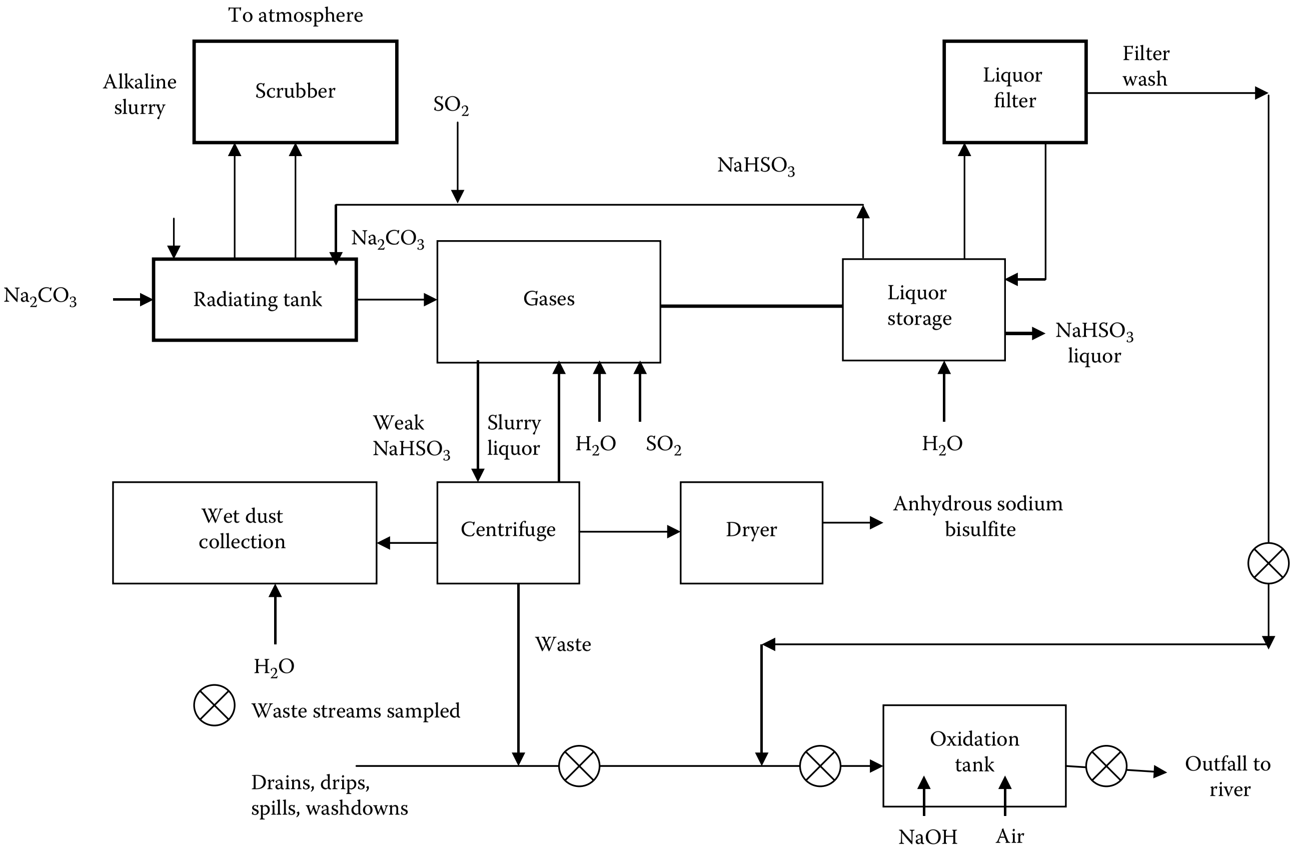

FIGURE 22.13 A typical plant production of sodium bisulfite indicating water use and wastewater generation.

TABLE 22.15
Summary of Raw Waste Loading Found in Screening and Verification Sampling of Sodium Bisulfite

Pollutant	Maximum Raw Waste Loading (kg/Mg) × 10^{-4}
Arsenic	0.3[a]
Antimony	0.8
Cadmium	0.17
Chromium	220
Copper	10
Lead	2
Mercury	0.1
Nickel	7
Zinc	88
Silver	1.7
Thallium	4.2

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 0.3 (kg/Mg) × 10^{-4} = 0.00003 kg/10^6 g.

which is then precipitated as chromium hydroxide out of the solution. Zinc is equally reduced and precipitated with further treatment of the wastewater with sulfite. The wastewater generated from this plant is treated in the same manner and sent to settling tanks where the precipitates and other suspended solids are settled before discharging the overflow.

Flow diagram of the general wastewater treatment process at a typical sodium dichromate plant is shown in Figure 22.14.

A more appropriate and improved method of treatment is still under study. The ion exchange and xanthate processes have not proved to be effective in treating the raw waste associated with this industry.

TABLE 22.16
Summary of Raw Waste Loading Found in Screening and Verification Sampling of Sodium Dichromate

Pollutant	Maximum Raw Waste Loading (kg/Mg) × 10^{-3}
Chromium	3300[a]
Lead	0.09
Copper	0.67
Nickel	5.0
Silver	0.28
Zinc	2.5
Selenium	<0.04
Arsenic	<0.04

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 3300 (kg/Mg) × 10^{-3} = 3.3 kg/10^6 g.

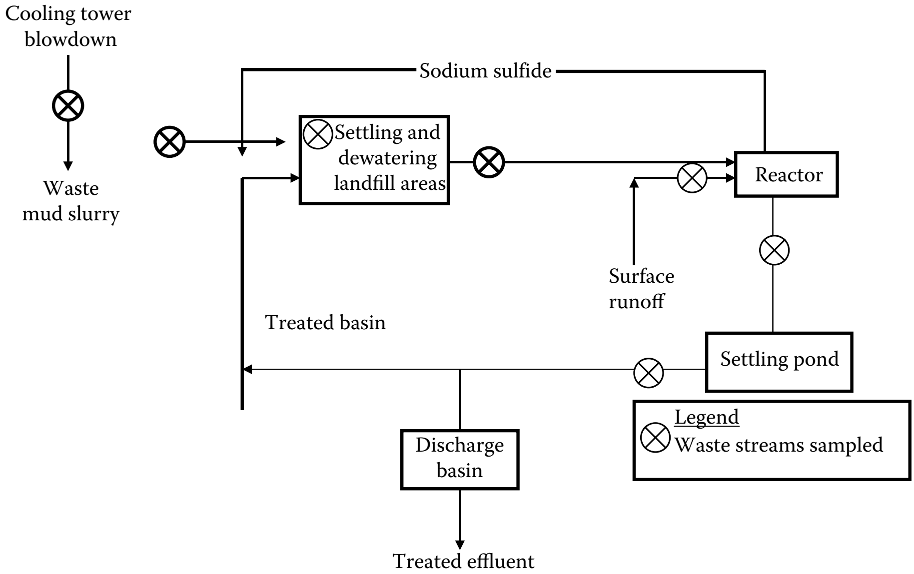

FIGURE 22.14 Flow diagram of the general wastewater treatment process at a typical sodium dichromate plant.

22.3.10 SODIUM HYDROSULFITE

22.3.10.1 Description and Production Process

22.3.10.1.1 Formate Process

Sodium hydrosulfite is produced through the Formate process where sodium formate solution, sodium hydroxide, and liquid sulfur dioxide reacted in the presence of a recycled stream of methanol solvent. Other products are sodium sulfite, sodium bicarbonate, and carbon monoxide. In the reactor, sodium hydrosulfite is precipitated to form a slurry of sodium hydrosulfite in the solution of methanol, methyl formate, and other coproducts. The mixture is sent to a pressurized filter system to recover sodium hydrosulfite crystals that are dried in a steam-heated rotary drier before being packaged. Heat supply in this process is highly monitored in order not to decompose sodium hydrosulfite to sulfite. Purging is periodically carried out on the recycle stream, particularly those involving methanol, to avoid excessive buildup of impurities. Also, vaporized methanol from the drying process and liquors from the filtration process are recycled to the solvent recovery system to improve the efficiency of the plant.

22.3.10.1.2 Zinc Process

Sodium hydrosulfite can also be produced through the zinc process, where pure sulfur dioxide from oleum or liquid sulfur dioxide is bubbled through zinc dust (suspended in water), in a well-agitated reactor. The zinc hydrosulfite formed flows into another similar reactor where it is reacted with a calculated amount of caustic soda to produce sodium hydrosulfite. The mixture is filtered to collect zinc hydroxide residue, while the filtrate is further processed in the clarifier and later crystallized out. The crystals are filtered in a vacuum filter, washed with ethyl alcohol, and finally dried in a vacuum dyer before being packaged. This process is losing patronage because of environmental reasons. Sodium hydrosulfite is widely used as a reducing agent in the textile dyeing, wood pulp bleaching, vegetable oil, and soap industries.

22.3.10.2 Wastewater Characterization

Water use in this process is for contact and noncontact use. The noncontact use is mainly for cooling, scrubbing, drying, and as washdowns and blowdowns. Reaction solution makeup and steam generation in the rotary dryers are the main processes involving contact use of water in the plant. The scrubber wastewater is recycled to the methanol recovery distillers and eventually goes to the plant wastewater stream in addition to the voluminous aqueous residue from the distillation column bottoms. This wastewater contains concentrated reaction coproducts. Dilute wastewaters resulting from leaks, spills, washdowns, and other wash water are collected and sent to the biological treatment system.

A typical plant production of sodium hydrosulfite is shown in the process diagram (Figure 22.15).

Results of raw waste load found in verification sampling for a sodium hydrosulfite plant are given in Table 22.17.

22.3.10.3 Wastewater Treatment Process

Zinc and other heavy metals are the major toxic pollutants associated with the zinc process of the sodium hydrosulfite process; thus the zinc process is not a favored industrial process unlike the Formate process. Heavy metal impurities such as zinc, nickel, lead, chromium, copper, and trace amounts of cyanide are pollutants resulting from the Formate process. The resulting wastes from various forms of sulfite, methyl formate, and residual methanol after the solvent recovery process are characterized by high chemical oxygen demand (COD) and low level of phenolic compounds. The heavy metals can be removed through alkaline precipitation and sulfide treatment. Chromium concentration can be controlled at a higher pH. The COD of the generated wastewater can be controlled by various forms of chemical and biological oxidation. Aeration systems such as submerged air diffusion, induced air, or mechanical surface aeration facilitate effective contact with oxygen, which oxidizes sulfite to sulfate. Organic pollutants such as formate, phenols, methanol, and chlorinated hydrocarbons are removed through trickling filtration, rotating biological discs, or activated sludge processes. Microorganisms and nutrients such as nitrogen, phosphorus, and urea are added to the wastewater to facilitate digestion and eventual removal of the pollutants as sludge. Liquid effluent is further treated with chlorine before being sent to a final tank for settling, equalization, and eventual discharge.

22.3.11 TITANIUM DIOXIDE

22.3.11.1 Description and Production Process

Production of titanium dioxide in the industry can be achieved through two different processes—the sulfate and chloride processes.

22.3.11.1.1 Sulfate Process

The ore is often dried in a continuous, direct fired rotary kiln and then ground to finely divided solid to facilitate effective reaction with sulfuric acid. The resulting product is dissolved in water and then flocculated continuously to classify the insoluble impurities such as silicon, zirconium, and unreacted ore. The concentrated liquor is further mixed with water and heated to form titanium hydrate that is precipitated out of the mixture and filtered. The accompanying residue is mixed with water and conditioning agents, such as compounds of potassium, zinc, antimony, and calcium and phosphate salts, to improve the size, color, dispersability, and photochemical stability. This improved mixture is further filtered and calcinated to precipitate and remove residual acid and iron originally present in the ore. The resulting product of this process is titanium dioxide pigment, which is further repulped, milled, washed, and dried, depending on the end use.

A typical plant production of titanium dioxide (sulfate process) is shown in the process diagram (Figure 22.16).

22.3.11.1.2 Chlorine Process

This process involves the reaction of dried rutile ore and coke with chlorine in the chlorinator to produce titanium tetrachloride. The liquefied titanium tetrachloride is sent to the distillation unit to remove impurities and then to a fluidized bed reactor to react with oxygen to form titanium dioxide and chlorine. Solid titanium dioxide formed at this stage is vacuum degassed before being treated

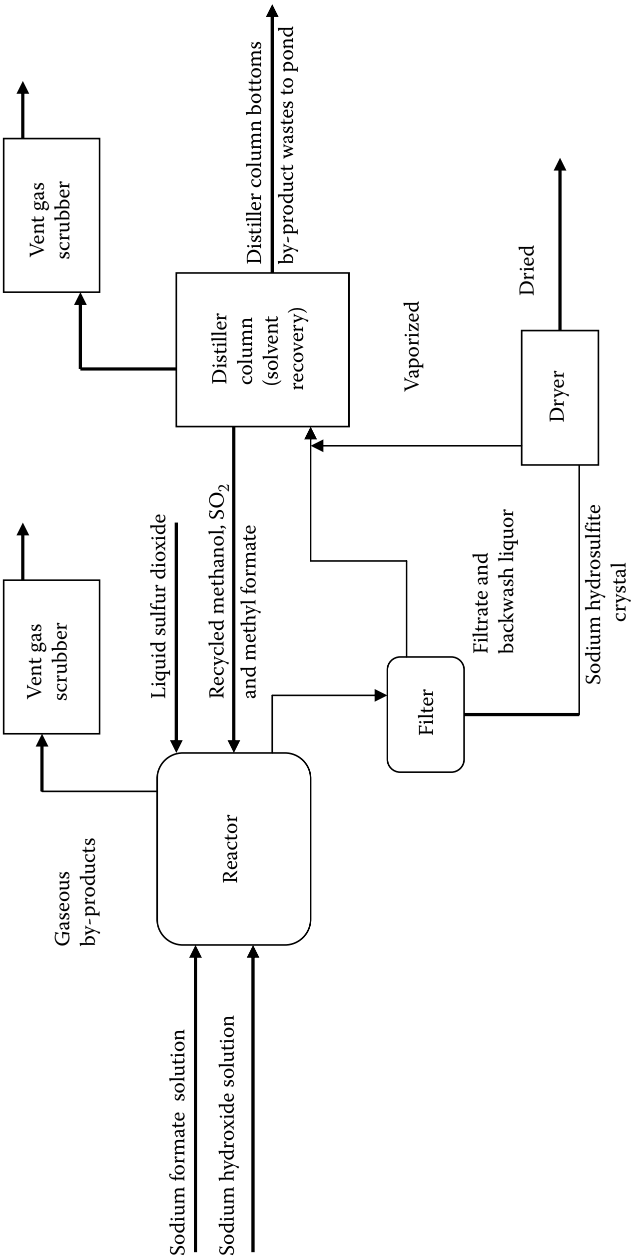

FIGURE 22.15 Flow diagram of a typical plant production of sodium hydrosulfite.

TABLE 22.17
Summary of Raw Waste Loading Found in Screening and Verification Sampling of Sodium Hydrosulfite (Formate Process)

Pollutant	Maximum Raw Waste Loading (kg/Mg) × 10^{-3}
Arsenic	0.12[a]
Cyanide	0.039
Cadmium	0.033
Chromium	0.56
Copper	0.19
Lead	1.0
Mercury	0.02
Nickel	1.6
Silver	0.16
Zinc	24
Pentachlorophenol	0.83
Phenol	0.15
Selenium	0.03

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.

[a] 0.12 (kg/Mg) × 10^{-3} = 0.00012 kg/10^6 g.

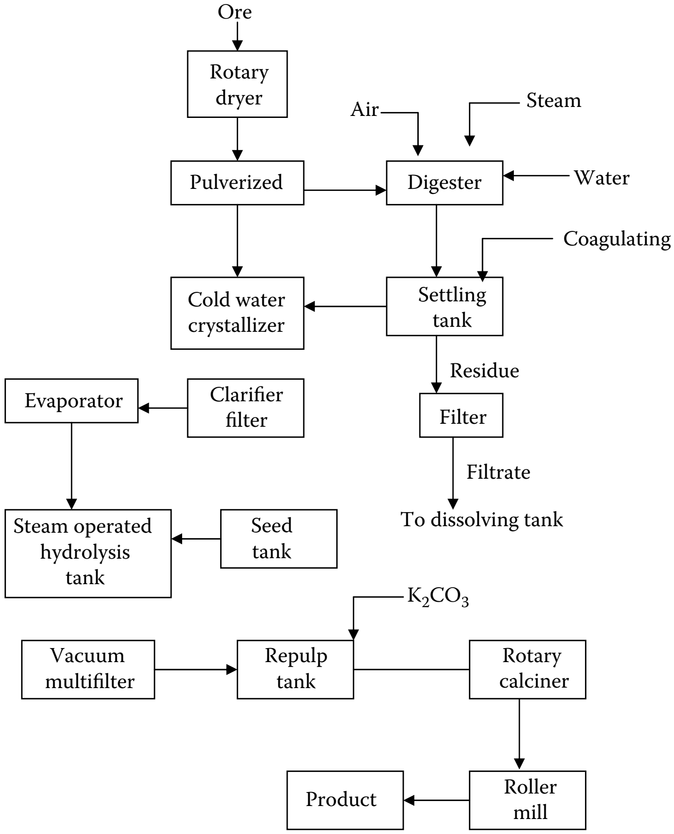

FIGURE 22.16 General production flow diagram of a typical plant production of titanium dioxide (the sulfate process).

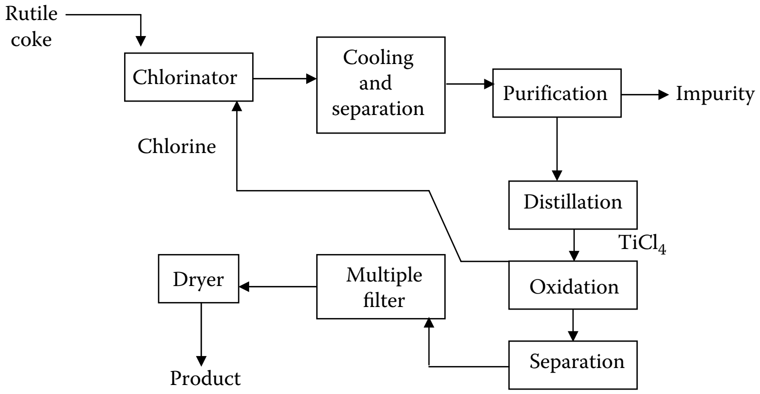

FIGURE 22.17 General production flow diagram of a typical plant production of titanium dioxide (the chlorine process).

with alkali and a small amount of water to absorb chlorine and hydrochloric acid in the mixture. The final product is processed for handling and use. The chlorine generated and scrubbed in the production process is refrigerated, liquefied, and finally recycled. The bulk of titanium dioxide is used as a pigment in the production of paints, varnishes, lacquers, ceramics, ink, rubber, and in the paper and plastic industries.

A typical plant production of titanium dioxide (the chlorine process) is shown in the process diagram (Figure 22.17).

22.3.11.2 Wastewater Characterizations

Water employed in the sulfuric process of titanium oxide production is mainly used for noncontact cooling, process reactions, and air emission control. Wastewater generated as a result of the scrubbing process in the scrubber contains titanium dioxide particulates, sulfur trioxide, sulfur dioxide, and acid mist. Water is also used in the wet milling unit of the plant, where the titanium dioxide pigment is rendered to desired size and surface character. The process requires steam and water for repulping of titanium dioxide and for making a solution of caustic soda. Wastewater from this unit contains titania, sodium sulfate, and other additives employed to achieve desired properties of the products. Furthermore, sulfates, resulting from the digestion of the ore in sulfuric acids, are dissolved in water before being sent to the clarifier or filter to remove insoluble impurities such as silica, alumina, sulfuric acid, and unreacted iron. Water is also used in the washing of the titanium dioxide at some stages; this generates weak and strong acid liquors that contain some impurities, such as iron sulfate, titania, heavy metal, and sulfuric acid. Again, a large volume of water is used in cleaning the kiln gases and in the finishing operations, thus producing wastewater that contains impurities common to other waste streams in the plant. The wastewater is treated with chlorine before being sent to a final tank for settling, equalization, and eventual discharge (Table 22.18).

In the chloride process, water is mainly employed for noncontact cooling, scrubbing of tail gases, and in the finishing operation of titanium dioxide. Water use for cooling the gases emanating from the chlorinator generates a wastewater stream containing solid particles of unreacted ore, iron cake, and some heavy metals and heavy metal chlorides, which is further mixed with water to facilitate its movement to the treatment plant. Wet scrubbing is employed to remove hydrogen chloride, chlorine phosgene, and titanium tetrachloride from the cooling chlorinator gas. Steam waste generated in the scrubber also contains titanium dioxide particles; when caustic soda is used, sodium hypochlorate forms part of the pollutants in the wastewater stream. Like in the sulfate process, a large volume of water is used in the finishing operation of this pigment. The wastewater generated is characterized by suspended solids of titanium dioxide and dissolved sodium chloride.

TABLE 22.18
Summary of Raw Waste Loading Found in Screening and Verification Sampling of Titanium Dioxide (the Sulfate Process)

Pollutant	Maximum Raw Waste Loadings (kg/Mg)
Antimony	0.22
Arsenic	0.032
Cadmium	0.02
Chromium	3.4
Copper	0.12
Lead	0.42
Nickel	0.15
Thallium	0.008
Zinc	0.55
Selenium	<0.66

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.
Note: 1 kg/Mg = 1 kg/10^6 g.

In both processes, wastewater is equally generated as a result of equipment and plant washes, leaks, spills, and blowdowns (Table 22.19).

22.3.11.3 Wastewater Treatment Process

Common pollutants in a titanium dioxide plant include heavy metals, titanium dioxide, sulfur trioxide, sulfur dioxide, sodium sulfate, sulfuric acid, and unreacted iron. Most of the metals are removed by alkaline precipitation as metallic hydroxides, carbonates, and sulfides. The resulting solution is subjected to flotation, settling, filtration, and centrifugation to treat the wastewater to acceptable standards. In the sulfate process, the wastewater is sent to the treatment pond, where most of the heavy metals are precipitated. The precipitate is washed and filtered to produce pure gypsum crystals. All other streams of wastewater are treated in similar ponds with calcium sulfate before being neutralized with calcium carbonate in a reactor. The effluent from the reactor is sent to clarifiers and the solid in the underflow is filtered and concentrated. The clarifier overflow is mixed with other process wastewaters and is then neutralized before discharge.

TABLE 22.19
Summary of Raw Waste Loading Found in Screening and Verification Sampling of Titanium Dioxide (the Chloride Process)

Pollutant	Maximum Raw Waste Loadings (kg/mg)
Chromium	1.2
Lead	0.041
Nickel	0.041
Zinc	0.03

Source: U.S. EPA, *Treatability Manual*, Technical Report EPA-600-/2-82-001, U.S. Environmental Protection Agency, Washington, DC, 1982.
Note: 1 kg/Mg = 1 kg/10^6 g.

A typical wastewater treatment process diagram in a titanium dioxide (the sulfate process) plant is shown in Figure 22.18.

In the titanium dioxide production plant where the chlorine process is employed, the wastewater from the kiln, the distillation column, bottom residue, and those from other parts of the plant first settle in a pond. The overflow from this pond is neutralized with ground calcium carbonate in a particular reactor, while the scrubber wastewater is neutralized with lime in another reactor. The two streams are sent to a settling pond before being discharged.

A typical wastewater treatment process flow diagram in a titanium dioxide production plant (the chlorine process) is shown in Figure 22.19.

Ion exchange as well as lime treatment is another method that can be applied in this process to reduce some of the toxic trace metals in the wastewater from the plant.

22.4 SUMMARY

The pollution prevention strategy in the inorganic chemical industry is largely dependent on the age and size of the facility and the type and number of processes involved in a particular chemical industry. The above listed pollution prevention opportunities, aimed at reducing wastes and reducing materials use, have been embarked upon by some of these industries as the primary means of improving process efficiencies and increasing the profits. Most of the pollutants encountered in the production process are inherent in the raw materials and reflect as traces at many stages. The best substitution is to use a higher-purity feedstock and this can be accomplished by obtaining higher-quality feed or by installing purification equipment. Less toxic and less water-soluble materials will reduce water contamination, and materials with less volatile materials will reduce fugitive emissions.

The efficiency of a given reactor affects the quality of the product coming out of it. If its efficiency is high, despite the presence of impurities in the raw materials, effective reaction may greatly reduce the generation of such impurities in its output. Installations in the reactor, such as baffles, motors with high speed for agitation, multiple impellers, and pump recirculation system, and the use of improved blade design are some of the techniques to improve effective mixing. The method of feed introduction, particularly for a continuous flow system, can be improved to avoid spills and to allow thorough mixing within the residence time of the reactor. Most of the catalysts, particularly those of heavy metal origin, are oftentimes the sources of toxic metal pollutant in the inorganic chemical industries. Noble metal catalysts can be used in place of these conventional heavy metal catalysts to eliminate the wastewater contaminated with heavy metals. An active form of catalysts will reduce consumption of the catalyst and emissions and effluent generated in the processes.

Optimization processes in manufacturing industries are mainly employed to minimize loss and maximize profit. Wastes generation and the cost of removing them always lead to financial and even environmental impact on the operators of such industries. Processes in inorganic chemical industries can be optimized by the installation of computer control systems that are more efficient than usual manual control systems. Equalizing the reactor and storage tank vent lines during batch filling to minimize vent gas losses; addition of reactants and reagents in a well-ordered sequence to optimize yields and lower emissions; and well-sequenced washing operations are some of the methods of optimization of production processes in manufacturing plants involving inorganic chemicals.

Most of the reactions involving production of inorganic chemicals are exothermic, and in other processes they are heated to initiate reaction. As a result, heat generation is high and thus facilitates waste emission generation. Heat exchangers are common equipment in this industry but improvement in their efficiency will minimize emission generation. Using noncorroding tubes, reducing the tube wall thickness, increasing the effective surface area, monitoring, and prevention of fouling of the heat exchanger tubes are some of the techniques to improve the efficiencies of the heat exchangers and invariably the reduction of waste.

Larger parts of the waste generated in the inorganic chemicals production process are found in the wastewater emanating from the industry. However, if the wastewater generation could be

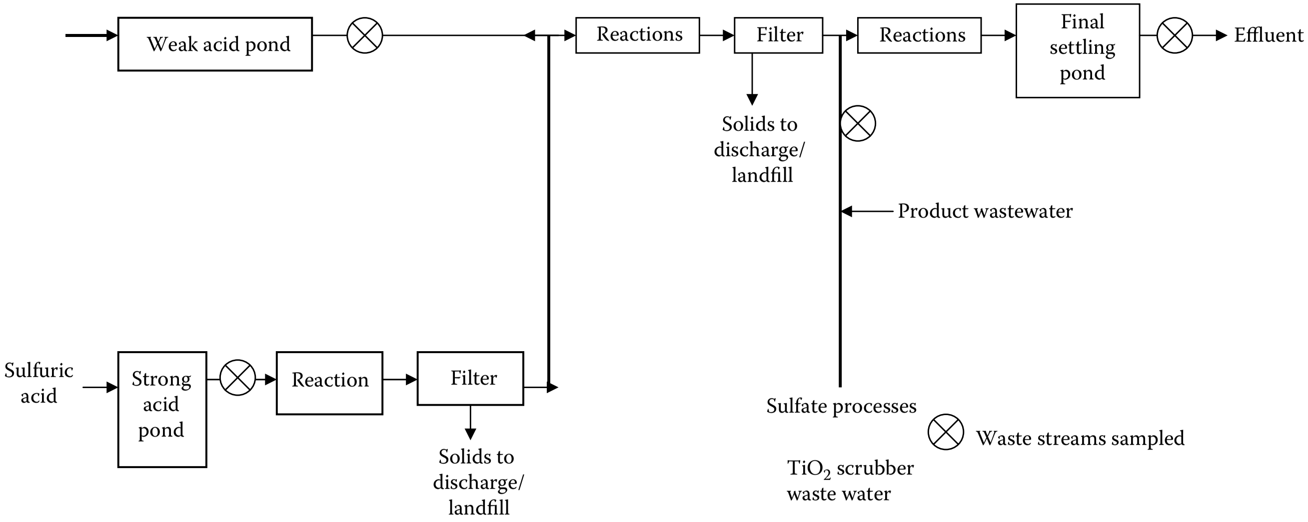

FIGURE 22.18 Flow diagram of a typical wastewater treatment process in a titanium dioxide plant (the sulfate process).

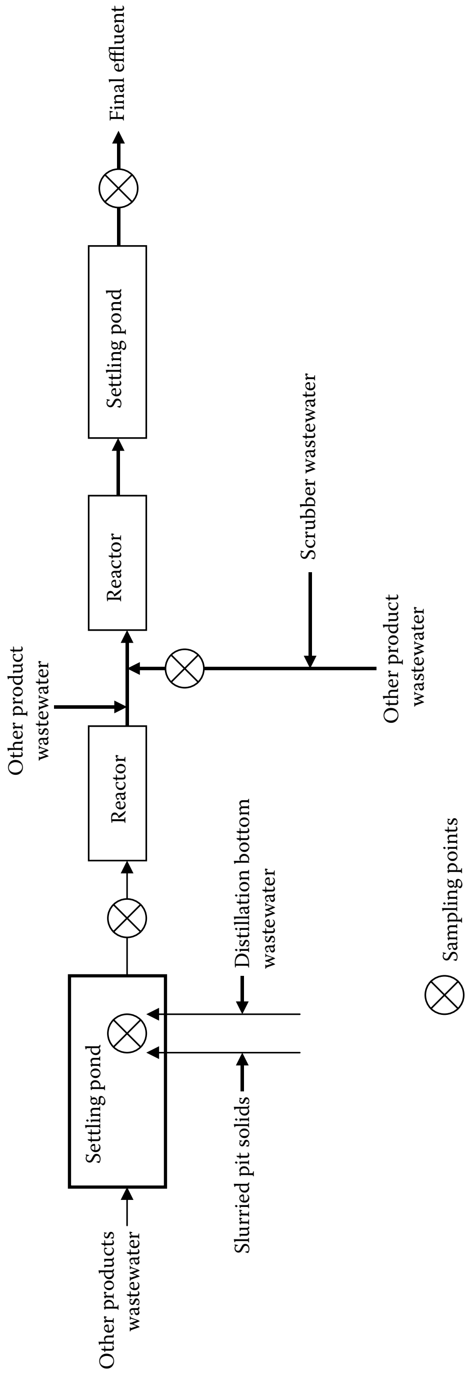

FIGURE 22.19 Flow diagram of a typical wastewater treatment process in a titanium dioxide plant (the chlorine process).

minimized or effectively treated, less pollutant from the industries will reach the environment. Improved wastewater treatment technologies such as ion exchange, electrolytic cells, reverse osmosis, evaporation, dewatering, and improved distillation can be added or used to replace existing treatment systems. More importantly, most of the wastewater treatment streams can be recycled before or after treatment to reduce the rate and volume of discharges into the environment. Prevention or elimination of leaks and spills of reactants, products, or wastewater in the inorganic chemical industries is an effective means of pollution prevention. This can be achieved by installing seamless pumps, a leak detection program, and maintaining a rapid response solution in the case of leaks or spills.

Packaging, storage area, and safety programs are important for most of the products coming from the inorganic chemical industries since they are in transit within the premises until purchased by interested manufacturing industries. Good inventory in terms of the amount used, returning of unused, and reducing the likelihood of accidental release are some of the ways to manage the generation and emission of wastes from the storage end of the industry.[30–33]

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23 Incineration and Combustion of Hazardous Wastes

Nazih K. Shammas and Lawrence K. Wang

CONTENTS

In the United States, more than 3.1 million tons of hazardous waste were disposed of through combustion in 2005. This figure represents 7.2% of the approximately 44 million tons of hazardous waste generated.[1] The state of Texas, which ranked first in hazardous waste production, generated 15.2 million tons, while the state of Louisiana that ranked second produced 5.5 million tons.[2] These two states alone contributed almost 50% of the total U.S. hazardous waste generation.

There are two categories of combustion units for solid and liquid hazardous wastes:

1. Incinerators—used primarily for waste destruction.
2. Boilers and industrial furnaces (BIFs)—used primarily for energy and material recovery.

Incinerators are used to burn hazardous waste primarily for waste destruction/treatment purposes; however, some energy or material recovery can occur. When performed properly, incineration destroys the toxic organic constituents in hazardous waste and reduces the volume of the waste.[3] Since metals will not combust, incineration is not an effective method for treating metal-bearing hazardous wastes.

BIFs are typically used to burn hazardous waste for the significant energy and material recovery potential, with waste treatment being a secondary benefit. Boilers typically combust waste for energy recovery, whereas industrial furnaces burn waste for both energy and material recovery.[3] A boiler is defined as an enclosed device that uses controlled flame combustion to recover and export energy in the form of steam, heated fluid, or heated gases. An industrial furnace is a unit that is an integral part of a manufacturing process and uses thermal treatment to recover materials or energy.

Resource Conservation and Recovery Act (RCRA) regulations governing incinerators can be found at 40 CFR Part 264/265, Subpart O-Incinerators.[4] RCRA regulations governing BIFs can be found at 40 CFR Part 266, Subpart H-Hazardous Waste Burned in BIFs.[5]

Hazardous waste combustors (HWCs) also are regulated under the Clean Air Act (CAA).[6] The CAA protects human health and the environment from the harmful effects of air pollution by requiring significant reductions in the emissions of the most dangerous air pollutants. These pollutants are known or suspected to cause serious health problems such as cancer or birth defects, and are referred to as hazardous air pollutants (HAPs).

As originally enacted, the CAA required that the U.S. Environmental Protection Agency (U.S. EPA) establish National Emission Standards for Hazardous Air Pollutants (NESHAPs) on a chemical-by-chemical basis. Under this mandate, U.S. EPA established NESHAPs for seven HAPs. However, the 1990 amendments to the CAA changed U.S. EPA's approach to regulating HAPs, so that NESHAPs are now established based on the maximum achievable control technology (MACT) for an industry group or source category (e.g., HWCs). These standards are based on emission levels that are already being achieved by the better-performing sources within the group.

The NESHAP was developed in two phases. Phase I addresses hazardous waste burning incinerators, cement kilns, and lightweight aggregate kilns and was originally promulgated on September 30, 1999. Hazardous waste burning industrial boilers, process heaters, and hydrochloric acid production furnaces were addressed in Phase II, which was signed on September 14, 2005. Replacement standards for Phase I also were signed on this date.

23.1 INCINERATORS

Incineration destroys organic compounds contained in hazardous wastes and reduces the volume of the wastes by removing liquids. To achieve those goals, the incinerator must be able to provide controlled burning (combustion) conditions that ensure the proper mixing of air, temperature, and gas, and adequate time to allow a thorough destruction of organic constituents to take place. A deficiency in any of those requirements can result in incomplete combustion and the production of smoke and possibly harmful air emissions. Such emissions are a potential public health hazard because nearby communities may be exposed to site contaminants via the air transport pathway. It should also be recognized that human exposure to airborne incinerator contaminants can occur indirectly by consumption of animals or plants raised in areas where deposition of emissions takes place.[7]

The specific equipment used for each step depends on the incinerator type and the physical and chemical characteristics of the wastes the incinerator is designed to burn. Wastes are fed into the incinerator in batches or in a continuous stream. Liquid wastes are often pumped and atomized into fine droplets that burn more easily. Solid wastes may be fed into the incinerator in bulk or in containers using a conveyer, a gravity system, or a ram feeder.[8]

As the wastes are heated, they are converted from solids or liquids into gases. The gases are mixed with air and pass through a hot flame. As the temperature of the gases rises, the organic compounds in the gases begin to break down and recombine with oxygen to form carbon dioxide and water. Depending on the waste composition, other organic and inorganic compounds may form.

In most hazardous waste incinerators, combustion occurs in two combustion chambers. Combustion is completed in the secondary combustion chamber after the compounds have been converted to gases and partially combusted in the first chamber.

Incineration produces gases and solids, in the form of ash and slag. Combustion gases are composed primarily of carbon dioxide and water, as well as small quantities of carbon monoxide, nitrogen oxides, and small concentrations of organic and inorganic compounds.

Following combustion, the combustion gases move through various devices that cool and cleanse the gases. A fan is typically used to pull the gases through the incinerator and the air pollution control equipment. Gases are quenched with a water mixture to reform any particulate matter (PM). Acids can be removed with wet or dry scrubbers. PM can be removed using either dry (baghouse) or wet systems.

When Congress enacted the RCRA in 1976, it directed U.S. EPA to establish performance, design, and operating standards for all hazardous waste treatment, storage, and disposal facilities

(TSDFs). U.S. EPA promulgated both general facility standards that apply to all TSDFs and requirements for specific types of units (e.g., incinerators, landfills, and surface impoundments) in 40 CFR Parts 264 and 265. The regulations under Parts 264 and 265, Subpart O, apply to owners and operators of facilities that incinerate hazardous waste.[4]

23.1.1 INCINERATOR DESIGN AND OPERATING CONSIDERATIONS

23.1.1.1 Overview of Combustion

Incineration is the controlled burning of substances in an enclosed area. During a burn, wastes are fed into the incinerator's combustion chamber. As the wastes are heated, they are converted from solids and liquids into gases. These gases pass through the flame and are heated further. Eventually, the gases become so hot that the organic compounds in the gases break down into their constituent atoms. These atoms combine with oxygen and form stable gases that are released to the atmosphere after passing through air pollution control devices (APCDs).

For incineration to be an effective method for destroying the hazardous properties of wastes, combustion must be complete. Three critical factors ensure the completeness of combustion in an incinerator[8]:

1. The temperature in the combustion chamber.
2. The length of time wastes are maintained at high temperatures.
3. The turbulence or degree of mixing of the wastes and the air.

23.1.1.2 Design Considerations

To minimize the public's potential exposure to site emissions, an incinerator must be designed and operated properly. The incinerator must be designed to burn waste materials thoroughly. The combustion chambers must be of a size and arranged in a way to provide adequate time for the gases produced by burning waste to mix with proper amounts of combustion air, and to maintain the high temperatures needed to ensure that the burning is completed.[9]

When an incinerator is designed, the waste to be burned must be characterized for properties such as heat content (fuel value), percent moisture, chlorine content, metals content, and physical characteristics. The size and physical layout of the incinerator should be based on those waste properties.

The incinerator must be designed and operated in a manner that minimizes production of nonstack, fugitive emissions. This can be accomplished by ensuring proper seals at all system connections, maintaining negative gas pressures throughout the combustion gas flow path, and by limiting the waste feed to prevent excessive and rapid releases of volatile compounds. Careful attention must also be given to the design and operation of waste handling systems to minimize fugitive emissions. Agency for Toxic Substances and Disease Registry (ATSDR) public health assessors have found that excavation and handling of soils at some Superfund sites, and waste unloading and repackaging operations at some RCRA facilities, have been major sources of airborne contaminants that have resulted in exposure of workers and/or nearby residents[10] to hazardous wastes.

Another critical part of the incinerator design is the pollution control system.[11] Pollution control systems directly influence the levels and kinds of pollutants that are released and that can potentially reach the public. Most modern hazardous waste incinerators are designed with extensive air pollution removal systems. For example, a common pollution control system might include a system that cools or "quenches" gases produced by burning waste, followed by a system that reduces acid gas emissions, and ultimately followed by a particulate removal system such as fabric filters (baghouses), electrostatic precipitators, venturi scrubbers, and others.[10]

Finally, current design of hazardous waste incinerators includes various safeguards, such as process monitoring devices (to monitor parameters such as temperature, air flow, and operating pressures); continuous emission monitoring systems (to measure air emissions of carbon monoxide, gas flow rates, and possibly other combustion performance indicators); and automatic waste feed shutoff devices (AWFSOs). AWFSOs, as required by RCRA regulations (40 CFR 264), automatically stop the waste feed to the incinerator when specified monitoring parameters exceed or fall below limits specified in the permit. The parameters that trigger the AWFSOs are established based on successful trial burns. AWFSOs are critical to ensure that the incinerator cannot operate in an improper condition for extended periods of time).[12]

23.1.1.3 Operating Considerations

Operating considerations of importance in protection of public health are described in the following subsections.[10]

23.1.1.3.1 Training of Operators

Even with all the proper design features, skilled operators are essential for a safe, effective incineration program. Operators should understand the principles of good combustion and be thoroughly familiar with all major and support systems at their plants. Careful attention to proper waste burn rates and waste blending, as needed, helps to ensure that the combustion systems are not overloaded and that the AWFSOs are not activated excessively. Routine maintenance, inspection, and instrument calibrations should be conducted and recorded. Safety and emergency response plans that thoroughly address likely failure scenarios (including power, systems, and operational failures) must be in place, documented, and shared with local officials. Emergency "release" drills should be conducted periodically with the knowledge and involvement of local emergency response personnel. In addition, all employees should be adequately trained in appropriate health and safety procedures for the safe day-to-day operation of the incinerator.

Figure 23.1 provides a compilation of information on reported emergency incidents at hazardous waste combustion facilities and other TSDFs regulated under the RCRA. It covers emergency incidents such as fires, explosions, hazardous waste spills, or unauthorized releases of hazardous waste. The reported incidents at 24 hazardous waste combustion units and 26 other TSDFs

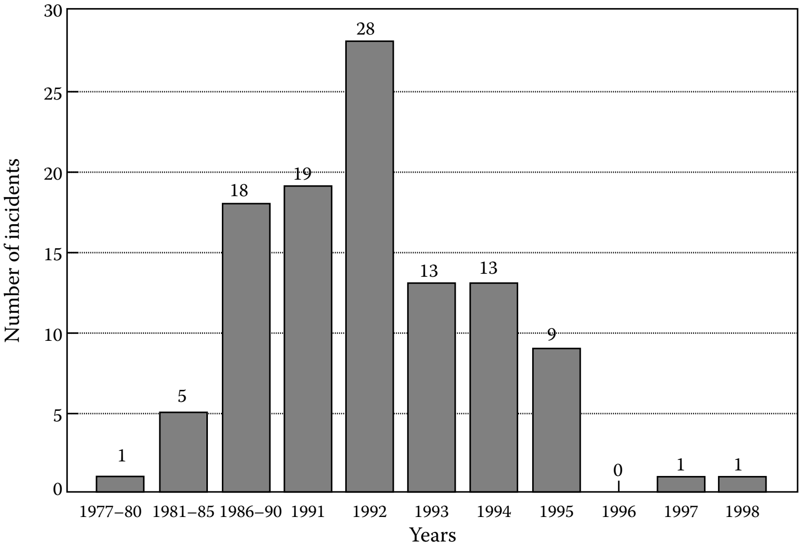

FIGURE 23.1 Number of incidents at combustion facilities and TSDFs. (Adapted from U.S. EPA, *Report on Emergency Incidents at Hazardous Waste Combustion Facilities and Other Treatment, Storage and Disposal Facilities (TSDFs)*, EPA530-R-99-014, U.S. Environmental Protection Agency, Washington, DC, June 1999.)

emphasize the importance of safety procedures for the safe day-to-day operation of incinerators. Of the incidents that have occurred, nine facilities experienced incidents that were directly related to the actual combustion of hazardous waste. The remaining incidents involved were not combustion related and consist of activities such as waste handling and storage. Detailed incident reports of the various combustion units can be found in a U.S. EPA Report.[13]

23.1.1.3.2 Siting of the Incinerator

Another consideration relevant to public health and frequently raised by the public is the location of the incinerator with respect to the community. More specifically, consideration should be given to the possible health impacts associated with living or working people in the path of incinerator emissions. To address those concerns, when reviewing the location of an incinerator, regulatory agencies use generally accepted air dispersion models[14] in conjunction with local meteorologic data to determine the permit conditions necessary to protect human health and the environment. Such modeling results can be particularly helpful in identifying prevailing wind transport patterns and their effect on downwind pollutant concentrations. Ideally, the site should not be where modeled high ground-level concentrations of stack emissions coincide with population centers. Dispersion models can also help evaluate the need for, and the location of, off-site air monitors used to detect fugitive emissions associated with incinerator operations and related hazardous materials-handling activities. If there is concern about the impact of incineration on a specific major food resource, such as a fish hatchery, and ATSDR has data regarding the uptake of the contaminants of concern by the particular food chain species, dispersion modeling can serve to estimate the concentration of emissions that would be available at ground level for food chain uptake.

23.1.1.3.3 Storage of Materials

In addition to the aforementioned issues regarding the incineration process, other concerns of relevance to public health need to be addressed. For example, hazardous waste to be fed to the incinerator and process effluents resulting from the incinerator should be stored in a manner that does not allow for uncontrolled environmental releases of potentially harmful substances. Dry, dusty materials should be enclosed or otherwise stored to prevent windborne transport of contaminated particulates. Wastes containing volatile organic compounds should be stored under conditions that safely collect and remove gases released from the wastes.

Similarly, wet wastes or process effluents should be stored in chemically compatible, leak-resistant containers. Storage areas for such liquid-bearing materials should have dikes or be designed to contain leakage. Processing of wastes, such as blending or shredding operations, may provide opportunities for aerosolization of contaminants. Such conditions should be adequately considered and waste-processing areas are designed to minimize the potential exposure to workers on-site, as well as to people living or working nearby.

23.1.1.3.4 Transportation of Wastes to the Incinerator

The means of transporting hazardous waste into the incinerator plant should be carefully considered. Routes of access should be selected to minimize accident (release) potential and to avoid residential and play areas if possible. For the remediation of Superfund sites, for which no over-the-road hauling is required, care is still needed to avoid spills and releases when transporting the wastes on-site.

23.1.1.3.5 Maintaining Good Performance

Some considerations relevant to public health concerns about modern and effective incineration systems have been described. However, local health officials and citizens of communities with hazardous waste incinerators have expressed to ATSDR their concern that they may not be able to judge a good operation, or that, once the initial trial burns and inspections are completed, the system may not be operated in the same manner as during the testing phase. Citizens have also expressed concern that burning rates will be exceeded or monitoring systems will be overridden.

ATSDR believes that one way to ensure that the system continues to operate in a manner consistent with operating conditions specified in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) contract[15] is for U.S. EPA to conduct frequent, random, unannounced facility inspections and to routinely provide the results to the public. Under some circumstances, permanent on-site inspectors might be advisable.

Another way to ensure continued satisfactory operation is to retest the incinerator periodically. This would be appropriate if the CERCLA incinerator operates at the site for an extended period of time, or there are other indications that it may not be operating properly.

Each time a CERCLA incinerator is relocated, ATSDR recommends that it be retested. A less rigorous trial burn may be appropriate if the incinerator has successfully passed a full trial burn on similar wastes at another site.

23.1.1.3.6 Community Right-to-Know

ATSDR also strongly recommends that information and data for an incinerator's design, testing, operation, and monitoring be shared with the public. The Agency endorses this approach as being consistent with the community right-to-know requirements already in place for industries that use and store hazardous substances in the community.

In addition, as a final caution, it must be remembered that each site is unique, and must be carefully evaluated individually and not by generic extrapolation of data from other sites or studies.

23.1.1.3.7 Summary of Public Health Considerations

The following is a summary of items that should be considered when evaluating proposed or existing hazardous waste incinerators for public health acceptability[10]:

1. The technology used or proposed to be used at a site is proven to be appropriate for, and compatible with, the materials to be burned.
2. In selecting a site for an incinerator, proximity to residential and other populations and local meteorologic conditions is considered to ensure a location that minimizes the prevailing wind transport of air emissions to affected populations.
3. Recognized, acceptable, and when possible, U.S. EPA-approved air modeling is used to help screen and identify potentially impacted areas as mentioned previously.
4. Trial burns, with appropriate stack sampling and analysis, and subsequent continuous emissions monitoring are conducted to demonstrate that the incinerator performs as specified.
5. Adequate training is provided to incinerator operators to ensure that the incinerator is operated in a manner that does not adversely affect the operators' or the community's health.
6. An active inspection program is instituted.
7. Where the incinerator must be at a site close to neighboring populations, local ambient air monitors are used to detect possible site releases to the air requiring corrective or emergency action.
8. Proper management of residual ash is part of the design and operation of the incinerator.
9. Procedures consistent with the community right-to-know philosophy are instituted.

23.1.2 REGULATORY SUMMARY

The standards for hazardous waste incinerators primarily regulate the emissions that result from the combustion process. Specifically, the regulations restrict the emissions of organics, hydrogen chloride (HCl), and PM, as well as fugitive emissions. A very important aspect of the regulations is that compliance with operating conditions specified in the permit is deemed to be compliance with the limits for organics, HCl, and PM.[16]

Incinerators in existence on May 19, 1980, were allowed to continue burning hazardous waste if the units complied with the Part 265, Subpart O,[4] interim status standards. On November 8, 1989, however, interim status was terminated for all existing hazardous waste incinerators unless the owner/operator had submitted a Part B permit application by November 8, 1986. Due to this deadline, there are very few incinerators currently operating under interim status. This chapter, therefore, focuses primarily on the requirements for permitted, rather than interim status, incinerators. There is a comparison of the requirements for permitted and interim status incinerators at the end of Section 23.1.

The stable gases produced by incineration are primarily carbon dioxide and water. Depending on waste composition, however, small quantities of carbon monoxide, nitrogen oxides, HCl, and other gases may form. Also, if combustion is not complete, compounds known as products of incomplete combustion (PICs) may be emitted. RCRA regulations control the amount of HCl released from the APCD.

Another by-product of the combustion process is ash. Ash is an inert solid material composed primarily of carbon, salts, and metals. During combustion, most ash collects at the bottom of the combustion chamber (bottom ash). When this ash is removed from the combustion chamber, it may be considered hazardous waste via the derived-from rule or because it exhibits a characteristic.[17] Some ash, however, is carried up with the gases as small particles, or PM. These particles are also collected in the APCD in accordance with RCRA-established limits.

As a hazardous waste management practice, incineration has two unique attributes[16]:

1. It permanently destroys toxic organic compounds contained in hazardous waste by breaking their chemical bonds and reverting them to their constituent elements, thereby reducing or removing their toxicity.
2. Incineration reduces the volume of hazardous waste by converting solids and liquids to ash. Land disposal of ash, as opposed to untreated hazardous waste, is therefore both safer and more efficient. Incineration, however, will not destroy inorganic compounds, such as metals, present in hazardous waste. Residue ash from incinerators is subject to applicable RCRA standards and may need to be treated for metals or other nonorganic constituents prior to land disposal.

23.1.2.1 Subpart O Applicability

The Subpart O standards apply to units that treat or destroy hazardous waste and which meet the definition of an incinerator. An incinerator is any enclosed device that uses controlled flame combustion and does not meet the criteria for classification as a boiler, sludge dryer, carbon regeneration unit, or industrial furnace. Typical incinerators[3] include rotary kilns, liquid injectors, fixed hearth units, and fluidized bed incinerators (Table 23.1). The definition of an incinerator also includes units that meet the definition of an infrared incinerator or plasma arc incinerator. An infrared incinerator is any enclosed device that uses electric-powered resistance as a source of heat and which is not listed as an industrial furnace. A plasma arc incinerator is any enclosed device that uses a high-intensity electrical discharge as a source of heat and which is not listed as an industrial furnace.

All devices classified as incinerators that burn hazardous waste must follow the Subpart O standards, with the following exception. The Regional Administrator must exempt an owner/operator applying for a permit from all of the incinerator standards in Subpart O, except waste analysis and closure, if the hazardous waste fed into an incinerator is considered as low-risk waste. The criteria for defining a waste as low risk are as follows[4]:

1. A waste is a hazardous waste if it is listed or is identified for ignitability, corrosivity, or both.
2. A waste is a hazardous waste if it is listed, or is identified for reactivity, and will not be burned with other hazardous wastes (this exemption does not apply to wastes that are reactive for generating toxic gases when mixed with water or cyanide or sulfide gases and to a waste contains none of the listed hazardous constituents).

TABLE 23.1
Lists of Devices That Are Considered to Be Incinerators and Industrial Furnaces

Incinerators	Industrial Furnaces
1. Rotary kilns	1. Cement kiln
2. Fluidized bed units	2. Lime kiln
3. Liquid injection units	3. Aggregate kiln
4. Fixed hearth units	4. Phosphate kiln
	5. Coke oven
	6. Blast furnace
	7. Smelting, melting, and refining furnace
	8. Titanium dioxide chloride process oxidation reactor
	9. Methane reforming furnace
	10. Halogen acid furnace
	11. Pulping liquor recovery furnace
	12. Combustion device used in the recovery of sulfur values from spent sulfuric acid

Source: U.S. EPA, *Hazardous Wastes Combustion*, U.S. Environmental Protection Agency, Washington, DC, 2008. Available at http://www.epa.gov/epaoswer/hazwaste/hazcmbst.htm.

23.1.2.2 Performance Standards

The Subpart O standards[4] for hazardous waste incinerators set performance standards that limit the quantity of gaseous emissions an incinerator may release. Specifically, the regulations set limits on the emission of organics, HCl, and PM. The following section outlines the requirements for each of these substances.

23.1.2.2.1 Organics

To obtain a permit, an owner/operator must demonstrate that emission levels set for various hazardous organic constituents are not exceeded. U.S. EPA's principal measure of incinerator performance is its destruction and removal efficiency (DRE). A 99.99% DRE means that one molecule of an organic compound is released to the air for every 10,000 molecules entering the incinerator. A 99.9999% DRE means that one molecule of an organic compound is released to the air for every 1 million molecules entering the incinerator.

Since it would be impossible to monitor the DRE results for every organic constituent contained in a waste, certain principal organic hazardous constituents (POHCs) are selected for monitoring and are designated in the permit. POHCs are selected based on high concentration in the waste feed and difficulty in burning compared with other organic compounds. If the incinerator achieves the required DRE for the selected POHCs, then it is presumed that the incinerator should achieve the same or better DRE for organic compounds that are easier to incinerate.

RCRA performance standards require a minimum DRE of 99.99% for POHCs designated in the permit and a minimum DRE of 99.9999% for dioxin-bearing wastes.

23.1.2.2.2 Hydrogen Chloride

HCl is an acidic gas that forms when chlorinated organic compounds in hazardous wastes are burned. An incinerator burning hazardous waste cannot emit more than 1.8 kg of HCl/h or more than 1% of the total HCl in the stack gas prior to entering any pollution control equipment, whichever is larger.

23.1.2.2.3 Particulate Matter

PM are tiny particles of ash that are carried along with the combustion gases to the incinerator's stack. The incinerator regulations control metal emissions through the performance standard for particulates, since metals are often contained in or attached to the PM. A limit of 180 mg PM/dscm of gas emitted through the stack has been discussed in section.

23.1.2.3 Operating Conditions

The goal of setting operating conditions for hazardous waste incinerators is to ensure compliance with the performance standards discussed in the previous section (i.e., for organics, HCl, and PM). An incinerator permit specifies operating conditions that have been shown in a trial burn to result in the incinerator meeting these performance standards. A very important aspect of the regulations is that compliance with the operating conditions specified in the permit is deemed to be compliance with the performance standards for organics, HCl, and PM.

A RCRA permit for a hazardous waste incinerator sets operating conditions that specify allowable ranges for, and requires continuous monitoring of, certain critical parameters. Operation within these parameters ensures that combustion is performed in the most protective manner and the performance standards are achieved. These parameters, or operating conditions, include[16]

1. Maximum allowable carbon monoxide levels in stack emissions
2. Allowable ranges for temperature
3. Maximum waste feed rates
4. Combustion gas velocity
5. Limits on variations of system design and operating procedures.

In addition, during the startup and shutdown of an incinerator, hazardous waste must not be fed into the unit unless it is operating within the conditions specified in the permit. An incinerator must cease operations when changes in waste feed, incinerator design, or operating conditions exceed the limits designated in its permit.

Operating conditions are also set to control fugitive emissions. Fugitive emissions are gases that escape from the combustion chamber (e.g., gases may escape through the opening where wastes are fed into the combustion chamber) and do not pass through pollution control devices. The two examples of fugitive emission control methods are[4]

1. Maintaining negative pressure in the combustion zone so that air will be pulled into the APCD rather than escaping into the ambient air.
2. Totally sealing the combustion chamber so that no emissions can escape to the environment.

23.1.2.4 Permit Phases

An owner/operator wishing to operate a new hazardous waste incinerator is required to obtain an RCRA permit before construction of the unit commences.

The purpose of a hazardous waste incinerator permit is to allow a new hazardous incinerator to establish conditions including, but not limited to, allowable waste feeds and operating conditions that will ensure adequate protection of human health and the environment. The incinerator permit covers four phases of operation: pretrial burn, trial burn, posttrial burn, and final operating conditions.

23.1.2.4.1 Pretrial Burn

The pretrial burn phase of the permit allows the incinerator to achieve a state of operational readiness necessary to conduct the trial burn. The pretrial burn permit conditions are effective for the minimum time (not to exceed 720 h) required to bring the incinerator to a point of operational readiness to conduct a trial burn. This phase is often referred to as the shakedown period.

23.1.2.4.2 Trial Burn

The trial burn can be seen as the "test drive" of the incinerator. It is the time when the owner/operator will bring the unit up to operational readiness, monitor the key operating conditions, and measure the emissions. The trial burn test conditions are based on the operating conditions proposed by the permit applicant in the trial burn plan submitted to U.S. EPA for evaluation. U.S. EPA establishes conditions in the permit necessary to conduct an effective trial burn, meaning that the burn will be representational of the incinerator's intended day-to-day operation and will yield meaningful data for analysis.

23.1.2.4.3 Posttrial Burn

The posttrial burn period is the time for U.S. EPA to evaluate all of the data that were recorded during the incinerator's trial burn. To allow the operation of a hazardous waste incinerator following the completion of the trial burn, U.S. EPA establishes permit conditions sufficient to ensure that the unit will meet the incinerator performance standards. This posttrial burn period is limited to the minimum time required to complete the sampling, analysis, data computation of trial burn results, and the submission of these results to U.S. EPA.

23.1.2.4.4 Final Operating Conditions

After reviewing the results of the trial burn, U.S. EPA will modify the permit conditions again, as necessary, to ensure that the operating conditions of the incinerator are sufficient to ensure compliance with incinerator standards and protection of human health and the environment. Owners/operators of incinerators must comply with the final permit conditions for the duration of the permit, or until the permit is modified.

23.1.2.4.5 Data in Lieu of Trial Burn

While most incinerators must undergo a trial burn, it is possible for a facility to submit extensive information in lieu of the trial burn. U.S. EPA believes that most combustion units will need to conduct trial burns in order to develop operating conditions that ensure compliance with the performance standards. Data submitted in lieu of the trial burn, therefore, must originate from a unit with a virtually identical design that will burn wastes under virtually identical conditions (i.e., located at the same facility).

23.1.2.5 Waste Analysis

During operation, the owner/operator of an incinerator must conduct sufficient waste analyses to verify that the waste feed is within the physical and chemical composition limits specified in the permit. This analysis may include a determination of a waste's heat value, viscosity, and content of hazardous constituents, including POHCs. Waste analysis also comprises part of the trial burn permit application. U.S. EPA stresses the importance of proper waste analysis to ensure compliance with emission limits.

23.1.2.6 Monitoring and Inspections

The specific monitoring and inspection requirements are that the owner/operator must perform, at a minimum, the following functions while incinerating hazardous waste[4,16]:

1. Monitor the combustion temperature, the waste feed rate, and the indicator of combustion gas velocity on a continuous basis.
2. Monitor carbon monoxide on a continuous basis at a point downstream of the combustion zone and prior to release into the atmosphere.

3. Sample and analyze the waste and exhaust emissions on the request of the Regional Administrator to verify that the operating requirements established in the permit can achieve the performance standards.
4. Conduct daily visual inspections of the incinerator and associated equipment.
5. Test the emergency waste feed cutoff system and associated alarms at least weekly unless otherwise directed by the Regional Administrator—as a minimum, operational testing must be conducted monthly.
6. Place the monitoring and inspection data in the operating log.

23.1.2.7 Management of Residues

If an incinerator burns a listed hazardous waste, the ash is also considered a listed waste. The derived-from rule states that any solid waste generated from the treatment, storage, or disposal of a listed hazardous waste, including any sludge, spill residue, ash, emission control dust, or leachate, remains a hazardous waste unless and until it is delisted. The owner/operator must also determine whether the ash exhibits any of the characteristics of a hazardous waste.

If an incinerator burns waste that only exhibits one characteristic of a hazardous waste, the owner/operator must determine whether the ash exhibits any of the other characteristics of a hazardous waste. Ash that exhibits one characteristic must be managed as a hazardous waste.

23.1.2.8 Closure

At closure, the owner/operator must remove all hazardous waste and hazardous residues from the incinerator equipment site. In addition, throughout the operating period, if the residue removed from the incinerator is a hazardous waste, the owner or operator becomes a generator of hazardous waste and must manage the residue in accordance with the requirements applicable.

23.1.2.9 Comparison of Permitted and Interim Status Incinerators

The requirements for interim status incinerators are very similar to the already discussed regulations for permitted units. The interim status regulations, however, are designed to be self-implementing as the facilities are already in operation on the effective date of the standards. Table 23.2 compares the requirements for permitted and interim status incinerators.

In addition, the trial burn process for interim status incinerators is different from that discussed previously in this chapter. As interim status units were already in operation on the effective date of the regulations, the facility would submit their trial burn plan for approval without ceasing operation. Once this plan is approved, the facility would conduct the trial burn test (or submit data in lieu of the trial burn) and continue operating under interim status until the final permit is issued.

23.1.3 REGULATORY DEVELOPMENTS

23.1.3.1 Notice of Intent to Comply

U.S. EPA carefully considered public participation when promulgating the streamlined permit modification procedures. In order to provide for public involvement early in a source's compliance planning process, U.S. EPA requires owners and operators of combustion facilities to submit a notification of intent to comply (NIC) within one year of promulgation of the final standards indicating whether the source intends to come into compliance with the new standards.[16] In addition to submitting the NIC, U.S. EPA requires covered facilities to provide notice of and host an informal meeting with the community to discuss plans for complying with standards and to submit a progress report within two years of promulgation of the final standards, which demonstrates progress made toward meeting the emissions standards.

TABLE 23.2
Comparison of Permitted and Interim Status Incinerator Requirements

Permitted (Part 264)	Interim Status (Part 265)
Waste Analysis	
Heating value	Heating value
Viscosity	Waste halogen and sulfur content
Appendix VIII	Waste lead and mercury content
Performance Standards	
99.99% DRE for POHCs	Burn hazardous waste only during steady-state operations
99.9999% DRE for POHCs for dioxin-bearing wastes	99.9999% DRE and certification for dioxin-bearing wastes
1.8 kg/h or 1% HCl emissions	
180 mg/dscm PM	
Monitoring and Inspections	
Combustion temperature	Monitor emission control system every 15 min
Waste feed rate	Daily inspection
Combustion gas velocity	Daily operations test
Carbon monoxide (CO)	
Daily inspections	
Weekly operations test	
Closure	
Remove all hazardous waste and residues	Remove all hazardous waste and residues

Source: U.S. EPA, *Introduction to Hazardous Waste Incinerators*, 40 CFR Parts 264/265, Subpart O, EPA530-R-99–052, U.S. Environmental Protection Agency, Washington, DC, February 2000.

23.1.3.2 Waste Minimization and Pollution Prevention

The CAA compliance deadline may cause companies to install simple end-of-pipe emissions controls, instead of pollution prevention process changes. In order to limit this practice and encourage waste minimization, U.S. EPA allows owners and operators of combustion facilities to request a one-year extension to the compliance period in cases where additional time is needed to install pollution prevention and waste minimization measures that reduce the amount of hazardous waste entering combustion feedstreams.[16] Requests for a one-year extension must reasonably document that the waste minimization measures could not be installed in time to meet the three-year compliance period. Decisions to grant the extensions will be made by U.S. EPA or authorized state programs.

23.1.4 SPECIAL ISSUES

As U.S. EPA continues to revise the regulatory program for incinerators in order to adequately protect human health and the environment, the omnibus permitting authority, site-specific risk assessments, and public participation issues have received greater attention. The following discusses both issues in greater detail.

23.1.4.1 Omnibus Permitting Authority

The omnibus provision, added by Congress in the Hazardous and Solid Waste Amendments (HSWA),[18] allows the U.S. EPA Regional Administrator or state to incorporate into a permit any provision deemed necessary to protect human health and the environment. Even if a facility submits a permit application that is complete and technically adequate, if site-specific factors at the facility suggest that typical permit conditions or performance standards will not ensure protection of human health and the environment, U.S. EPA can impose additional conditions to ensure such protection. Regulators can invoke the omnibus authority whenever a facility owner/operator is seeking a new permit or reissue of an expiring permit or when existing permits are reopened for modification (in appropriate circumstances).

U.S. EPA has recommended that permit writers invoke the omnibus provision to more stringently control emissions for toxic metals, HCl, and PICs and to enhance public participation in the combustion permitting process. Also, under the Strategy for Hazardous Waste Minimization and Combustion, U.S. EPA has directed states and regions to conduct site-specific risk assessments[19] using the omnibus authority. These risk assessments can be conducted by either the implementing agency or the facility (with agency oversight) during the permitting process.

23.1.4.2 Public Participation

U.S. EPA published the final Public Participation Rule[20] expanding the role of public participation in the RCRA permitting process. This rule affects incinerators by increasing the extent of public participation during the trial burn process. Specifically, the permitting agency is required to issue a public notice prior to approving a facility's trial burn plan, and must announce the commencement and completion dates for all trial burns. The Public Participation Rule also included some changes to the procedural requirements for permitting interim status facilities.

23.2 BOILERS AND INDUSTRIAL FURNACES

Combustion is a technology employed to burn hazardous waste for energy or materials recovery. This occurs in a group of units collectively known as BIFs. The following sections will provide an overview of the regulation of these units, found in 40 CFR Part 266, Subpart H.[5,21]

When U.S. EPA instituted the RCRA[22] hazardous waste regulations in 1980, it only regulated the combustion of hazardous waste in destruction units. The Agency determined that further study was needed to determine appropriate regulation for units that burn waste to recover energy or materials. This distinction was in line with the Agency's policy of encouraging all types of recycling and reclamation.

However, the HSWA[18] mandated that U.S. EPA examine the risks posed by combustion activities and consider what controls should be placed on the burning of hazardous waste for energy recovery. The first phase of this occurred on November 29, 1985 when U.S. EPA promulgated regulations covering the burning of hazardous waste for energy recovery in BIFs. These standards were largely administrative, covering only the management of the waste prior to burning and notification and recordkeeping. The combustion devices themselves were not subject to technical performance or emissions standards; nor were the facilities governed by the TSDF requirements.

The second phase in developing regulations for BIFs has dramatically changed the requirements for burning hazardous waste in BIFs by subjecting BIFs to almost all of the TSDF standards, including extensive emission controls, waste analysis, and permitting requirements. The regulations were expanded to cover more devices and place some limitations on specialized units. Also, as a result of this final rule, previous standards were entirely removed and the regulations governing the burning of hazardous waste in BIFs were codified in Part 266, Subpart H.[5]

The following sections are designed to familiarize the reader with the regulations affecting hazardous waste processed in BIFs.

23.2.1 REGULATORY SUMMARY

Of the 3 million tons of hazardous waste sent for combustion, about half was processed in BIFs. Boilers are normally used for energy recovery. Hazardous waste fuels provide about 50% of a boiler's fuel requirements and are normally mixed with natural gas or other fuels.[21] There are around

900 boilers operating in the United States ranging from very small boilers to huge utility class boilers. Industrial furnaces, on the other hand, are usually involved in not only energy recovery but also materials recovery. These units are normally commercial facilities that handle the hazardous waste of others for a fee. There are <50 hazardous waste-burning industrial furnaces currently operating in the country.

The following is a summary of the regulations affecting hazardous waste processed in BIFs. These requirements include the general TSDF facility standards, extensive emission control regulations, standards for the direct transfer of waste from a transportation vehicle to a unit, and regulation of residues. Some units are subject to special reduced requirements depending on the type of waste processed in the unit and the unit's capacity. Because of the technically extensive nature of these regulations, only a summary of the requirements is provided here.

23.2.1.1 Applicability and Exemptions

There are two classes of units covered under the Part 266, Subpart H regulations—BIFs. U.S. EPA defines a boiler as an enclosed device that uses controlled flame combustion to recover and export energy in the form of steam, heated fluid, or heated gases. Boilers must have a combustion chamber and a primary energy recovery system of integral design to ensure the effectiveness of the unit's energy recovery system and to maintain a thermal energy recovery efficiency of at least 60%. Finally, in order to meet U.S. EPA's definition of boiler, the unit must export and use at least 75% of the recovered energy off-site.

An industrial furnace is a unit that is an integral part of a manufacturing process and uses thermal treatment to recover materials or energy. The 12 devices that are considered to be industrial furnaces can be found in Table 23.1. An example of such industrial furnaces[23] is shown in Figure 23.2.

23.2.1.1.1 Exemptions

Not all units that meet the definition of boiler or industrial furnace are subject to the BIF standards. The individual unit must first be evaluated against a number of exemptions found in the applicability

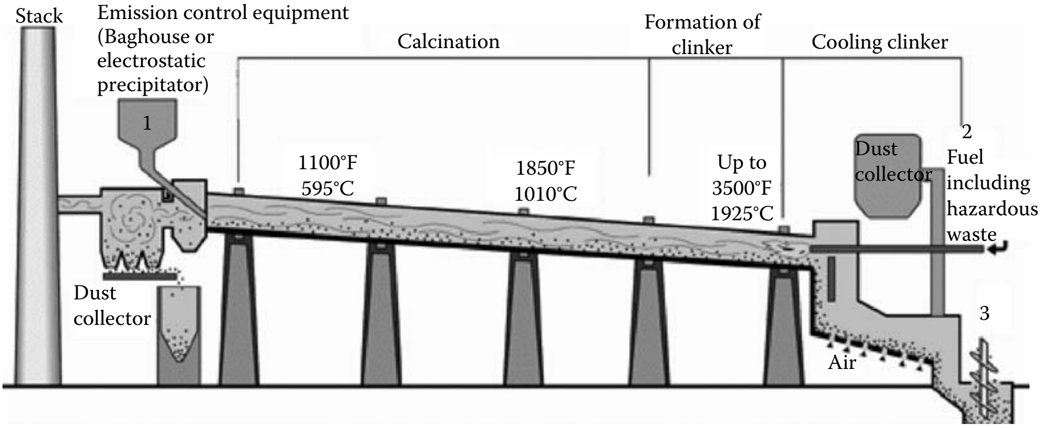

FIGURE 23.2 The dry process of a typical cement kiln. (1) Ground limestone and other raw materials are placed in rotating kiln, (2) the ground materials are heated by fuel (which can include hazardous wastes), introduced at the opposite end of the kiln, and (3) the final product, called "clinker," is cooled and later ground and mixed with gypsum to form cement. (Adapted from Texas Environmental Profiles, *Using Incineration to Reduce Hazardous Characteristics of Waste, State of Texas*, 2009. Available at http://www.texasep.org/html/wst/wst_4imn_incin.html.)

section of the regulations. For a variety of reasons, U.S. EPA determined that the following units do not require stringent regulation under Part 266, Subpart H[5,21]:

- Units burning used oil for energy recovery.
- Units burning gas recovered from hazardous or solid waste landfills for energy recovery.
- Units burning hazardous wastes exempt from regulation under Section 261.
- Units burning hazardous waste produced by conditionally exempt small quantity generators.
- Coke ovens that burn only decanter tank tar sludge from coking operations.

23.2.1.1.2 Conditionally Exempt Units

In addition to these exemptions, there are three types of units that are conditionally exempt from the regulations. These are metal recovery furnaces, precious metal recovery units, and certain other special industrial units. In order to claim these exemptions, owners/operators must provide a one-time written notice claiming the exemption, conduct sampling, and analysis, and maintain records to demonstrate compliance with all applicable requirements. Any waste management prior to burning in this type of unit, and any resulting residues, are subject to applicable hazardous waste regulation.

23.2.1.1.2.1 Metals Recovery Owners/operators of smelting, melting, and refining furnaces that process hazardous waste solely for metal recovery are conditionally exempt from regulation under this subpart. The Agency has established three criteria to determine if hazardous waste is being legitimately burned for metals recovery[5,21]:

1. The heating value of the waste does not exceed 5000 Btu/lb (if so, the waste is considered to be burned for energy recovery).
2. The concentration of Part 261 organic constituents does not exceed 500 mg/kg (if so, the waste is considered to be burned partially for destruction).
3. The waste must have demonstrated recoverable levels of metals. Units that may be covered by this exemption include pyrometallurgical devices such as cupolas, sintering machines, roasters, and foundry furnaces, but do not include cement kilns or halogen acid furnaces.

23.2.1.1.2.2 Precious Metals Recovery Metal recovery units engaged in precious metals recovery are also conditionally exempt from Part 266, Subpart H. Precious metal recovery is defined as the reclamation of economically significant amounts of gold, silver, platinum, palladium, iridium, osmium, rhodium, ruthenium, or any combination of these metals. Provided the owner/operator complies with the alternative requirements, the unit would be exempt from all BIF requirements except for the regulations concerning the management of residues.

23.2.1.1.2.3 Special Industries Certain industrial units, such as secondary lead and nickel–chromium smelters and mercury recovery furnaces, and other units that process wastes from metals recovery normally do not meet the conditions required for being considered as legitimately burned for metals recovery. U.S. EPA revised the BIF standards to conditionally exclude those wastes that are processed for metals recovery, but do not meet the criteria. Waste streams in these units must contain recoverable levels of metals and the waste must not contain more than 500 mg/L of the toxic organics listed in Part 261 to be considered for this conditional exemption.

23.2.1.1.3 Small Quantity Burners

Owners/operators of facilities that burn small quantities of hazardous waste with a heating value of 5000 Btu/lb are also exempt from Part 266, Subpart H.[5] They must, however, comply with the quantity restrictions based on stack height and the surrounding terrain. Also, the hazardous waste firing rate may not exceed 1% of the total fuel requirements. These units are prohibited from burning any waste that contains or is derived from dioxin-bearing wastes. Small quantity burners are required to notify U.S. EPA and maintain facility records documenting compliance with these restrictions. Small quantity burners are also exempt from the requirements in Parts 264/265, Subparts A through L, and Part 270 with respect to the storage of mixtures of hazardous waste and primary fuel, if the waste is stored in tanks that feed fuel directly into the burner.

23.2.1.2 Emission Standards

BIFs are required to comply with strict air emission standards to ensure adequate protection of human health and the environment. These standards are divided into four contaminant categories: organics, PM, metals, and HCl and chlorine (Cl_2). For each category or type of emission, the regulations establish compliance methods and alternatives. Each is addressed in Table 23.3.

23.2.1.2.1 Organics

Burning hazardous waste that contains toxic organic compounds under poor combustion conditions can result in substantial emissions of toxic compounds. This includes both those compounds originally present in the waste as well as the emission of other compounds formed by the partial or incomplete combustion of the waste constituents. These types of emissions can result in an array of adverse health effects, including an increased lifetime cancer risk to humans. U.S. EPA controls organic emissions from BIFs by implementing two types of organic emission performance standards. The first requires the measurement of the unit's DRE, and the second limits the unit's output of PICs.[5]

23.2.1.2.1.1 Destruction and Removal Efficiency The primary measure of the BIF's organic emissions is its DRE. This is basically a measure of how efficiently the BIF is destroying organics. Since it would be impossible to monitor the DRE results for every organic constituent in the waste, certain POHCs are selected for this monitoring. These POHCs are selected based on their high concentration in the waste stream and their difficulty to burn. If the BIF achieves the required DRE for the POHCs, then it should be able to achieve the same, or better, DRE for all other, easier to burn, organics in the waste stream. POHCs are designated in the unit's trial burn plan and permit.

The BIF must achieve a DRE of 99.99% for each POHC in the hazardous waste stream during the unit's compliance test, known as the trial burn.[5] This means that for every 10,000 molecules entering the unit, only one molecule of the POHC is released to the atmosphere. In addition, due to an increased threat to human health and the environment from dioxin, the required DRE for POHCs in dioxin-bearing wastes has been established at 99.9999%, or one released molecule for every 1 million burned. It is important to note that this DRE standard applies only to permitted units.

Under certain conditions, a BIF owner/operator may obtain an exemption from the DRE requirements when burning low-risk waste. Waste can be shown to be low risk if, under a reasonable, worst-case scenario, emissions of organics, and metals do not exceed acceptable levels.

TABLE 23.3
Compliance Methods for Each Category of Emission

Contaminant	Emission Standard	Regulatory Citation Section
Organics	DRE and CO limits	266.104
PM	180 mg/dscm	266.105
Metals	Tiered approach	266.106
Chlorine	Tiered approach	266.107

Source: U.S. EPA, *Boilers and Industrial Furnaces*, 40 CFR Part 266, Subpart H, EPA530-R-99-042, U.S. Environmental Protection Agency, Washington, DC, February 2000.

TABLE 23.4
Options for Owners/Operators of BIFs to Meet Emission Standard

Option	CO Concentration	HC Concentration
Option 1	100 mL/L	No limit
Option 2	Determined in trial burn	20 mL/L

Source: U.S. EPA, *Boilers and Industrial Furnaces*, 40 CFR Part 266, Subpart H, EPA530-R-99-042, U.S. Environmental Protection Agency, Washington, DC, February 2000.

23.2.1.2.1.2 Products of Incomplete Combustion Poor combustion conditions result in the release of a high concentration of organic materials formed during the combustion process. These PICs may be present in the original waste stream or may be new compounds that form during the thermal breakdown and subsequent recombination of organic compounds. In order to control the emission of PICs, U.S. EPA places limits on carbon monoxide (CO) emissions or, if necessary, hydrocarbon (HC) emissions from the unit. The presence of carbon monoxide is an indicator of incomplete combustion. Therefore, a high level of carbon monoxide in emissions is an indicator of incomplete combustion and thus an indication of a high release of PICs. The BIF owner/operator has two options to meet this CO emission standard. They may meet a CO emission standard of 100 mL/L, with no limits on HC emissions, or they may meet an HC limit of 20 mL/L, with CO emission limits based on levels demonstrated during the unit's trial burn (Table 23.4).

23.2.1.2.2 Particulate Matter

The second emission U.S. EPA regulates is PM. PM consists of small dust-like particles emitted from BIFs. Although the particles themselves may cause adverse health effects (e.g., increased asthma), they also provide a point of attachment for toxic metals and organic compounds. The particulates may become caught in the lungs or be absorbed into the environment. To minimize these adverse conditions, U.S. EPA set an emission limit of 180 mg/dscm. BIFs that qualify for the low-risk waste exemption mentioned above, however, are not subject to the PM standard.[5]

23.2.1.2.3 Metals

The third aspect of the emissions standards involves limits on metals. Metals regulated under the BIF standards are categorized as either noncarcinogenic (i.e., antimony, barium, lead, mercury, silver, and thallium) or carcinogenic (i.e., arsenic, cadmium, chromium, and beryllium). The owner/operator can determine the allowable feed or emission rate for each regulated metal by selecting any one of three approaches, called tiers (Figure 23.3). Each tier differs in the amount of monitoring and, in some cases, modeling the owner/operator is required to do.[21]

Factors that may be considered in selecting a tier include the physical characteristics of the facility and surrounding terrain, the anticipated waste compositions and feed rates, and the level of resources available for conducting the analysis. The main distinction between the tiers is the focal

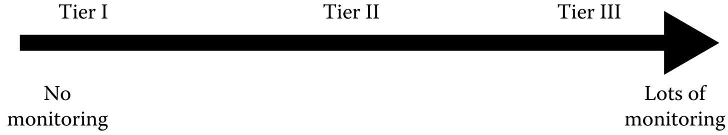

FIGURE 23.3 Continuum of tiers and monitoring. (Adapted from U.S. EPA, *Boilers and Industrial Furnaces*, 40 CFR Part 266, Subpart H, EPA530-R-99-042, U.S. Environmental Protection Agency, Washington, DC, February 2000.)

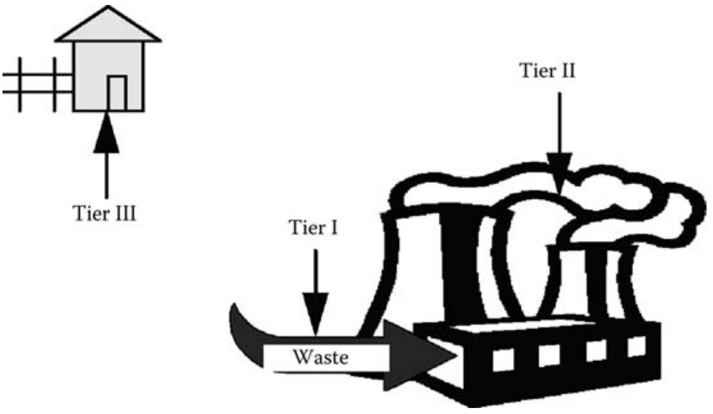

FIGURE 23.4 Focal point of tiers. (Adapted from U.S. EPA, *Boilers and Industrial Furnaces*, 40 CFR Part 266, Subpart H, EPA530-R-99-042, U.S. Environmental Protection Agency, Washington, DC, February 2000.)

point (Figure 23.4). This is the point at which the owner/operator must ensure that the metal concentration of their waste will be below U.S. EPA's acceptable exposure levels for that constituent.

23.2.1.2.3.1 Tier I The focal point of Tier I is the waste feed. This tier limits the hourly feed rate of individual metals into the combustion device. These limits have been developed by U.S. EPA and can be found in Part 266, Appendix I.[5] U.S. EPA established these feed rate limits by considering flue gas flows, stack height, terrain, and land use in the vicinity of the facility. It determined acceptable air quality levels for each type of metal as a function of terrain, stack height, and land use in the vicinity of the facility. This value is also the waste feed rate, as Tier I assumes that 100% of the metals that are fed into the unit will be released into the atmosphere.

23.2.1.2.3.2 Tier II The focal point of Tier II is the stack. This tier limits the emissions of individual metals from the stack. As with Tier I, emission limits have been predetermined by U.S. EPA by considering a number of different factors (i.e., stack height, terrain, and surrounding land use) and can be found in Part 266, Appendix I.[5] Tier II differs from Tier I, however, in that owners/operators are able to conduct emission testing to take credit for reduced metal emissions achieved either by the partitioning of pollutants to bottom ash or products or by the removal of the pollutants through the facility's APCD. By conducting tests to determine how much of the metals fed into the BIF are emitted through the stack, owners/operators using Tier II can conceivably increase the amount of metals in the waste feed by accounting for waste partitioning and pollution control activities.

23.2.1.2.3.3 Tier III The focal point of Tier III is the surrounding environment. Tier III limits must be set such that the metals will not adversely affect the ambient air quality. It allows the owner/operator to use site-specific factors to back calculate from the ambient levels to determine the unit's waste feed. Tier III standards are implemented in the same way as Tier II, by placing emission limits on metals, but unlike Tiers I and II, there are no predetermined levels established by U.S. EPA. Instead, the facility owner/operator determines emission levels by testing emission rates for each individual metal using air dispersion modeling techniques[14,24–26] to predict maximum ground-level metal concentrations that will not adversely affect human health and the environment, and by demonstrating that ambient air levels will not be exceeded.

23.2.1.2.3.4 Adjusted Tier I A BIF owner/operator may choose to adjust the feed rate limits that have been established by combining some of the aspects of Tier I and Tier III. This alternative is implemented in the same way as the Tier I standards, by regulating feed rates into the BIF, but allows for limits that are more relevant to a given facility. As with the Tier III methodology, owners/operators may back calculate maximum allowable emission rates for their facility from acceptable ambient air levels using site-specific air dispersion modeling. These emission limits then become the adjusted feed rate limits for that facility.

23.2.1.2.3.5 Alternative Implementation Owners/operators are also allowed to use a combination of the Tier II and Tier III methodologies. Under this approach, rather than monitoring metal feed rates, a BIF would monitor the emission rates contingent upon approval from the Regional waste management director.

23.2.1.2.4 HCl and Chlorine Gas

The final emission standard under the BIF regulations limits the unit's output of HCl and chlorine gas (Cl_2). These compounds combine with water in the air to form acid rain. They are also a known cause of human respiratory problems. The emission controls are implemented in the same way as the metal emissions, using the tiered approach. The owner/operator has a choice of three tiers with varying focal points. The Tier I and Tier II screening levels for waste feed and stack emission limits are located in Part 266, Appendices II and III.[5]

23.2.1.3 Operating Requirements

Operating requirements for BIFs are determined on a site-specific basis, and serve as day-to-day requirements that the facility must follow in order to ensure compliance with the emission standards set by the regulations. The BIF regulations do not specify precise operating requirements that all units must follow; rather, units must establish operating standards that allow them to meet the emission standards in the regulations. In addition to the general operating standards discussed below, the BIF may establish operating standards for feed rate, combustion temperature, flue gas temperature, contaminant concentrations in stack gases, and other conditions as determined necessary.

23.2.1.3.1 Management Prior to Burning

The management of hazardous waste prior to burning in a BIF is subject to all applicable RCRA regulations. Generators of hazardous waste are required to comply with Part 262 regulations, while transporters of hazardous waste are subject to Part 263. In addition, any storage prior to burning is subject to the hazardous waste storage regulations in Parts 264/265[4] and the permitting requirements of Part 270 unless the unit is a small quantity burner. This management requirement includes storage activities conducted by the burner as well as any intermediaries.

23.2.1.3.2 TSDF Standards

Permitted BIFs are subject to all of the general TSDF standards including general operating standards, preparedness and prevention, contingency plan, use of the manifest system, closure and financial assurance, and corrective action.

23.2.1.3.3 Hazardous Waste Analysis

The BIF owner/operator must perform a waste analysis[27] to identify the type and quantity of hazardous constituents that may be reasonably expected to be found in the waste. The facility must provide an explanation for any constituents not included in the analysis. In addition to the initial analysis, the owner/operator must conduct periodic sampling and analysis to ensure that the hazardous waste is within the limits of the facility's permit.

23.2.1.3.4 Fugitive Emissions

The BIF must be operated such that emissions escaping from the combustion chamber are minimized. The owner/operator has two options from which to choose[21]:

1. Maintain a negative pressure in the combustion zone so that air is pulled into the unit rather than escaping into the atmosphere.
2. Totally seal the combustion chamber so that no emissions can escape to the environment.

23.2.1.3.5 Direct Transfer

Facilities that transfer hazardous waste directly from a transport vehicle (e.g., a tanker truck) to the BIF without first storing the waste must comply with special requirements.[5] Generally, direct transfer operations must be managed in a manner similar to that required by the regulations for hazardous waste storage tanks and containers. In addition, the direct transfer equipment must have a secondary containment system, the owner/operator must visually inspect the operation at least once every hour, and the facility must keep records of these inspections.

23.2.1.3.6 General Standards

In addition to the standards described above, the BIF owner/operator must fulfill requirements for establishing an automatic waste feed cutoff system. The facility must also conduct inspection and monitoring, maintain certain records, and close in accordance with given regulations.

23.2.1.4 Permit Process

An owner/operator wishing to operate a new hazardous waste BIF is required to obtain an RCRA permit before beginning construction of the unit. The purpose of this permit is to allow the new BIF to establish operating conditions that will ensure adequate protection of human health and the environment. The BIF permit process consists of four operational phases: pretrial burn, trial burn, posttrial burn, and final operating conditions.

23.2.1.4.1 Pretrial Burn

The pretrial burn phase of the permit allows the BIF to achieve the state of operational readiness necessary to conduct the trial burn. The pretrial burn permit conditions are effective for the minimum time (not to exceed 720 h) required to bring the BIF to a point of operational readiness to conduct a trial burn. This phase is often referred to as the shakedown period.

23.2.1.4.2 Trial Burn

The trial burn can be seen as the "test drive" of the BIF. It is the time when the owner/operator will bring the unit up to operational readiness, monitor the key operating conditions, and measure the emissions. These conditions are based on the operating conditions proposed by the permit applicant in the trial burn plan submitted to U.S. EPA for evaluation. U.S. EPA establishes the conditions in the permit that are required for conducting an effective trial burn, meaning that the burn will be representational of the BIF's intended day-to-day operation and will yield meaningful data for analysis.

23.2.1.4.3 Posttrial Burn

The posttrial burn period is the time for U.S. EPA to evaluate all of the data that were recorded during the BIF's trial burn. To allow the operation of a hazardous waste BIF following the completion of the trial burn, U.S. EPA establishes permit conditions that are sufficient to ensure that the unit will meet the BIF performance standards. This posttrial burn period is limited to the minimum time required to complete the sampling, analysis, data computation of trial burn results, and the submission of these results to U.S. EPA.

23.2.1.4.4 Final Operating Conditions

After reviewing the results of the trial burn, U.S. EPA will modify the permit conditions again as necessary to ensure that the operating conditions of the BIF are sufficient to ensure compliance with BIF standards and protection of human health and the environment. Owners/operators of BIFs must comply with the final permit conditions for the duration of the permit, or until the permit is modified. The unit must be managed in accordance with all of the operating conditions described in the permit and established by the trial burn.[5]

23.2.1.4.5 Data in Lieu of Trial Burn

While most BIFs must undergo a trial burn, it is possible for a facility to submit extensive information in lieu of the trial burn. U.S. EPA believes that most combustion units will need to conduct trial burns in order to develop operating conditions that ensure compliance with the performance standards. Data submitted in lieu of the trial burn, therefore, must originate from a unit with a virtually identical design that will burn wastes under virtually identical conditions (i.e., located at the same facility).

23.2.1.4.6 Omnibus Authority

The omnibus provision allows the Regional Administrator or state to incorporate into a permit any provision deemed necessary to protect human health and the environment. Specifically, this allows U.S. EPA to incorporate additional terms or conditions not found in the regulations, if site-specific circumstances dictate this result.[21] Under the U.S. EPA Strategy for Hazardous Waste Minimization and Combustion, U.S. EPA directed the states and Regions to conduct site-specific risk assessments (incorporating direct and indirect exposures) into a combustion unit's permit using this omnibus authority. These risk assessments can be conducted by either the implementing agency or the facility (subject to agency oversight) during the permitting process.

23.2.1.4.7 Public Participation

On December 11, 1995, U.S. EPA published a final rule expanding the role of public participation in the RCRA permitting process. This rule affects BIFs by increasing the extent of public participation during the trial burn process. Specifically, the permitting agency is required to issue a public notice prior to approving a facility's trial burn plan and must announce the commencement and completion dates for all trial burns. The Public Participation Rule[20] also included some changes to the procedural requirements for permitting interim status facilities.

23.2.1.5 Interim Status Facilities

To qualify for interim status, the facility must have been in existence on or before August 21, 1991, and must have submitted a Part A permit application by this date. If the facility already had a permit for another activity, owners/operators must have submitted a permit modification under interim status. If the facility was already operating under interim status for another activity, then it was required to comply with the requirements for changes under interim status.

Until U.S. EPA calls in the facility's Part B permit application, where precise permit conditions will be established through a trial burn, owners/operators of interim status BIFs must ensure compliance with emission standards by showing certification of precompliance and certification of compliance. As the deadlines for these certifications have already passed, all interim status BIFs, except for possible extenuating circumstances, should be in the compliance stage.

23.2.1.5.1 Certification of Precompliance

In order to certify precompliance, the owner/operator established operating conditions under which the BIF would meet emissions standards. These operating conditions must have included feed rates of hazardous waste, metals, chlorine and chloride, and ash. The operating conditions should have been documented in a certification of precompliance, submitted by August 21, 1991. Prior to submitting this certification of compliance, interim status owners/operators were not allowed to feed hazardous waste with a heating value of <5000 Btu/lb into a boiler or industrial furnace (5).[5] By requiring burners to demonstrate that a waste's heating value is greater than or equal to 5000 Btu/lb, the Agency was able to ensure a high enough temperature and long enough residence time in the boiler to destroy hazardous constituents at a rate that is protective of human health and the environment.

23.2.1.5.2 Certification of Compliance

Owners/operators that were required to submit a certification of precompliance must have conducted compliance testing to verify the operating conditions on or before August 21, 1992. Within 90 days after compliance testing, the owner/operator must have submitted a certification of compliance containing operating conditions based on the results of the testing. The certification included a description of any changes that had taken place since precompliance, as well as the test data and results of quality assurance and quality control work. Throughout the remainder of interim status, the BIF is required to comply with the operating limits contained in this certification.

As mentioned above, interim status BIFs must be operated much in the same way as those facilities with permits. As with permitted BIFs, owners/operators of interim status BIFs must comply with all applicable TSDF regulations in Part 265. In addition, because interim status facilities have not yet conducted trial burns to ensure compliance with the standards, U.S. EPA has placed some restrictions on their use and what types of hazardous waste these facilities may burn. These restrictions are discussed below.

23.2.1.5.3 Prohibition on Burning Dioxin-Containing Waste

A BIF operating under interim status may not burn dioxin-containing hazardous wastes or any material derived from one of these wastes.

23.2.1.5.4 Special Requirements for Interim Status Furnaces

Interim status furnaces are required to comply with all of the performance standards with the exception of the DRE. In addition, U.S. EPA established special interim status requirements for industrial furnaces to ensure adequate combustion of hazardous waste until more stringent, permitted conditions could be established through completion of the facility's trial burn. These conditions include minimum temperatures, assurance of adequate oxygen, and continuous hydrocarbon monitoring.

These requirements do not apply to a furnace that burns hazardous waste solely as an ingredient. The requirements also do not apply to any furnace that feeds the hazardous waste into the hot end of the furnace, where products are normally discharged and fuels are normally fired.

23.2.1.6 Regulation of Residues

Under the traditional hazardous waste regulations, the derived-from rule requires that anything derived from the treatment, storage, or disposal of a hazardous waste is, itself, a hazardous waste. Thus, any residue generated from the burning of hazardous waste in a BIF would normally be considered a hazardous waste under RCRA. The Bevill Amendments,[21] however, provide three statutory exclusions from the definition of hazardous waste for certain residues: residues from the burning of coal and fossil fuels; cement kiln dust; and residues from the processing of certain mining wastes. Some questions have arisen as to whether these exemptions should apply to residues that are produced when both hazardous waste and fossil fuels are burned. U.S. EPA has ruled that the exemptions may stand if the coburning does not significantly affect the character of the waste residues.

The regulations retain the Bevill exclusion for residues from certain BIFs as long as the burning or processing of the hazardous waste does not significantly affect the character of the residue. These BIFs include[21]

1. Boilers burning primarily coal (i.e., at least 50% coal).
2. Industrial furnaces processing primarily normal ores or minerals (i.e., at least 50% normal nonhazardous raw materials).
3. Cement kilns processing primarily normal raw materials (i.e., at least 50% normal raw materials).

To determine whether the character of a residue has been significantly affected by the burning or processing of hazardous waste, and thus whether the Bevill exemption can be claimed, one of two criteria must be met. As long as the residue meets either criterion, it will qualify for the Bevill exclusion.

The first criterion compares the hazardous waste residues to waste residues that would be found if the BIF were not burning hazardous waste at all. A statistical test describes methods that should be used when comparing the waste-derived residues with these baseline levels to determine whether the character of the residue has been significantly affected.[21] The second criterion compares the concentrations of toxic constituents found in the waste-derived residue with health-based constituent limits.

Provided the residues meet these standards, they would not be regulated as hazardous waste. If results from either part of this test indicate that the character of the residue has not been significantly altered, the BIF residue qualifies for the Bevill exemption. Figure 23.5 describes this process.

23.2.2 REGULATORY DEVELOPMENTS

On April 19, 1996, U.S. EPA published a proposed rule, called the MACT rule, under the joint authority of the RCRA and the CAA, to upgrade the emission standards for HWCs. Specifically, this rule will affect incinerators, cement kilns, and lightweight aggregate kilns. It proposes emission standards for dioxins, furans, mercury, cadmium, lead, PM, hydrochloric acid, chlorine,

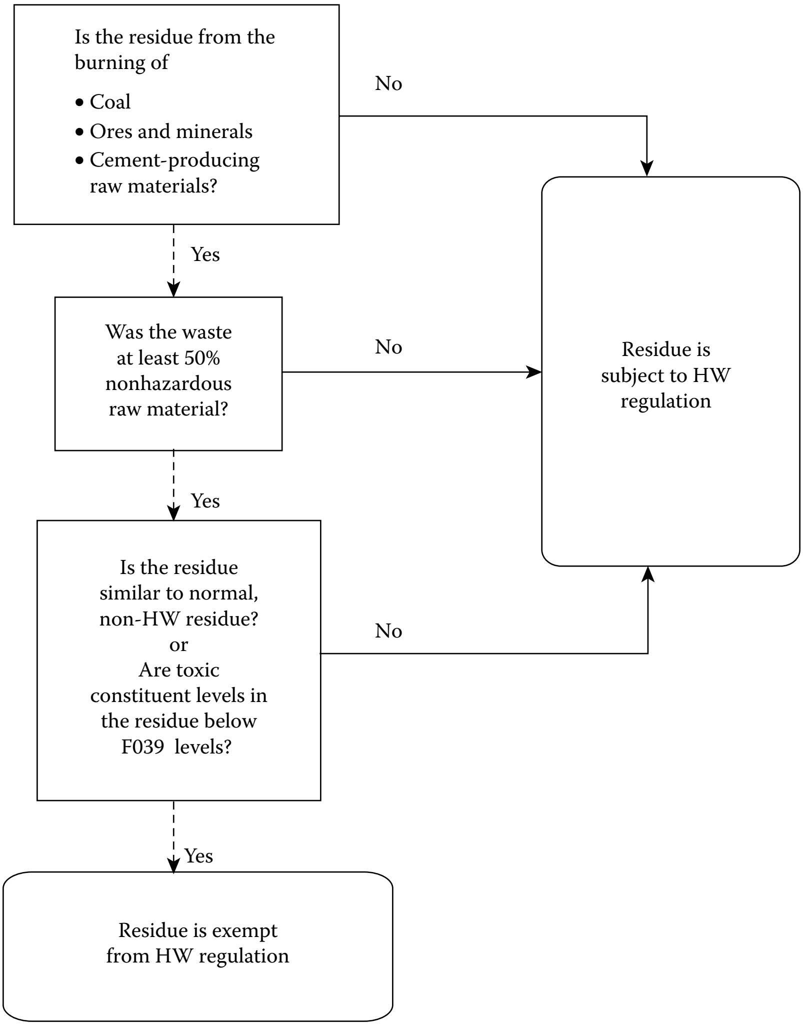

FIGURE 23.5 Regulation of residue from BIFs. (Adapted from U.S. EPA, *Boilers and Industrial Furnaces*, 40 CFR Part 266, Subpart H, EPA530-R-99-042, U.S. Environmental Protection Agency, Washington, DC, February 2000.)

hydrocarbons, carbon monoxide, and several low-volatile metals. U.S. EPA plans to address boilers and other industrial furnaces in another rulemaking. This rule fulfills U.S. EPA's commitment to upgrade emission standards as stated in its 1994 Strategy for Hazardous Waste Minimization and Combustion.

On June 19, 1998, U.S. EPA finalized the first phase of the MACT rule. This final rule includes the comparable fuels exclusion and amendments to the permit modification procedures for combustion facilities.

Many combustion facilities operating under RCRA permits will need to modify their permits in order to comply with the MACT emission standards. The old permit modification procedures are time consuming and may hinder facilities from meeting the three-year compliance deadline established by the CAA. To facilitate meeting the deadline, U.S. EPA revised the RCRA permit modification procedures to explicitly address changes to a facility's design or operations that are necessary to comply with the MACT standards. U.S. EPA designated such changes as Class 1 modifications that require prior Agency approval. It also incorporated a time default of 90 days, with a possible one-time 30-day extension, for the permitting agency to make a decision about the requested modification. If the Agency fails to make a decision within the default time frame, the permittee may consider the request approved. In authorized states, owners and operators of facilities subject to the MACT standards will only be able to take advantage of the revised permit modification procedures if the state has become authorized for the revised modification provisions.

Interim status combustion facilities subject to the MACT standards also have to meet the three-year deadline. Interim status facilities are allowed to implement certain facility changes if the changes do not amount to reconstruction. To ensure that the reconstruction clause does not present an obstacle for interim status facilities trying to implement changes to meet the new MACT emissions levels, U.S. EPA exempted changes necessary to comply with the MACT standards from the reconstruction limit.

23.2.2.1 Notice of Intent to Comply

U.S. EPA considered public participation when promulgating the streamlined permit modification procedures. In order to provide for public involvement early in a source's compliance planning process, U.S. EPA requires owners and operators of combustion facilities subject to the MACT standards to submit a NIC within one year of promulgation of the final standards indicating whether the source intends to come into compliance with the new standards. In addition to submitting the NIC, U.S. EPA requires covered facilities to provide notice of and host an informal meeting with the community to discuss plans for complying with the MACT standards and to submit a progress report within two years of promulgation of the final standards, which demonstrates progress made toward meeting the emission standards.

23.2.2.2 Waste Minimization and Pollution Prevention

The CAA compliance deadline may cause companies to install simple end-of-pipe emission controls, instead of pollution prevention process changes. In order to limit this practice and encourage waste minimization, U.S. EPA allows owners and operators of combustion facilities to request a one-year extension to the MACT compliance period in cases where additional time is needed to install pollution prevention and waste minimization measures that reduce the amount of hazardous waste entering combustion feedstreams. Requests for a one-year extension must reasonably document that the waste minimization measures could not be installed in time to meet the three-year compliance period. Decisions to grant the extensions will be made by U.S. EPA or authorized state programs.

The rule proposes emission standards for dioxins, furans, mercury, cadmium, lead, PM, hydrochloric acid, chlorine, carbon monoxide, hydrocarbons, and several low-volatile metals. It also proposes a new comparable fuels exclusion and makes significant changes to the existing combustion regulations.

23.3 EMISSION STANDARDS FOR COMBUSTORS

U.S. EPA promulgated action plans for the removal of hazardous substances from the environment by reducing air pollutants from HWCs. U.S. EPA's NESHAPs[28,29] achieve significant long-term ecological and human health benefits without imposing significant regulatory burdens on HWCs.

The NESHAPs were issued by U.S. EPA for air quality protection from HWCs. The standards implement a section of the CAA by requiring HWCs to meet HAP emission standards reflecting the application of the MACT.[30]

The combustors affected by this rule detoxify or recover energy from hazardous waste and include incinerators, cement kilns, lightweight aggregate kilns, boilers and process heaters, and hydrochloric acid production furnaces. U.S. EPA estimates that 145 facilities operate 265 devices that burn hazardous waste. These technology-based standards reduce emissions of hazardous pollutants, including lead, mercury, arsenic, dioxin and furans, and HCl and chlorine gas. In addition, emissions of PM are also reduced.

Better control of air pollutants is expected to result in fewer cases of chronic bronchitis, reduced hospitalizations for severe respiratory conditions and cardiovascular problems in adults and children, and fewer cancer cases.[30] Populations residing near HWCs may benefit the most from implementation of these standards.

U.S. EPA promulgated MACT standards for most HWCs on September 30, 1999. These emission standards created a technology-based national cap for HAP emission from the combustion of hazardous waste in these devices. A number of parties, representing both industrial and environmental communities, requested judicial review of this rule, and challenged its emission standards and several implementation provisions. On July 24, 2001, the United States Court of Appeals for the District of Columbia Circuit vacated the emission standards; however, it allowed EPA to promulgate interim standards that were in place since February 13, 2002. U.S. EPA issued the new Final Rule and standards on April 20, 2004. Today's standards[30,31] shown in Tables 23.5 and 23.6 result from the above judiciary and regulatory actions.

U.S. EPA's recommendations regarding stack emission tests, which may be performed at hazardous waste combustion facilities for the purpose of supporting MACT standards and multipathway, site-specific risk assessments, where such a risk assessment has been determined to be necessary by the permit authority, can be found in the U.S. EPA document on Risk Burn Guidance for Hazardous Waste Combustion Facilities.[32] The applicability of the new standards has been demonstrated in the management of hazardous waste incinerators, whose performance was shown to clearly surpass the regulatory requirements in all tested areas.[33]

Readers interested in reviewing information on the implementation of legislation on hazardous waste combustion in the European Union member states are referred to the Europa website.[34]

ACRONYMS

APCD	Air pollution control device
ATSDR	Agency for Toxic Substances and Disease Registry
AWFSOs	Automatic waste feed shutoff devices
BIFs	Boilers and industrial furnaces
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DRE	Destruction and removal efficiency
dscf	Dry standard cubic foot
dscm	Dry standard cubic meter
HAPs	Hazardous air pollutant(s)
HSWA	Hazardous and Solid Waste Amendments
HWCs	Hazardous waste combustors

TABLE 23.5
Summary of Emission Limits for Existing Sources

	Incinerators	Cement Kilns	Lightweight Aggregate Kilns	Solid Fuel-Fired Boilers[a]	Liquid Fuel-Fired Boilers	Hydrochloric Acid Production Furnaces
Dioxin/furans [ng toxicity equivalence (TEQ)/dscm]	0.20 or 0.40 and temperature control <400°F at APCD inlet	0.20 or 0.40 and temperature control <400°F at APCD inlet	0.20 or rapid quench below 400°F at kiln exit	CO or HC and DRE standard as a surrogate	0.40 for dry APCD sources; CO or HC and DRE standard as surrogate for others	CO or HC and DRE standard as surrogate
Mercury	130 μg/dscm	Hazardous waste feed restriction of 3.0 ppmw and 120 μg/dscm maximum theoretical emission concentration (MTEC) or 120 μg/dscm total emissions	120 hazardous waste MTEC feed restriction or 120 μg/dscm total emissions	11 μg/dscm	4.2 E-5lb/MMBtu or 19 μg/dscm depending on Btu content of hazardous waste	Total chlorine (TCl) standard as surrogate
PM	0.013 gr/dscf	0.028 gr/dscf and 20% opacity	0.025 gr/dscf	0.030 gr/dscf	0.035 gr/dscf	TCl standard as surrogate
Semivolatile metals (lead + cadmium)	230 μg/dscm	7.6 E-4 lb/MMBtu and 330 μg/dscm	3.0 E-4 lb/MMBtu and 250 μg/dscm	180 μg/dscm	8.2 E-5 lb/MMBtu or 150 μg/dscm depending on Btu content of hazardous waste	TCl standard as surrogate

Low-volatile metals (arsenic + beryllium + chromium)	92 µg/dscm	2.1 E-5 lb/MMBtu and 56 µg/dscm	9.5 E-5 lb/MMBtu and 110 µg/dscm	380 µg/dscm	1.26 E-4 lb/MMBtu or 370 µg/dscm depending on Btu content of hazardous waste	TCl standard as surrogate
TCl (HCl + chlorine gas)	32 ppmv	120 ppmv	600 ppmv	440 ppmv	5.08 E-2 lb/MMBtu or 31 ppmv, depending on Btu content of hazardous waste	150 ppmv or 99.923% system removal efficiency
Carbon monoxide (CO) or hydrocarbons (HC)	100 ppmv CO or 10 ppmv HC		100 ppmv CO or 20 ppmv HC	100 ppmv CO or 10 ppmv HC		
DRE	99.99% for each principal organic hazardous pollutant. For sources burning hazardous waste F020, F021, F022, F023, F026, or F027, however, 99.9999% for each principal organic hazardous pollutant					

Source: U.S. EPA, *Fact Sheet—Maximum Achievable Control Technology (MACT) Standards*, EPA530-F-05-018, U.S. Environmental Protection Agency, September 2005 and U.S. EPA, 40 CFR Parts 9, 63, 260, 264, 265, 266, 270 and 271, National emission standards for hazardous air pollutants: Final standards for hazardous air pollutants for hazardous waste combustors, final rule, *Federal Register*, 70, 196, October 12, 2005.

[a] Standards expressed as mass of pollutant per million Btu contributed by the hazardous waste.

TABLE 23.6
Summary of Emission Limits for New or Reconstructed Sources

	Incinerators	Cement Kilns	Lightweight Aggregate Kilns	Solid Fuel-Fired Boilers[a]	Liquid Fuel-Fired Boilers	Hydrochloric Acid Production Furnaces
Dioxin/furans (ng TEQ/dscm)	0.11 for dry APCD and/or waste heat boiler (WHB) sources; 0.20 for other sources	0.20 or 0.40 and temperature control <400°F at APCD inlet	0.20 or rapid quench <400°F at kiln exit	CO or HC and DRE standard as a surrogate	0.40 for sources with dry APCD; CO or HC and DRE standard as surrogate for other sources	CO or THC and DRE standard as surrogate
Mercury	8.1 μg/dscm	Hazardous waste feed restriction of 1.9 ppmw and 120 μg/dscm MTEC or 120 μg/dscm total emissions	120 hazardous waste MTEC feed restriction or 120 μg/dscm total emissions	11 μg/dscm	1.2 E-6 lb/MMBtu or 6.8 μg/dscm depending on Btu content of hazardous waste	TCl as surrogate
PM (gr/dscf)	0.0015	0.0023 and 20% opacity	0.0098	0.015	0.0087	TCl as surrogate
Semivolatile metals (lead + cadmium)	10 μg/dscm	6.2E-5 lb/MMBtu and 180 μg/dscm	3.7 E-5 lb/MMBtu and 43 μg/dscm	180 μg/dscm	6.2 E-6 lb/MMBtu or 78 μg/dscm depending on Btu content of hazardous waste	TCl as surrogate
Low-volatile metals (arsenic + beryllium + chromium)	23 μg/dscm	1.5E-5 lb/MMBtu and 54 μg/dscm	3.3 E-5 lb/MMBtu and 110 μg/dscm	190 μg/dscm	1.41 E-5lb/MMBtu or 12 μg/dscm depending on Btu content of hazardous waste	TCl as surrogate
TCl (HCl + chlorine gas)	21 ppmv	86 ppmv	600 ppmv	73 ppmv	5.08 E-2 lb/MMBtu or 31 ppmv depending on Btu content of hazardous waste	25 ppmv or 99.987% SRE
Carbon monoxide (CO) or hydrocarbons (HC)	100 ppmv CO or 10 ppmv HC		100 ppmv CO or 20 ppmv HC	100 ppmv CO or 10 ppmv HC		
DRE	99.99% for each principal organic hazardous pollutant. For sources burning hazardous waste F020, F021, F022, F023, F026, or F027, however, 99.9999% for each principal organic hazardous pollutant					

Source: U.S. EPA, *Fact Sheet—Maximum Achievable Control Technology (MACT) Standards*, EPA530-F-05-018, U.S. Environmental Protection Agency, September 2005 and U.S. EPA, 40 CFR Parts 9, 63, 260, 264, 265, 266, 270 and 271, National emission standards for hazardous air pollutants: Final standards for hazardous air pollutants for hazardous waste combustors, final rule, *Federal Register*, 70, 196, October 12, 2005.

[a] Standards are expressed as mass of pollutant per million Btu contributed by the hazardous waste.

MACT	Maximum Achievable Control Technology
MMBtu	Million British thermal unit
MTEC	Maximum theoretical emission concentration—feed rate divided by gas flow rate
NESHAPs	National Emission Standards for Hazardous Air Pollutants
ng	Nanograms
NIC	Notification of intent to comply
PICs	Product of incomplete combustion
PM	Particulate matter
POHCs	Principal organic hazardous constituents
ppmv	Parts per million by volume
ppmw	Parts per million by weight
RCRA	Resource Conservation and Recovery Act
SRE	System removal efficiency
TCl	Total chlorine
TEQ	Toxicity equivalence
TSDFs	Treatment, storage, and disposal facilities
U.S. EPA	U.S. Environmental Protection Agency
WHB	Waste heat boiler

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24 Remediation from MTBE and Other Fuel Oxygenates

Nazih K. Shammas

CONTENTS

24.1 INTRODUCTION

Fuel oxygenates, including methyl tertiary-butyl ether (MTBE), have been widely used in the United States for the past several decades as an additive to gasoline intended either to boost octane ratings or to reduce air pollution. The gasoline containing these oxygenates has been stored in aboveground and underground storage tanks (ASTs and USTs) at a wide range of facilities, including refineries, terminals, service stations, and by end users; gasoline has been transported throughout the United States via pipeline, barge, rail, and truck. As a result of leaks and spills, MTBE, other fuel oxygenates, and other gasoline components have been found in soil and groundwater at these sites. Federal and state studies have found that these components, including MTBE, have reached drinking water sources in many locations, including areas where the use of oxygenated fuel has not been mandated.

The United States Environmental Protection Agency (U.S. EPA) has identified several hundred MTBE-contaminated sites that have performed treatment of soil and groundwater to remove or destroy MTBE.[1] Many of these sites have also treated other fuel components, primarily benzene, toluene, ethylbenzene, and xylene (BTEX), and some have treated fuel oxygenates other than MTBE. Although others have reported about treatment technologies for MTBE cleanup,[2] only limited information has been published about cleanup of other oxygenates. These oxygenates include ether compounds, such as ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), diisopropyl ether (DIPE), and tert-amyl ethyl ether (TAEE), as well as alcohol compounds, such as tert-butyl alcohol (TBA), tert-amyl alcohol (TAA), ethanol, and methanol.

This chapter provides an overview of the treatment technologies used to remediate groundwater, soil, and drinking water contaminated with MTBE and other fuel oxygenates. The treatment methods discussed include air sparging, soil vapor extraction (SVE), multiphase extraction (MPE), *in situ* and *ex situ* bioremediation, *in situ* chemical oxidation (ISCO), pump-and-treat, and drinking water treatment. Information in this chapter can be used to help evaluate these technologies based on their effectiveness at specific sites. The chapter summarizes available performance and cost information for these technologies, examples of where each has been used, and additional sources of information.

This chapter may be useful to cleanup professionals and researchers; federal, state, and local regulators; remediation consultants; water treatment plant designers and operators; and other interested parties. The chapter is intended to be a screening tool that can be used to identify treatment technologies for soil, groundwater, and drinking water contaminated with MTBE and other fuel oxygenates. The applicability of a particular treatment technology is site-specific, and depends heavily on factors such as site conditions and treatment goals. Decisions about the use of a specific treatment approach will require analysis, possibly including treatability or pilot-scale studies.

U.S. EPA's MTBE Treatment Profiles Website[3] provides site-specific data about the use of *in situ* and *ex situ* technologies that have been used to treat MTBE in groundwater, soil, and drinking water. The website contains information about more than 400 projects, including information about the technology used, project scale, performance, and cost. The treatment performance and cost data presented in this chapter provide readers with

1. Data from actual field applications, focusing on full-scale and relatively large field demonstrations, including design and operation information about the use of treatment technologies in hundreds of projects.
2. Information about both conventional and innovative technologies that have been used to successfully treat MTBE.
3. Preliminary information about treatment of fuel oxygenates other than MTBE.
4. Lessons learned about the application of these technologies to clean up media contaminated with MTBE and other fuel oxygenates.

Treatment performance and cost are site-specific and depend on many factors. These factors include site conditions (such as soil types, permeability, conductivity, redox conditions, and degree of heterogeneity), technology design and operation, and regulatory considerations such as cleanup levels. Additional factors include duration of the release (such as a gasoline leak), presence of downgradient water supply wells, and distribution of contaminants in soil and groundwater.[4]

While U.S. EPA has not promulgated a federal cleanup level for MTBE, some states have established cleanup levels. However, these vary by state, ranging from 5 to 202,000 μg/L, a difference of more than three orders of magnitude.[1] Because of the variation in MTBE cleanup levels, after-treatment MTBE concentrations are reported based on information provided in the source documents, and are not compared against a common cleanup level for all projects.

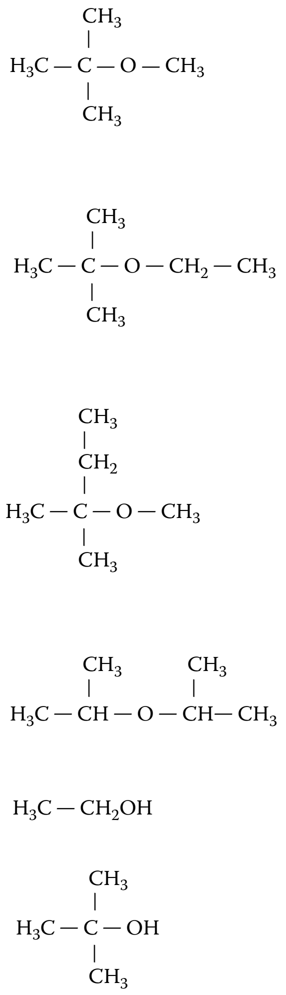
24.2 BACKGROUND

24.2.1 Fuel Oxygenates

Fuel oxygenates are oxygen-containing compounds used as gasoline additives to increase octane ratings and produce cleaner burning fuel. The common oxygenates fall into two major chemical groups: ether compounds, consisting of organic compounds characterized by an oxygen atom linking two hydrocarbon groups, or alcohols, consisting of an alkyl group (such as methyl, ethyl, or isopropyl) bonded to a hydroxyl (oxygen–hydrogen) group. In addition to MTBE and ethanol, other common oxygenates include TBA, TAME, ETBE, and DIPE. TAEE, TAA, and methanol have also been used to a lesser extent. Figure 24.1 shows the molecular structure of commonly used oxygenates. Some of these oxygenates could also be present in commercial formulations of other oxygenates as by-products or degradation products. For example, TBA is often found in commercial formulations of MTBE.

Oxygenates came into widespread use in the United States in the late 1970s as an octane booster, replacing alkyl lead additives, which were being phased out in an effort to reduce lead emissions from vehicles. The use of oxygenates in gasoline was increased after the passage of the 1990 Clean Air Act Amendments that included requirements to increase the oxygen content of fuel to reduce air emissions. The amendments required the use of oxygenated fuel (Oxyfuel) with a minimum of 2.7% by weight oxygen in 39 carbon monoxide nonattainment areas during wintertime and reformulated gasoline (RFG) with a minimum of 2.0% by weight during the remainder of the year.[5]

In 1998, approximately 30% of all gasoline in the United States contained oxygenates. At that time, MTBE was the most common fuel oxygenate, present in more than 80% of oxygenated fuels. However, due to increasing restrictions on the use of MTBE, this percentage has decreased over the past several years. In 1998, ethanol was the second most common fuel oxygenate, present in about



Methyl tert-butyl ether (MTBE)

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H_3C - & C & - O - CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Ethyl tert-butyl ether (ETBE)

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H_3C - & C & - O - CH_2 - CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Tert-amyl methyl ether (TAME)

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ & CH_2 & \\ & | & \\ H_3C - & C & - O - CH_3 \\ & | & \\ & CH_3 & \end{array}$$

Diisopropyl ether (DIPE)

$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ H_3C - & CH & - O - & CH & - CH_3 \end{array}$$

Ethanol

$H_3C - CH_2OH$

Tert-butyl alcohol (TBA)

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ H_3C - & C & - OH \\ & | & \\ & CH_3 & \end{array}$$

FIGURE 24.1 Molecular structures of common fuel oxygenates. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

15% of oxygenated fuels. Other oxygenates were used in the remaining 5% of oxygenated fuels. As of 2002, 17 states and the District of Columbia were required to use gasoline that contains MTBE or other oxygenates to reduce air pollution. Recent surveys have found that MTBE is present in states that did and did not use RFG. MTBE has been found in gasoline, as well as heating oil and diesel fuel. Sources of MTBE included areas used for storage, transportation, and use.[5] The Refs [5–7] contain additional information on the historic use of oxygenates.

24.2.2 Sources of Oxygenates in the Environment

Oxygenates have been widely used in the United States for the past several decades as an additive to gasoline intended either to boost octane ratings or to reduce air pollution. A significant proportion of more than 100 billion gal of gasoline used in the United States annually has contained MTBE and other oxygenates at >10% by volume. The volume of MTBE, ethanol, and other oxygenates used in RFG and Oxyfuel in 1997 was estimated to be about 11 million, 2 million, and 700,000 gallons, respectively.[8] The gasoline containing these oxygenates is stored in ASTs and USTs at a wide range of facilities, including refineries, terminals, service stations, and by end users; gasoline has been transported throughout the United States via pipeline, barge, rail, and truck. There are an estimated 3.7 million USTs in the United States, including 700,000 regulated gasoline USTs at approximately 250,000 facilities and approximately 3 million underground fuel storage tanks that are exempt from federal regulations (e.g., certain farm and residential and home heating oil tanks).[5] Gasoline has been released to the environment through spills and leaks from ASTs and USTs, as well as from manufacturing, storage, and transport operations.

24.2.3 Prevalence of Contamination by Oxygenates in the Environment

MTBE has been detected nationwide in soil and groundwater. Federal and state studies have found that MTBE contamination has reached drinking water sources in many locations, including areas where the use of oxygenated fuel has not been mandated.[9] This MTBE contamination has also been documented in surface water bodies resulting from direct spills, storm water runoff, and emissions from watercraft. Additional information on the extent of contamination by MTBE can be found in several references of federal and state studies.[9–13]

Of the 44 states that reported testing for MTBE at leaking tank sites, 35 states reported finding MTBE in the groundwater at least 20% of the time they sampled for it. Twenty-four states reported finding MTBE at least 60% of the time.[9]

Information about the prevalence of other oxygenates in the environment is limited. However, there is evidence that other oxygenates may be found at sites contaminated with MTBE; non-MTBE oxygenates were identified as a contaminant at 29 of the projects in U.S. EPA's database. In addition, several surveys have assessed the nature and extent of contamination with other oxygenates within the United States.[11,14,15]

24.2.4 Concerns about Contamination with Oxygenates

There have been several assessments of research concerning the health effects of MTBE and other oxygenated fuels.[16,17] Recently, results of a study of the movement of MTBE between tissues in human volunteers were published.[18] U.S. EPA is currently updating its assessment of the health effects of MTBE.

There is uncertainty as to what levels of MTBE in drinking water cause a risk to public health.[9] U.S. EPA has issued an advisory suggesting that drinking water should not contain MTBE in concentrations >20–40 μg/L, based on taste and odor concerns, but has not issued a federal maximum contaminant level (MCL) for MTBE, which will be based on the ongoing U.S. EPA studies.[1]

In addition, 31 states have established standards, guidelines, advisory levels, or action levels (some based on the U.S. EPA advisory concentrations) for the maximum concentration of MTBE allowable in drinking water. California Department of Health Services established a primary MCL of 13 μg/L, corresponding to the *de minimis* cancer risk derived from animal studies and a secondary MCL of 5 μg/L for taste and odor concerns.[19] Forty-two states have established cleanup levels or guidelines (some site-specific) for MTBE in soil and groundwater. MTBE drinking water standards range from 5 to 240 μg/L, with 90% of state standards ≤100 μg/L. Soil cleanup levels range from 5 to 280,000 μg/kg and groundwater cleanup levels range from 5 to 202,000 μg/L, considering both potable and nonpotable uses for groundwater.[10,20,21] More than 75% of the states have groundwater cleanup values <100 μg/L.

Only limited information is available about the health risks of oxygenates other than MTBE. Fewer states have established standards and cleanup levels for these contaminants than for MTBE. Currently, there are no federal drinking water advisory or cleanup levels for these other fuel oxygenates. Several states have established, and some states have plans to establish, cleanup levels for other oxygenates.[21] Table 24.1 summarizes the number of states that have cleanup levels for fuel oxygenates along with the range of cleanup levels established for each.

24.2.5 ASSESSMENT OF OXYGENATES IN THE ENVIRONMENT

Analytical methods for petroleum hydrocarbons (usually BTEX) are well established and some of these protocols have been modified to include oxygenates as individual target compounds. Until recently, validated U.S. EPA analytical methods existed for only a few fuel oxygenates (specifically ethanol, methanol, and TBA). Methods that were developed for analysis of petroleum hydrocarbons in water samples may not be appropriate for fuel oxygenates for several reasons, such as analytical instruments may not routinely be calibrated for oxygenates, inappropriate methods may be used for sample analysis, detection limits (particularly for alcohols) may be higher than regulatory standards, or acid-catalyzed hydrolysis (breakdown) of ethers may occur during sample processing and analysis. In April 2003, U.S. EPA published a fact sheet[20] that specifies steps that may be taken to address potential analytical problems with oxygenate analysis. U.S. EPA has found that using its approach consistently results in detection limits of 5 μg/L or lower for MTBE, TBA, ETBE, TAME, TAEE, TAA, DIPE, and acetone.

Other researchers have provided additional information related to the methods used for the analysis of fuel oxygenates. The following references provide more detailed information about this subject.[8,22,23]

TABLE 24.1
State Cleanup Levels for Fuel Oxygenates in Groundwater

Fuel Oxygenate	States with Cleanup Level 2004	Lowest Cleanup Level (μg/L)	Highest Cleanup Level (μg/L)
MTBE	42	13	202,000
TBA	11	12	11,000
DIPE	7	0.438	20,000
TAME	6	25	980
ETBE	5	24	50
Ethanol	6	50	1,900,000
Methanol	11	50	16,000

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

24.2.6 Migration of Oxygenates in the Environment

MTBE and other oxygenates typically enter the environment blended with gasoline or other refined fuel products. However, these oxygenates migrate differently within the environment because of the differences in physical properties between oxygenates and the other components of gasoline, such as BTEX, of which benzene is typically the most common contaminant of concern. Table 24.2 contains a summary of some properties that influence the migration of MTBE and other oxygenates in the environment. These physical properties also influence the treatability of MTBE and other oxygenates.

Fuel oxygenates generally exhibit the following physical properties relative to benzene:

1. Greater tendency to partition into the vapor phase from the nonaqueous phase (vapor pressure) (with the exception of TBA, ethanol, and TAME).
2. Greater solubility in water.
3. Lesser tendency to partition to organic matter in soil (soil adsorption coefficient).
4. Lesser retardation factor (slowing of migration with groundwater due to sorption to aquifer matrix).
5. Lesser tendency to partition into the vapor phase from the aqueous phase (Henry's law constant).

Because of their relatively higher vapor pressure, ether-based oxygenates in fuel will tend to volatilize from releases (nonaqueous phase) exposed to the open air more rapidly than benzene. Alcohol-based oxygenates will volatilize less rapidly than benzene. However, once fuel oxygenates enter the subsurface and become dissolved in groundwater (aqueous phase), they are significantly less volatile (lower Henry's constant) than benzene. Oxygenates are many times more soluble than benzene; the concentrations of MTBE in groundwater as high as 1,000,000 μg/L are not uncommon. Also, because MTBE dissolved in groundwater will partition (as a function of its soil adsorption coefficient) to the organic matter in the surrounding soil less readily than benzene, a dissolved MTBE plume typically migrates faster than a dissolved benzene plume (lower retardation factor). As a result, MTBE contamination can result in a relatively larger groundwater plume, compared with plumes originating from gasoline constituents.[24,25]

While all fuel oxygenates are more water soluble than other gasoline components (benzene), variations in molecular structures result in a range of physical properties and affect the way each of them migrate in the environment. Figure 24.2 summarizes the physical properties discussed above for each of the common fuel oxygenates relative to benzene, which is most often the chemical of concern in gasoline. While the physical properties for each oxygenate are different, there are similarities among the alcohols and ethers. For example, as shown in Figure 24.3, alcohol-based oxygenates have a relatively greater water solubility and a much lower Henry's constant than the ether-based oxygenates. Other properties such as the soil partition coefficient, vapor pressure, and retardation factor do not adhere to these same groupings.

24.2.7 Effect of Oxygenates' Properties on Their Treatment

The properties of MTBE and other oxygenates, including water solubility, vapor pressure, soil adsorption coefficient, retardation factor, and Henry's law constant, affect their fate and transport in the environment relative to other contaminants. These same properties also affect the selection and design of remediation technologies used to address soil and water contaminated with oxygenates. In general, the same types of treatment technologies have been applied for the treatment of BTEX and MTBE; however, design and operating conditions for MTBE may not be the same as for treatment of BTEX. For example, carbon-based adsorption materials that work well for BTEX may not be effective in the removal of MTBE.

TABLE 24.2
Properties of Fuel Oxygenates and Other Fuel Constituents

Chemical	Pure Phase Solubility (mg/L)[a]	Solubility into H_2O from Gasoline (mg/L)[a]	log K_{oc}	Vapor Pressure at 25°C, at 20°C (mm Hg)[a]	Henry's Law Constant (Dimensionless)	Retardation Factor		Molecular Weight (g/mol)	Boiling Point (°C)	Density (g/L)	Octane Number	Taste Threshold in Water (mg/L)	Odor Threshold (mg/L)
						Soil A[b]	Soil B[c]						
Benzene	1780	<100	1.5–2.2	76–95.2 73	0.22	1.59	3.38	78.11	80.1	0.88	94	500	0.5
MTBE	43,000–54,300 48,000	5500 3393 5241	1.0–1.1	245–256 240	0.024–0.12	1.09	1.38	88.2	55.2	0.74	110	20–40	0.053
TBA	Miscible	25,000	1.57	40–42 41	0.00048–0.00059	1.31	2.25	74.1	82.4	0.79	100	NA	21
DIPE	2039–9000 at 20°C	804 745	1.46–1.82	149–151 at 20°C	0.195–0.41	1.37	2.47	102.2	68	0.73	NA	NA	NA
ETBE	26,000 12,000	3300 1018 1365	1.0–2.2	152 130	0.11	1.33	2.34	102.2	72.2	0.74	112	47	0.013
TAME	20,000 12,000	2400 1210 1220	1.3–2.2	68.3 75	0.052	1.47	2.89	102.2	86.3	0.77	105	128	0.027
Ethanol	Miscible	57,000	0.20–1.21	49–56 544	0.00021–0.00026	1.04	1.17	46.1	78.5	0.79	115	NA	49
Methanol	Miscible	NA	0.44–0.92	121.6	0.00011	1.04	1.16	32.1	64.7	0.79	NA	NA	NA

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

[a] Data from various locations.

[b] Soil condition A: Organic fraction $f_{oc} = 0.001$ mg/mg, bulk density = 1.75 kg/L, porosity = 0.25.

[c] Soil condition B: $f_{oc} = 0.004$ mg/mg, bulk density = 1.75 kg/L, porosity = 0.25.

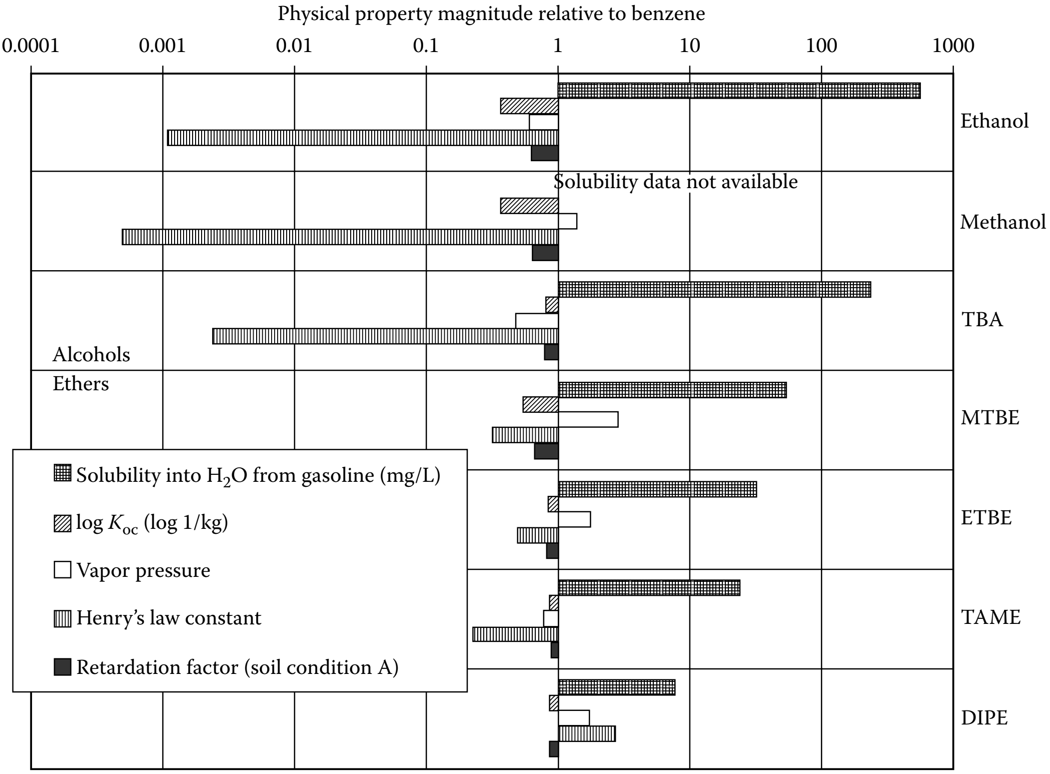


FIGURE 24.2 Physical properties of fuel oxygenates relative to benzene. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

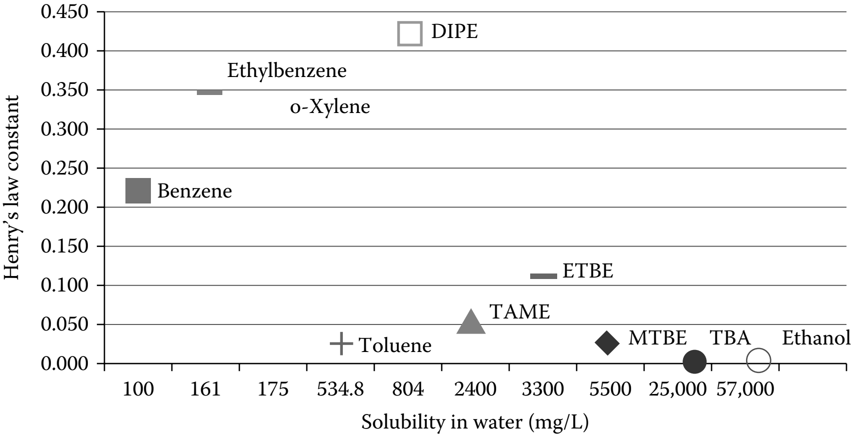


FIGURE 24.3 Relative solubility and Henry's law constants for selected fuel oxygenates. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

BTEX is the contaminant group most often targeted for treatment at gasoline spill sites, and in many cases the treatment systems have been specifically designed to reduce concentrations of benzene. In some cases, a treatment system designed to remove benzene can also remove the oxygenate contamination. However, because of the differences in the physical properties of oxygenates relative to benzene, certain oxygenates might not be effectively treated by a system designed to treat benzene. Also, because the physical properties of individual oxygenates also differ from one another, a treatment system designed to treat one oxygenate may not effectively treat another oxygenate. An overview of the effects of the physical properties of oxygenates on the effectiveness of various remediation technologies is included in the following sections. Primary considerations related to the treatment of oxygenates include

1. The vapor pressures of most oxygenates, with the exception of ethanol, TBA, and TAME, can result in them being more readily volatilized from soil using certain technologies, such as SVE or MPE.[25,26]
2. The relatively low Henry's constants (the ratio of a compound's concentration in air relative to its concentration in water) of oxygenates can result in them being more difficult to strip from contaminated groundwater via air sparging or air stripping as part of a pump-and-treat remedy.
3. The presence of an ether bond or hydroxyl group in oxygenates results in these compounds being significantly less likely to partition to organic matter (K_{oc}), such as in the use of granular activated carbon (GAC) in pump-and-treat remedies.
4. Because they can be chemically oxidized or biologically degraded, chemical oxidation and biodegradation technologies (both *in situ* and *ex situ*) can be effective in the treatment of oxygenates.

24.2.8 TYPES OF TECHNOLOGIES FOR TREATMENT OF SOIL, GROUNDWATER, AND DRINKING WATER CONTAMINATED WITH OXYGENATES

Technologies that have been used to treat groundwater and soil contaminated with oxygenates include air sparging, SVE, MPE, *in situ* bioremediation, ISCO, groundwater extraction, aboveground treatment (i.e., pump-and-treat or drinking water treatment), and phytoremediation. Aboveground treatment for extracted groundwater includes technologies such as air stripping, activated carbon, chemical oxidation, and bioremediation. Air sparging, SVE, and MPE rely generally on the use of air flow to remove contaminants. Bioremediation and ISCO rely on biological and chemical reactions to destroy MTBE and other oxygenates, while pump-and-treat and drinking water treatment rely primarily on physical and chemical parameters to separate MTBE and oxygenates from water. Other discussed technologies, such as phytoremediation, *in situ* thermal treatment, and permeable reactive barriers (PRBs), have also been used at sites contaminated with oxygenates, although less often at the sites in U.S. EPA's MTBE database. Nontreatment remedies that have been used include excavation, free product recovery, monitored natural attenuation (MNA), and institutional controls (ICs). Additional sources of information that discuss treatment of MTBE using multiple technologies include Refs [27,28].

24.2.9 THE USE OF TECHNOLOGIES TO TREAT SOIL AND WATER CONTAMINATED WITH OXYGENATES

Remediation of a site contaminated with MTBE and other fuel oxygenates is often conducted using a phased approach. Often, the first phase of remedial action at a site focuses on protecting receptors at the site, such as nearby buildings or drinking water supplies. The second phase generally involves controlling the source of the contamination, for example, excavation of leaking USTs or contaminated soil, or free product removal. The next phase typically involves the active cleanup of residual and dissolved contamination using one or more treatment technologies. Active cleanup of residual and dissolved contamination is often followed by MNA.[29]

Technologies might be applied sequentially or simultaneously in different parts of a contaminated site, depending on the concentration of oxygenates and potential risks to receptors. For example, at a gasoline service station site with a leaking UST, excavation, free product removal, or SVE might be performed at the source area; air sparging, ISCO, or *in situ* bioremediation in the plume area (these technologies could also be used for source area treatment at some sites); or pump-and-treat as the plume gets closer to a receptor. If concentrations are sufficiently low, MNA might be used instead of an active bioremediation technology or pump-and-treat for the residual plume. When considering MNA as a potential remedy, remediation time frame is an important factor to consider. Treatability studies (bench or pilot-scale) often are performed to evaluate how a technology would perform on the actual soil or groundwater at a site. The results of these studies are used in preparing a design for full-scale remediation.[30]

24.2.10 Additional Technical Considerations Associated with Remediating Sites Contaminated with Oxygenates

Other technical considerations related to remediation of sites contaminated with MTBE and oxygenates include

1. Contaminant concentration
2. Cleanup goals
3. Presence of other contaminants at the site
4. Site-specific considerations that may affect the selection and design of treatment technologies.

There tends to be wide variability in the range of concentrations of MTBE or other oxygenates in soil and groundwater at sites. The concentration of MTBE in contaminated groundwater and soil ranges from 5 to 1,000,000 μg/L. In addition, soil and groundwater treatment goals for MTBE-contaminated sites are currently based on state-specific standards and risk-based levels that range from 5 to 280,000 μg/L in soil and from 5 to 200,000 μg/L in groundwater. State-established primary drinking water limits for MTBE range from 5 to 240 μg/L.[21] High contaminant concentrations at sites with low cleanup goals can result in the need for treatment technologies and system designs that are able to achieve higher removal efficiencies and more aggressive remediation.

Many other factors can affect the performance and cost of implementing a technology at a given site, including the nature and extent of contamination, depth of contamination, physical and chemical characteristics of a site (such as dimensions and hydrogeology), design and operation of a treatment system, regulatory requirements, and logistical issues. Typically, these factors are quantified before an engineering level design is made for the use of a technology at a given site.

In addition, it is important to recognize that sites with spilled or leaked gasoline contain 200–300 distinct chemicals that can contaminate soil and groundwater; approximately 6–10% of the spilled/leaked gasoline typically consist of fuel oxygenates such as MTBE.[6]

24.3 OVERVIEW OF TREATMENT TECHNOLOGIES

This section contains an overview of the nine technologies that have been used to treat sites contaminated with MTBE and other fuel oxygenates:

1. Air sparging
2. SVE
3. MPE

4. *In situ* bioremediation
5. ISCO
6. Pump-and-treat
7. Phytoremediation
8. PRBs
9. *In situ* thermal treatment

The comparison is based primarily on information reported on the 323 MTBE remediation technology projects at U.S. EPA's MTBE Treatment Profile website[31] as well as information available from published literature sources.

24.3.1 TYPES OF REMEDIATION TECHNOLOGY

The U.S. EPA's MTBE remediation projects employed primarily air sparging, SVE, MPE, bioremediation, ISCO, and pump-and-treat to remediate MTBE and other oxygenates in groundwater and soil. Some sites also used phytoremediation, PRBs, or *in situ* thermal treatment. Table 24.3 summarizes the number of projects that used each of these technologies, as well as the scale (full-scale, pilot-scale, or bench-scale) and status (completed or ongoing) of the projects reviewed, and the number of projects for which performance and cost data were available. Among the six technologies, air sparging, SVE, bioremediation, and pump-and-treat were used more frequently to remediate groundwater and soil contaminated with MTBE and other oxygenates, and MPE, ISCO, phytoremediation, PRBs, and thermal treatment were used less frequently. Nearly 25% of the projects have been completed, with the remaining 75% ongoing. Eighty percent of the projects provided some type of performance data, and more than 30% provided cost data. Performance and cost data were provided most often for projects using air sparging, bioremediation, and pump-and-treat.

24.3.2 PERFORMANCE OF REMEDIATION TECHNOLOGIES

As shown in Table 24.3, performance data were available for all 323 of the MTBE remediation projects in the dataset. However, most of these projects with performance data are ongoing. To evaluate the performance of specific technologies and projects, 105 completed projects with performance data were identified, along with the minimum, median, and maximum of the highest

TABLE 24.3
Description of MTBE Remediation Technology Projects (323 Projects)

Technology	Number of Projects	Project Scale			Project Status		Number of Projects with Performance Data	Number of Projects with Cost Data
		Bench	Pilot	Full	Completed	Ongoing		
Air sparging	123	1	2	120	19	104	113	39
SVE	138	0	1	137	19	119	129	24
MPE	13	0	4	9	4	9	10	2
Bioremediation	73	7	13	53	35	38	68	28
ISCO	21	0	4	17	8	13	20	2
Pump-and-treat	100	0	16	84	22	78	76	43
Phytoremediation	8	3	4	1	5	3	1	0
PRB	6	0	2	4	4	2	4	0
Thermal treatment	1	0	0	1	1	0	1	0

Source: U.S. EPA. Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

TABLE 24.4
Performance Data for the Completed MTBE Remediation Technology Applications (105 Projects)

Technology	Number of Completed Projects with Performance Data	Initial MTBE Concentration (μg/L) in Groundwater			Final MTBE Concentration (μg/L) in Groundwater		
		Minimum	Median	Maximum	Minimum	Median	Maximum
Air sparging	19	5	2100	62,000	2	16	2070
SVE	19	5	2600	44,400	2	21	3200
MPE	3	11	55	6140	79	435	791
Bioremediation	35	5	3880	100,000	<1	30	33,000
ISCO	8	55	11,700	475,000	5	75	68,400
Pump-and-treat	21	3	1610	475,000	<1	11	68,400

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

concentration of MTBE measured in the groundwater before treatment (initial) and after treatment (final), as shown in Table 24.4. Limited performance data were available about the projects that employed phytoremediation, PRBs, and thermal treatment, and are not presented in this table.[31]

24.3.3 COSTS OF REMEDIATION TECHNOLOGIES

Table 24.5 summarizes the cost information reported for 127 MTBE remediation technology applications. Only costs reported as total project costs are summarized in this table. Note that these include both completed and ongoing projects. Because of the wide variation in the components that were included in the reported total project costs, these data should only be used as a general reference about costs and should not be used as a sole basis to estimate costs for future MTBE remediation projects or to compare the cost of technologies. In addition, U.S. EPA prepared a more detailed

TABLE 24.5
Total Project Cost Data for MTBE Remediation Technology (127 Applications, 2002 USD)[a]

Technology	Number of Projects with Cost Data	Total Project Costs Reported in 2002 USD		
		Minimum	Median	Maximum
ISCO	2	60,000	103,000	146,000
Bioremediation	30	4000	137,000	5,200,000
SVE	24	14,700	206,000	4,600,000
Air sparging	39	13,700	247,000	1,050,000
MPE	2	130,000	257,000	383,000
Pump-and-treat	43	65,000	327,000	4,000,000

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

[a] 2009 USD = 1.18 × 2002 USD.

analysis of treatment cost for *in situ* treatment of fuel oxygenates.[32] All costs in this chapter (except if mentioned otherwise) are in terms of 2002 U.S. Dollars (USD). Any cost index table can be used to update the costs from the year 2002 to reflect current costs. The U.S. Army Corps of Engineers (U.S. ACE) Cost Index for Utilities (see Appendix) is a good example that serves this purpose. Using this U.S. ACE Cost Index indicates that the cost in 2007 USD is 1.11 times the cost in 2002 USD.

The cost data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website. There was variation among the profiles in the level of detail for cost data by project, with many of the treatment profiles containing only limited information about treatment cost. Treatment cost is site-specific and depends on many of the same factors that also affect performance, such as site conditions, project scale, technology design and operation, and regulatory considerations.[1] Therefore, these cost data are intended to give a broad indication of the types of costs associated with cleanup projects, and users should be cautious about drawing conclusions about the cost of cleanup projects at specific sites based on these data.

For some of the treatment profiles, the specific components that make up the total cost were not provided in the source materials, such as for capital or operation and maintenance activities. In other cases, the types of contaminants present at the sites, other than MTBE, were not identified in the source materials. Sites may have been contaminated with gasoline components such as petroleum hydrocarbons, as well as oxygenates, and the treatment costs reported are for cleanup of both the gasoline components and oxygenates.

Costs for most of these projects were provided as a total remedial cost. Some projects also included the cost for ancillary treatment processes, monitoring costs, or source removal costs in the total cost. For most of the projects, reported costs were based on actual incurred costs. For other projects, costs were estimated as projected full-scale costs based on a scaleup of pilot-scale projects or on engineering estimates. Because most of the costs for the use of the treatment technologies are related to system design, installation, and startup, these partial or estimated costs may be relatively close to the eventual total project cost. However, the reported project costs should still be considered estimates because the cost components for each project are not consistent and it is possible that significant costs could be associated with system operation, maintenance, monitoring, and decommissioning. Further information about normalizing cost data is provided in Ref. [33].

24.3.4 FACTORS TO BE CONSIDERED WHEN IDENTIFYING TECHNOLOGIES TO TREAT FUEL OXYGENATES

Table 24.6 summarizes the general factors to be considered when identifying technologies to treat sites contaminated with fuel oxygenates. These general factors were developed based on the U.S. EPA's data from the 323 technology applications,[31] as well as from the Remediation Technology Screening Matrix and Reference Guide[34] and other industry references. As shown in Table 24.6, these general factors include type of treatment, relative time to complete, and relative cost.

Table 24.7 summarizes some of the general factors that are often considered when selecting a remediation technology for sites contaminated with fuel oxygenates. These include potential benefits (such as minimal site disturbance, integration with other treatment technologies, or applicability to challenging site conditions) and limitations (such as types of contamination not suited to treatment, undesired migration or transformation of contamination, or health and safety considerations).

For practitioners of *in situ* technologies, note that U.S. EPA has issued a policy statement that reinjection of contaminated groundwater is allowed under Resource Conservation and Recovery Act (RCRA)[35,36] as long as certain conditions are met. This policy is intended to apply to remedies involving *in situ* bioremediation and other forms of *in situ* treatment. Under this policy, groundwater may be reinjected if it is treated aboveground prior to reinjection. Treatment may be by a "pump-and-treat" system or by the addition of amendments meant to facilitate subsurface treatment. Also, the treatment must be intended to substantially reduce hazardous constituents in the groundwater (either before or after reinjection); the cleanup must be protective of human health and the environment; and the injection must be part of a response action intended to clean up the environment.[37]

TABLE 24.6
Factors to Consider When Identifying a Remediation Technology for Sites Contaminated with Oxygenates

	Type of Treatment				
Technology	***In Situ/Ex Situ***	**Media**	**Source/Plume**	**Relative Time to Complete**	**Relative Cost**
Air sparging	*In situ*	GW	Plume	Average	Average to lower
SVE	*In situ*	Soil	Source	Average to longer	Lower
MPE	*In situ*	Both	Source	Average	Average to higher
In situ bioremediation	*In situ*	Both	Plume	Average to shorter	Lower
ISCO	*In situ*	Both	Source	Shorter	Average to lower
Pump-and-treat	*Ex situ*	GW	Plume	Longer	Higher
Phytoremediation	*In situ*	Both	Plume	Longer	Lower
PRB	*In situ*	GW	Plume	Longer	Lower
In situ thermal treatment	*In situ*	Both	Source	Shorter	Average

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.
GW = Groundwater.

The following sections summarize the available information on nine treatment technologies that have been applied to treat MTBE and other oxygenates in groundwater, soil, and drinking water. Table 24.8 provides a brief description of these technologies, along with each technology's applicability to treat groundwater, soil, or both to treat oxygenates either *in situ* or *ex situ*. Groundwater contaminated with MTBE has most often been treated using air sparging, bioremediation, ISCO, pump-and-treat, and MPE. To date, soil contaminated with MTBE has been treated primarily with SVE. Drinking water contaminated with MTBE and other fuel oxygenates is typically treated using the same aboveground treatment technologies associated with pump-and-treat, such as air stripping, adsorption, chemical oxidation, or bioremediation. In addition to these treatment technologies, several nontreatment remedies (excavation, product recovery, and MNA) have been used to enhance MTBE source removal or plume management remedies.

24.4 AIR SPARGING

24.4.1 Air Sparging Process

Air sparging is an *in situ* technology that removes volatile organic compounds (VOCs) such as MTBE and other oxygenates from the groundwater through the injection of air, which induces a phase transfer of VOCs from a dissolved state to a vapor state that can be extracted from the subsurface or allowed to attenuate in the vadose zone. During air sparging, biodegradation of contaminants (including MTBE and other oxygenates) can also be promoted by the oxygen in the injected air. In some cases, pure oxygen or air amended with other gases, such as triethylphosphate (a nutrient), or butane or propane (cometabolic substrates), are injected to further promote biodegradation of contaminants. For the purpose of this chapter, technology applications that rely on biodegradation as a primary pathway for contaminant remediation are considered to be bioremediation projects, and are discussed under a different section.

TABLE 24.7
Factors to Consider When Selecting a Remediation Technology for Sites Contaminated with Oxygenates

Technology	Potential Benefits	Potential Limitations
Air sparging	• Causes minimal disturbance to site operations • Addition of oxygen to the subsurface may enhance aerobic biodegradation • Can be a cost-effective alternative for sites with groundwater contamination	• May cause a lateral spread of dissolved or separate phase contaminant plume • Contamination may be transferred from groundwater to the vadose zone • Has limited applicability at sites with confined aquifers
SVE	• Reduces the potential for migration of vapors into buildings or leaching into groundwater • Causes minimal disturbance to site operations • Can be a cost-effective alternative for sites with soil contamination and, in some cases, free product	• Low soil permeability or other heterogeneous conditions may reduce effectiveness • Shallow depths to groundwater or fluctuations in groundwater table can cause upwelling and interference with airflow • Off-gas typically requires treatment
MPE	• May increase groundwater recovery rates, compared with conventional pumping practices in equivalent settings • Can be used to recover free product • May be used to remediate the capillary fringe and smear zone • Can be a cost-effective alternative for sites with contamination in both soil and shallow groundwater	• NAPL emulsions and VOC-laden vapors may increase treatment requirements • Initial startup and adjustment periods may be relatively long • Some MPE configurations have depth limitations • Off-gas typically requires treatment
In situ bioremediation	• Causes minimal disturbance to site operations • Often biodegradation can be enhanced by the use of other technologies, such as air sparging, SVE, MPE, thermal, or ISCO • Can be a cost-effective alternative for sites with contamination in both soil and groundwater	• Presence of other organic contaminants may inhibit biodegradation • Degradation pathways for anaerobic processes not as well understood as aerobic pathways; anaerobic processes typically slower • High concentrations of contaminants may be toxic and/or not bioavailable • May be difficult to implement in low-permeability aquifers • Reinjection wells or infiltration galleries may require permits or may be prohibited • Biodegradation pathways may be site-specific, potentially requiring pilot testing or treatability studies
ISCO	• Can be a cost-effective alternative for hot spots that may not be amenable to bioremediation • Contaminants are treated rather than transferred to a vapor phase	• A relatively large amount of oxidant may be needed for treatment of large contaminant mass • Maybe low contact between oxidant and contaminant in heterogeneous conditions or in areas with low permeability

continued

TABLE 24.7 (continued)

Technology	Potential Benefits	Potential Limitations
	• Causes minimal disturbance to site operations	• Special precautions may be needed to protect worker health and safety during operation • Oxidation reactions may form toxic by-products in the groundwater or in off-gases, and off-gas may require capture and treatment
Pump-and-treat	• Can be a cost-effective alternative to treat an aquifer or to provide hydraulic containment for sites contaminated with fuel oxygenates	• May require an extended operation and maintenance period • Cost of constructing, operating, and maintaining the treatment system can be relatively high • Biofouling of extraction wells can reduce system performance • The typical design of common above-ground treatment systems may not be effective for oxygenates
Phytoremediation	• Can be a cost-effective alternative for remediating or containing relatively low concentration, shallow, and widespread soil or groundwater plumes	• Limited information available about the specific processes used in phytoremediation that reduce concentration of fuel oxygenates • Typically lengthy startup period • Phytoremediation generally less applicable to higher concentrations or deeper groundwater plumes
PRB	• Can be a cost-effective alternative for preventing the migration of contaminated groundwater plumes	• May affect natural groundwater flow gradients at a site, potentially resulting in lateral or vertical migration of the contaminant plume • Requires a high degree of engineering for design and installation
In situ thermal treatment	• Can be a cost-effective alternative for remediating source areas in soil or groundwater • Tends to remove oxygenates when used to treat other petroleum contaminants (such as petroleum hydrocarbons)	• May not be cost effective for use at small sites such as service stations • Requires a high degree of engineering for design, installation, and operation

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

24.4.2 EFFECT OF THE PROPERTIES OF MTBE AND OTHER OXYGENATES ON TREATMENT

In an air sparging system, the primary mechanism for contaminant removal is by the transfer of contaminants from the dissolved to the vapor phase. The extent to which this transfer can take place during air sparging depends on the Henry's law constant, which is an indication of the extent to which each will partition between the dissolved state and the vapor state under equilibrium conditions. A contaminant with a greater Henry's law constant is more readily stripped from groundwater by air sparging than one with a lower Henry's law constant.

Figure 24.3 shows the Henry's law constants for the common fuel oxygenates. As shown in the figure, all of the common oxygenates (with the possible exception of DIPE) have Henry's law

TABLE 24.8
Types of Technologies Used to Treat MTBE and Other Fuel Oxygenates

Treatment Technology	**Groundwater**	**Soil**	***In Situ* or *Ex Situ***	**Description**
Air sparging	•		*In situ*	Injection of air into the groundwater to strip out VOCs
SVE		•	*In situ*	Application of a vacuum to the soil to extract VOCs and treatment using aboveground processes
MPE	•	•	*In situ*	Simultaneous extraction of VOCs from soil and free product/groundwater and treatment using aboveground processes
In situ bioremediation	•	•	*In situ*	Addition of oxygen or other amendments to stimulate and enhance biodegradation
ISCO	•	•	*In situ*	Injection of chemicals such as ozone, hydrogen peroxide, or permanganate into the subsurface to oxidize contaminants
Groundwater extraction for pump-and-treat and drinking water treatment	•		*Ex situ*	Extraction of contaminated groundwater for treatment prior to use or disposal
Aboveground treatment technologies for extracted groundwater	•		*Ex situ*	Treatment of extracted groundwater using *ex situ* processes such as air stripping, adsorption, biological reactors, or oxidation
PRBs	•		*In situ*	Placement of a reactive zone that treats contaminants as groundwater flows through the zone
Phytoremediation	•	•	*In situ*	Use of trees and other higher plants to remove or destroy contaminants
In situ thermal treatment	•	•	*In situ*	Use of heat to mobilize or destroy contaminants

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

constants that are lower than those for BTEX, which range from 0.22 for benzene to more than 0.3 for xylene. Because of this, an air sparging system designed to remediate BTEX may not adequately address oxygenates. Research has shown that the removal of MTBE requires 5–10 times more airflow than would have been used for BTEX alone.[38] In addition, the ether-based oxygenates have Henry's law constants that are about two to three orders of magnitude greater than those for alcohol-based oxygenates, suggesting that ether-based oxygenates, such as MTBE, can be removed more readily using air sparging than alcohol-based oxygenates, such as TBA. However, alcohol-based oxygenates may be more readily biodegraded or may have less stringent (higher concentration) cleanup goals at some sites than ether-based oxygenates. Thus, it is possible that air sparging could be used to remediate sites contaminated with both alcohol- and ether-based oxygenates.

24.4.3 APPLICATION OF AIR SPARGING TO TREATMENT OF OXYGENATES

During air sparging, compressed air is forced into the saturated zone through one or more injection points, such as vertical or horizontal wells or engineered trenches, screened beneath the water table. The injected air flows and rises through the saturated zone. As the injected air passes through groundwater containing dissolved volatile contaminants, these contaminants partition to the injected air based on their individual physical properties. In addition, oxygen present in the injected air will dissolve into the groundwater at the gas–water interface and diffuse into the surrounding groundwater, potentially stimulating biodegradation of contaminants. When the injected air reaches the vadose zone, it can be extracted using SVE. Extracted vapors may be treated using aboveground technologies or are allowed to attenuate naturally in the vadose zone through dispersion and biodegradation. Air sparging has been used without SVE when contaminant concentrations are relatively low or potentially affected receptors are far from the area being treated.[39]

The design and configuration of air sparging systems to treat oxygenates varies widely based on site-specific conditions and is typically established through pilot-scale testing to determine the radius of influence (ROI) or zone of influence (ZOI) of an air sparging well under site conditions. The ROI or ZOI is the area around an injection well where there is adequate sparge pressure and airflow to enhance the transfer of contaminants from the dissolved phase to the vapor phase. Spacing between air sparging wells typically ranges from 1.5 to 12m (5–40ft), depending on the surrounding soil characteristics, and airflow rates commonly range from 1.7 to >68m^3/h (1 to >40scfm). Pilot testing is typically employed to determine an appropriate airflow rate (maximizing the ROI/ZOI while limiting the potential for unintended subsurface fracturing and over-mobilization of the contamination) for a given site. The flow of air through the sparging wells can be continuous or pulsed. Pulsed systems have been shown to increase mass transfer removal in some instances.[34,40,41]

More detailed information relevant to the application of air sparging at sites in general or those contaminated with MTBE and other fuel oxygenates is available in Refs [26,39,41–43].

24.4.4 TYPES OF PROJECTS USED IN AIR SPARGING TREATMENT OF OXYGENATES

Most of the 123 air sparging projects were conducted at full scale (120 projects) and were ongoing (104 projects) at the time the profile was prepared. In addition, while most (87) of the projects used air sparging alone or in conjunction with SVE, 36 projects supplemented air sparging treatment with pump-and-treat or other technologies, such as MPE, bioremediation, free product recovery, and ISCO.

The 123 air sparging projects primarily used vertical wells; three projects reported use of horizontal wells. Of 69 projects for which information about the number of air sparging wells was available, 48 used 2–8 wells per project, with a range of 1–30 wells. One project identified an ROI of 8.23 m (27ft). Three projects reported continuous airflow, two reported pulsed flow, and the remainder provided no information on the type of airflow. Of the 74 projects that used air sparging with SVE, the number of SVE wells used ranged from 1 to 23 wells per project, with 30 projects in the range of 2–5 wells per project. Four of these 74 projects reported the type of air emission treatment used, with two reporting use of GAC, one of catalytic oxidation, and one of thermal oxidation.[1]

24.4.5 PERFORMANCE OF AIR SPARGING IN TREATMENT OF OXYGENATES

The treatment performance data for 123 projects show that air sparging (either alone or in combination with other technologies) has been used to reduce MTBE in groundwater from concentrations >1,000,000 to <50 μg/L. The median project duration for the 19 completed sites ranged from 1 to 5 years. Although two of the 123 projects listed TBA as a cocontaminant, neither of these projects reported TBA concentrations before or after treatment; no data for other fuel oxygenates were reported.

24.4.6 COSTS OF AIR SPARGING TREATMENT OF MTBE

The median reported total cost for the 39 air sparging projects that reported costs in 2002 was approximately USD250,000, with most projects having a total cost between USD100,000 and USD350,000. For seven of these projects that used air sparging alone, the total cost ranged from USD20,000 to USD345,000 per project. For the 17 projects that used air sparging with SVE, the total cost ranged from USD27,000 to USD1,051,000 per project. The total cost for 15 of the projects ranged from USD96,000 to USD672,000 per project.

Because the area, volume, or mass treated was not consistently available for the 39 air sparging projects, no unit costs were calculated. The cost per volume of groundwater treated (identified as tons of saturated soil) was reported by U.S. EPA in 1995 as ranging from USD20 to USD50 per ton of saturated soil for air sparging in general.[40] The Federal Remediation Technologies Roundtable (FRTR)[34] in 2002 identified the unit cost as USD371,000–865,000 per hectare (USD150,000–USD350,000 per acre) of groundwater plume treated for air sparging in general. The cost of air sparging is generally considered to be better than the average of the costs for the remediation technologies used, for treatment of contaminated groundwater.[40] Because of the relative airflow requirements necessitated by the lower Henry's law constants of MTBE and other oxygenates, the unit costs for the remediation of sites contaminated with MTBE and other oxygenates could be at the upper end of these ranges.

24.4.7 FACTORS THAT AFFECT THE PERFORMANCE AND COST OF OXYGENATE TREATMENT USING AIR SPARGING

Because ether- and alcohol-based oxygenates exhibit different properties (specifically, Henry's law constant) than other common fuel contaminants such as BTEX, their presence may affect the size and design of the air sparging system required to remediate the site and, as a result, the cost of remediation. Research has shown that the removal of MTBE (ether-based) requires 5–10 times more airflow than used for BTEX alone.[38] The other common ether-based oxygenates have higher Henry's law constants than MTBE and are theoretically more amenable to treatment via air sparging (although still less amenable than BTEX components). The common alcohol-based oxygenates have Henry's law constants two to three orders of magnitude lower than those of the ether-based oxygenates, and may theoretically require 100–1000 times greater airflow. In practice, air sparging may not be feasible if high enough airflow rates cannot be achieved without causing unwanted subsurface fracturing or contaminant mobilization. However, the biodegradation potential of both ether- and alcohol-based oxygenates will also influence system design and may reduce the airflow and time required for remediation.

In addition to the oxygenate-specific factors described above, additional variables may also affect the performance and cost of an air sparging system. These factors include the concentration, mass, and distribution of contaminants in the groundwater; subsurface geology and hydrogeology; cleanup goals; and requirements for site cleanup. For example, heterogeneity within the subsurface may result in preferential pathways that prevent injected air from contacting contaminated areas. These factors affect the number and spacing of air sparging wells, flow rates, and the length of time required for treatment, which typically will be determined during pilot testing. Air sparging also has potential to cause a lateral spread of dissolved or separate phase contaminant plumes. For example, in formations with laterally oriented clays interbedded with sand, there is a possibility of spreading the contamination when using air sparging.

24.4.8 ADVANTAGES AND LIMITATIONS

The advantages of applying air sparging are as follows[34,40]:

1. Generally considered to be easy to construct, operate, and maintain.
2. Configurations can be designed to cause minimal disturbance to site operations.

3. In some cases, such as areas of lower contaminant concentrations or in remote locations, contaminants stripped from the groundwater may be allowed to attenuate naturally in the vadose zone.

The limitations to applying air sparging are as follows[34,40]:

1. Often contaminants stripped from the groundwater must be extracted and treated aboveground using SVE.
2. High airflow rates may result in unintended fracturing leading to nonuniform flow or short-circuiting of injected air in the subsurface, or may result in unintended mobilization of contaminants as nonaqueous phase liquids (NAPL), dissolved in groundwater, or in soil gas.
3. Has limited applicability at sites with confined aquifers and stratified layers; soil heterogeneities may limit effectiveness.
4. Has the potential to cause a lateral spread of dissolved or separate phase contaminant plumes.

24.4.9 Example Projects

24.4.9.1 Air Sparging at Exxon and Mobil Service Stations, Smithtown, New York

A full-scale cleanup was performed using air sparging, SVE, and groundwater pump-and-treat to prevent further off-site migration of MTBE, TBA, and BTEX in groundwater originating from two service stations in Smithtown, New York. The lithology of the site consists of fine to course-grained sands with varying amounts of silt and fine gravel. At the Exxon service station, a 142-standard L/s (300-scfm) air sparging system in conjunction with SVE was used to replace pump-and-treat remediation. Operation of the air sparging system began in April 2001. Initial MTBE concentrations were 15,600 μg/L and initial TBA concentrations were 365 μg/L. The cleanup goal for MTBE is 1000 μg/L.[32]

24.4.9.2 Air Sparging at Eaddy Brothers Service Station, Hemingway, South Carolina

A full-scale cleanup is being performed using air sparging and SVE to treat MTBE and other contaminants at a service station in Hemingway, South Carolina. Soil at the site consists of silty clays with clayey sand lenses. The SVE system consisted of 70 m (230 ft) of horizontal SVE piping installed immediately below the asphalt parking lot surface of the site. Extracted vapors were treated using a thermal oxidizer. The air sparging system, which began operating two weeks after the SVE system was activated, consisted of 10 vertical sparging wells, each installed at a depth of 7.93 m (26 ft) with 1.52 m (5 ft) well screens. The wells were connected to an air sparge compressor operating at 4.78 kg/cm^2 (68 psi). Site-specific target levels (SSTLs) for this site ranged from 5 to 80 μg/L per contaminant. As of June 2003, the maximum concentrations of MTBE and BTEX in the groundwater decreased, with the SSTLs being met for toluene, ethylbenzene, and xylenes. Maximum MTBE concentrations were reduced from >1,000,000 to 568 μg/L (99.99% reduction), and maximum BTEX concentrations reduced to 9690 μg/L. The cost for this application was USD195,515.[44]

24.5 SOIL VAPOR EXTRACTION

24.5.1 SVE Process

SVE is an *in situ* technology in which VOCs such as MTBE and other oxygenates are removed with soil vapor from the vadose zone. It involves the application of a vacuum to the soil to create a negative pressure gradient that induces subsurface vapor flow toward one or more extraction points. Soil vapors are collected from the extraction points and generally are captured and then treated with one or more aboveground treatment technologies prior to being discharged to the atmosphere.

SVE is used to reduce the concentration and mass of MTBE and other oxygenates in the vadose zone, which reduces its potential to migrate as vapors into buildings or to act as a continuing source of groundwater contamination. SVE may also reduce groundwater contaminants through the enhanced evaporation of the NAPL, volatilization of contaminants dissolved in pore water, and stimulation of biodegradation. SVE is also used as a component of air sparging or other systems to collect injected gases that have stripped contaminants from groundwater.

24.5.2 EFFECT OF THE PROPERTIES OF MTBE AND OTHER OXYGENATES ON TREATMENT

In an SVE system, the primary mechanism for contaminant removal from the soil to the vadose zone is the volatilization of contaminants present in the pure or adsorbed phase onto soil into the vapor phase, as the vapor phase is continually extracted. The property that shows the extent to which this transfer can take place during SVE is vapor pressure, which provides an indication of the extent to which each contaminant will partition between the liquid phase and the vapor state at equilibrium conditions. Generally, a contaminant with a greater vapor pressure more readily volatilizes than one with a lesser vapor pressure.

Figure 24.4 shows the vapor pressures, in units of millimeters of mercury (mm Hg), for the common fuel oxygenates as compared with BTEX.[1] Generally, contaminants with vapor pressures greater than 10 mm Hg are considered to be amenable to treatment using SVE. As shown in the figure, each of the common oxygenates has vapor pressures >10 mm Hg, with ether-based oxygenates generally having greater vapor pressures than alcohol-based oxygenates. In addition, most of the common oxygenates (with the exception of TBA, TAME, and ethanol) have greater vapor pressures than BTEX, suggesting that they are more readily extracted using SVE than BTEX, which are commonly addressed with SVE.

24.5.3 APPLICATION OF SVE TO TREATMENT OF OXYGENATES

During SVE, contaminated soil vapors are extracted by inducing a vacuum at one or more extraction points that are typically constructed as vertical vapor extraction wells. Horizontal extraction wells or trenches have also been employed as extraction points. In general, SVE is applied at depths

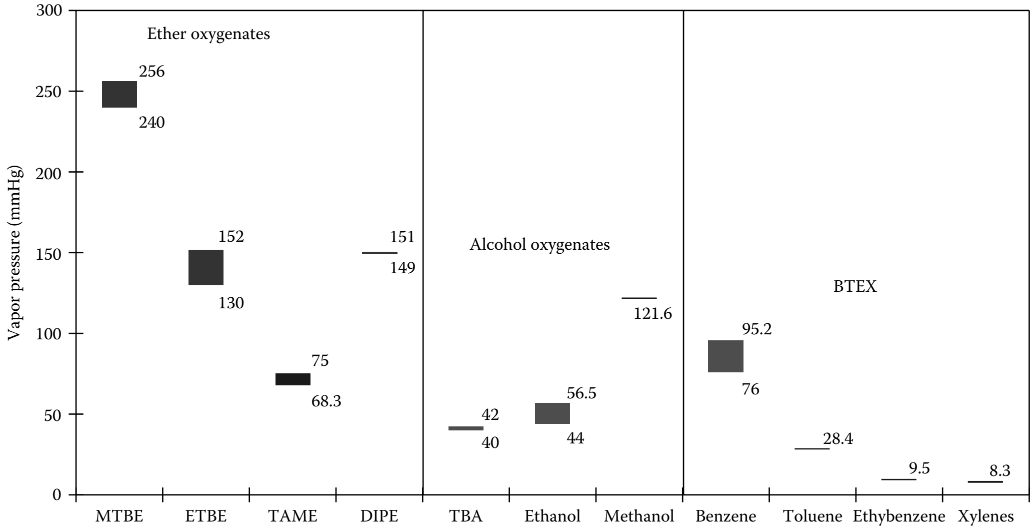


FIGURE 24.4 Ranges of vapor pressures for common fuel oxygenates. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

ranging from 10 to 50 ft below ground surface, but has been applied as deep as 300 ft.[40] Shallower applications typically employ some manner of a surface seal to minimize short-circuiting of the system by ambient air. Typical flow rates for extracted soil vapors range from 60 to 700 ft^3/min. The vacuum pressures required at the top of the vapor extraction well (wellhead vacuum) to produce the desired vapor extraction rate typically range from 3 to 100 in. of water, and vary depending on soil permeability.[34,40] The ROI of an extraction well is used to determine the number and spacing of extraction wells. The ROI is the distance from an extraction well to the point at which a vacuum can be induced to enhance volatilization and extraction of contaminants from the soil.

SVE is considered to be most effective in more homogeneous and higher-permeability geologies because subsurface preferential pathways may result in short circuiting and tighter formations may minimize the ROI of extraction points. In general, vapor extraction points are designed and spaced to provide for a reduced pressure gradient throughout the contaminated zone. Remediation of MTBE and other oxygenates using SVE may also potentially benefit from the aerobic conditions generated by subsurface air flow that may result in conditions that are amenable to *in situ* biodegradation of contaminants. At some sites, groundwater or free product extraction equipment may be incorporated into vapor extraction points.

Extracted soil vapors, containing volatilized contaminants, are routed to an aboveground treatment system prior to being discharged to the atmosphere. The types of aboveground vapor treatment technologies that have been used for treating MTBE and other fuel oxygenates include the following[39]:

1. *Adsorption*—Processes in which vapor-phase contaminants are adsorbed onto a medium, such as GAC or resin, as driven by equilibrium forces.
2. *Thermal treatment*—Processes in which vapor-phase contaminants are destroyed via high-temperature oxidation; the primary categories of thermal treatment used to treat MTBE and other oxygenates include thermal oxidation, which employs a flame to generate the high temperatures needed to oxidize contaminants, and catalytic oxidation, which employs lower temperatures in the presence of a catalyst (typically platinum, palladium, or other metal oxides) to destroy contaminants.
3. *Biofilters*—Processes in which contaminants are biodegraded in a fixed-film bioreactor, typically consisting of a bed of high surface area filter media, such as GAC, that acts as a support matrix for a thin film consisting of microbes that are acclimated to the biodegradation of MTBE or other contaminants.

The type of vapor treatment that is used will depend on factors such as the contaminant concentrations in the extracted vapors and the air emission discharge limitations for the site. Highly contaminated vapors at a site with stringent air emission limitations may require a multistep vapor treatment train, such as thermal oxidation, followed by carbon adsorption. Less contaminated vapors at a site with less stringent air emission limitation may require minimal or no vapor treatment. Fields et al.[38] described the following rules of thumb for selecting vapor treatment:

- Thermal oxidation for VOC concentrations greater than 2000 ppmv.
- Catalytic oxidation for VOC concentrations between 100 and 2000 ppmv.
- GAC treatment for VOC concentrations between 35 and 100 ppmv.
- Direct discharge for VOC concentrations <35 ppmv.

More detailed information on the application of SVE at sites contaminated with MTBE and other oxygenates in general is available in Refs [26,39,45].

24.5.4 TYPES OF PROJECTS USED IN SVE TREATMENT OF OXYGENATES

From the 323 projects listed in U.S. EPA's MTBE Treatment Profiles dataset, 138 projects were identified where MTBE was treated using SVE. Information on the treatment of oxygenates other than MTBE during these 138 projects is limited. Two projects reported treating these other oxygenates: one project reported TBA and one reported ethanol.

Most of the 138 SVE projects were full scale (137 projects). In addition, most of the projects used SVE in conjunction with air sparging (74 projects) or SVE alone (20 projects); the remaining projects supplemented SVE treatment with bioremediation, ISCO, pump-and-treat, or multiple technologies.

The 138 SVE projects primarily used vertical wells; three projects used horizontal wells. Of the 23 projects for which information about the number of SVE wells was available, 20 used 2–8 wells per project, with an overall range of 1–16 wells. Of the 74 projects that used air sparging with SVE, the number of SVE wells used ranged from 1 to 23 wells per project, with 30 projects in the range of 2–5 wells per project. Four of these 74 projects reported the type of air emission treatment used, with two reporting use of GAC, one of catalytic oxidation, and one of thermal oxidation. Eight of the SVE projects reported the types of aboveground treatment technologies that were employed to treat off-gas containing MTBE and other oxygenates. For seven of these eight projects, thermal treatment was employed; six projects used catalytic oxidation and one project used thermal oxidation. One of the projects used catalytic oxidation and another project used GAC adsorption to treat the SVE off-gas.

24.5.5 PERFORMANCE OF SVE IN TREATMENT OF OXYGENATES

Several approaches have been used to evaluate SVE performance for MTBE treatment, including analyzing the changes in MTBE concentrations in soil, soil vapor, or groundwater, or estimating the mass of contaminant removed. SVE is used to reduce the mass of contaminants that may leach or otherwise migrate from the vadose zone to the groundwater. This reduced leaching rate may result in lower concentrations of contaminants in groundwater, and the performance data provided are for MTBE concentrations in groundwater.[26]

The treatment performance data for the 19 completed projects presented in Table 24.9 show that SVE (either alone or in combination with other technologies) has been used to remediate MTBE in groundwater from concentrations >100,000 to <50 μg/L and has achieved MTBE concentration reductions >99%. The median project duration for the 19 completed sites ranged from 3 months to 5 years.

TABLE 24.9
Performance Summary for 19 Completed SVE Projects

Technology(ies)	Number of Projects	Initial MTBE Concentration (μg/L) Minimum	Median	Maximum	Final MTBE Concentration (μg/L) Minimum	Median	Maximum	Median Project Duration (months)
SVE Only	4	48	6900	8900	21	1800	3200	24
SVE with air sparging	2	99	218	337	NR			57
SVE with air sparging and pump-and-treat	5	5	203	2600	2	3	5	22
SVE with ISCO	1		17,000			31		9
SVE with multiple technologies	7	4151	10,800	44,400	NR			12

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

NR = Information not provided.

24.5.6 COSTS OF SVE TREATMENT OF MTBE

Project cost data were reported for 24 of the 138 SVE projects in the dataset. In most cases, the components that make up the project costs were not reported. However, it is likely that these incorporate different components, such as treatment, monitoring, design, oversight, and health and safety. The median reported total cost for all SVE projects was approximately USD206,000, with most projects having a total cost between USD100,000 and USD400,000.

The unit cost of SVE was reported in one literature source as ranging from USD13 to USD52 (USD10–USD40/yd^3) of soil treated. This source identified the cost of SVE as generally better than the average of the costs for remediation technologies for treatment of contaminated soil.[34]

In another source, the unit cost of SVE ranged from USD78 to USD458 (USD60 to nearly USD350/yd^3) of soil for projects treating <7650 m^3 (10,000 yd^3) of soil to <USD6.5 (USD5/yd^3) for projects treating >7650m^3 (10,000yd^3) of soil. This source also identified the unit cost as ranging from USD660 (USD300) to >USD22,000/kg (USD10,000/lb) of contaminant removed for projects where up to 1362 kg (3000 lb) of contaminant mass were removed, to <USD33/kg (USD15/lb) of contaminant removed for projects where larger quantities were removed.[33] These unit cost ranges represent treatment costs for the use of SVE in general and are not specific to its use for treatment of MTBE.

24.5.7 FACTORS THAT AFFECT THE PERFORMANCE AND COST OF OXYGENATE TREATMENT USING SVE

Key factors that affect the performance and cost of an SVE system include the following:

1. The concentration, mass, and distribution of contaminants in the soil.
2. Geology and heterogeneity of the subsurface.
3. Cleanup goals.
4. Requirements for discharging emissions to the atmosphere.

These factors affect the number of vapor extraction wells, vacuum level required, type of off-gas treatment, and length of time required for treatment.[34]

24.5.8 ADVANTAGES AND LIMITATIONS

The advantages of applying SVE are as follows[34,40]:

1. Removal of MTBE from soil is generally considered to be more cost effective than removal of MTBE that has dissolved in the groundwater.
2. SVE reduces the potential for MTBE to migrate as vapors into buildings or leach to the groundwater.
3. It is relatively low cost compared with other remediation technologies.
4. It causes minimal disturbance to site operations.

The limitations to applying SVE are as follows[34,40]:

1. Low soil permeability may limit vapor movement through the soil, reducing SVE effectiveness.
2. At heterogeneous sites, contaminants may be difficult to extract from low-permeability layers (soil vapors may be collected mainly from higher-permeability layers, while contaminants may be present in lower-permeability layers).

3. Shallow depths to groundwater or fluctuations in the groundwater table can cause upwelling and interference with airflow.
4. May not be capable of reaching very stringent soil cleanup levels (soil concentrations may reach an asymptotic level that is higher than the cleanup level).

24.5.9 Example Projects

24.5.9.1 SVE at Kansas Site U6-077-231, Atwood, Kansas

A full-scale cleanup was performed using SVE to treat MTBE from a UST site in Atwood, Kansas. Soil at the site consists of 0.3–5.5 m (1–18 ft) of silt and clay overlying 5.5–15.25 m (18–50 ft) of sand and gravel. The SVE system consisted of eight vapor extraction wells, installed to a depth of 3.66 m (12 ft) below ground surface. Operation of the SVE system began in February 1994 and the system is currently operational. As of June 2003, the concentration of MTBE in the groundwater has been reduced from 480 to 93 μg/L (an 80% reduction). The most recent cost data available depict a total remediation cost of USD298,040.[31]

24.5.9.2 SVE at Creek and Davidson Site G: Service Station, California

A full-scale cleanup was performed using SVE to treat MTBE and benzene from a UST leak at a service station in California. Soil at the site consists of 3 m (10 ft) of clay overlying sand and gravel. The SVE system consisted of five vapor extraction wells and a 19.8 m^3/min (700 ft^3/min) vacuum system. Thermal oxidation was used for off-gas treatment. After 2.2 years of SVE operation, the concentration of MTBE in the groundwater (measured in 11 monitoring wells) was reduced from as high as 8900 to 21 μg/L and the concentration of benzene was reduced from 670 to 0.5 μg/L (both more than 99% reductions). The thermal oxidizer destroyed greater than 95% of the VOCs in the off-gases, and remediation at the site is reported to be complete. As of June 2003, the cost data available depict a total remediation cost of USD140,000.[31]

24.6 MULTIPHASE EXTRACTION

24.6.1 MPE Process

The MPE process is a generic term for technologies that extract VOCs such as MTBE and other fuel oxygenates from the subsurface in soil, vapor, and groundwater, simultaneously. In addition, it can be used to remove free product or other NAPLs. MPE is referred to by several other names in the technical literature. Examples of terms referring to MPE and its configurations are dual-phase extraction (DPE), two-phase extraction (TPE), and vapor extraction/groundwater extraction (VE/GE). In general, all of these configurations couple SVE with groundwater (and in some cases NAPL) extraction and employ some form of aboveground water and vapor treatment technologies.[34,46]

24.6.2 Effect of the Properties of MTBE and Other Oxygenates on Treatment

The primary removal mechanisms for MPE are volatilization with subsequent air advection for the vapor phase and dissolution and aqueous advection in groundwater. Vapor pressure, solubility, and organic/water partition coefficient are the primary properties of MTBE and other oxygenates that correspond to these removal mechanisms. In general, contaminants with higher solubility and vapor pressure and lower partition coefficients, such as fuel oxygenates, are more appropriate for removal using MPE than BTEX. As shown in Table 24.10, the properties of both ether- and alcohol-based oxygenates suggest that they may be more favorably removed from the subsurface by the vapor and groundwater extraction components of MPE than BTEX constituents. One exception to this

TABLE 24.10
Contaminant Properties Relevant to MPE

Contaminant Category	Solubility into H_2O from Gasoline (mg/L)	Vapor Pressure (mm Hg)	Partition Coefficient (log *L*/kg)
BTEX constituents	3–100	8–95	1.5–3.2
Ether-based oxygenates (such as MTBE)	750–5500	68–250	1.0–2.2
Alcohol-based oxygenates (such as TBA)	> 25,000	40–120	0.2– 1.6

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

generalization is that certain alcohol-based oxygenates, specifically TBA and ethanol, may be less readily removed in the vapor phase because of their relatively low vapor pressures.

MPE provides several advantages when compared with the use of SVE or pump-and-treat alone. MPE provides for an increase in groundwater recovery rates, an increase in ROI in individual groundwater recovery wells, and recovery of shallow free product. By depressing the groundwater table in the vicinity of the extraction wells, MPE provides for remediation of the capillary fringe and smear zone, and remediation of volatile, residual contaminants located above and below the water table.[46]

However, while the contaminant properties are important considerations in the selection and design of an MPE system for a given site, the applicability of MPE is more dependent on media properties, primarily hydraulic conductivity, transmissivity, depth of the water table, and soil moisture.[46]

24.6.3 APPLICATION OF MPE TO TREATMENT OF OXYGENATES

MPE can be implemented in a variety of configurations, including single pump, two pump, and bioslurping. In the single-pump configuration, a single drop tube is employed to extract both liquid and vapor from a single well. The vacuum and liquid suction lift is achieved by one vacuum pump (liquid-ring pumps, jet pumps, and blowers are typical). In the two-pump configuration, a submersible pump is used for groundwater recovery in conjunction with a separate vacuum applied at the sealed wellhead. In this configuration, liquid and vapor streams are separate from one another. Depending on application, two-pump systems can use electric or pneumatic submersible pumps for groundwater recovery and liquid-ring pumps or blowers to induce vacuum. Applications that recover free product or light nonaqueous phase liquid (LNAPL) typically use pneumatic submersible pumps for liquid recovery. Bioslurping uses the same configuration as for a single-pump system; however, the drop tube is set at, or just below, the liquid–air interface. The extraction point alternates from recovering liquid to air, sending a slurping sound. This configuration has been effective in free product recovery, and also enhances *in situ* aerobic bioremediation, due to the increased airflow.

In some configurations, the vacuum used in MPE increases the effective drawdown of groundwater (i.e., the increase or lowering of the depth of the groundwater table) locally near the pumped well. This has the effect of increasing exposed soil in the saturated zone and the removal of volatile contaminants located above and below the original water table.

Extracted vapors and liquids are commonly treated aboveground. The types of technologies used for aboveground treatment are similar to those used for SVE and groundwater pump-and-treat, respectively, and they are discussed further under those technologies. More detailed information relevant to the application of MPE at sites in general or contaminated with MTBE and other oxygenates is available in Refs [47–49].

24.6.4 TYPES OF PROJECTS USED IN MPE TREATMENT OF OXYGENATES

From the 323 projects in EPA's MTBE Treatment Profiles dataset, 13 projects were identified where MTBE was treated using MPE. Information on the treatment of other oxygenates during these 13 projects is limited; no projects reported treating other oxygenates. Most of the 13 MPE projects were full scale (9 projects). Most of the projects (9) used MPE only; the remaining four projects supplemented MPE with air sparging (2 projects) and ISCO (2 projects). Short summaries for two projects, MPE at Service Station A, Maryland, and MPE at Sparks Solvent/Fuel Site, Sparks, Nevada, are included at the end of this section.

24.6.5 PERFORMANCE OF MPE IN TREATMENT OF OXYGENATES

For the 13 projects identified from 323 MTBE treatment profiles, MPE treated MTBE with concentrations as high as 100,000 μg/L (JFK International Airport, Jamaica City, New York) and achieved as low as 50 μg/L in groundwater after treatment. Table 24.11 provides a summary of seven projects.

24.6.6 COSTS OF MPE TREATMENT OF MTBE

The total project cost was reported for two of the 13 MPE projects identified above. The completed Kings Beach Swiss Mart, CA project, which employed MPE alone, reported a total project cost of USD130,000 and the completed Tahoe Boat Company, CA project, which employed MPE with air sparging, reported a total project cost of USD383,000. Both of these total costs were the amounts reported by the state cleanup fund. Because the area, volume, or mass treated was not available for this project, a unit cost was not calculated.

Little additional information was identified in the literature about the costs of using MPE for the treatment of MTBE and other oxygenates, or for other contaminants. The cost per volume of subsurface treated was reported in one literature source as ranging from USD47 to USD222/m^3 (USD36–USD170/yd^3) for sites contaminated with chlorinated solvents.[46] The cost of MPE is generally considered to be the average of the costs for remediation technologies for treatment of contaminated groundwater.[34] However, project costs will likely be driven primarily by the aboveground treatment required. The costs of aboveground water and vapor treatment technologies are discussed in other sections.

TABLE 24.11
Performance Summary for Seven Projects

MTBE Concentration Range	Number of Projects Reporting Initial MTBE Concentrations	Number of Projects with Last Reported MTBE Concentrations
Greater than or equal to 10,000 μg/L but less than 100,000 μg/L	1	0
Greater than or equal to 1000 μg/L but less than 10,000 μg/L	1	2
Greater than or equal to 100 μg/L but less than 1000 μg/L	2	0
Greater than or equal to 50 μg/L but less than 100 μg/L	0	1
Less than 50 μg/L	0	1

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

24.6.7 Factors That Affect the Performance and Cost of Oxygenate Treatment Using MPE

When MTBE or other oxygenates are present and must be remediated at a site, MPE, either alone or in combination with other technologies, may be a suitable remediation approach. MPE affects mass removal by volatilization, dissolution, and advective transport. In general, if both SVE and groundwater pump-and-treat are potentially applicable technologies, then MPE may be considered as a remedial alternative. The performance of MPE is governed, primarily, by media properties and, to a lesser extent, by contaminant properties. MPE is most applicable to fine-grained formations in the fine sand to silty sand range ($K = 10^{-3}$–10^{-5} cm/s) with low transmissivity <2.5 m^3/d/m (200 gallons/d/ft).

A typical result of conventional pumping in low conductivity and transmissivity formations is increased, and sometimes rapid, drawdown with steep gradients, with corresponding low recovery rates. This condition limits the influence of the conventional pumping well. MPE overcomes this limiting factor with the application of a vacuum. The vacuum enhancement of MPE also can overcome the capillary forces that can trap contaminants within the capillary zone. This allows better recovery of LNAPL, which tends to accumulate in the capillary zone at the air–water interface.

In addition to the technology-specific factors described above, additional factors may also affect the performance and cost of any MPE system. These factors include

1. The concentration, mass, and distribution of contaminants in the soil and groundwater.
2. Geology, hydrogeology, and heterogeneity of the subsurface; cleanup goals.
3. Requirements for air emissions and water discharges.

These factors affect the number and type of extraction wells, vacuum level, pumping rate, type of aboveground-water and off-gas treatments, and length of time required for treatment.[34]

24.6.8 Advantages and Limitations

The advantages of applying MPE are as follows[46]:

1. Increase in groundwater recovery rates compared with conventional pumping practices in equivalent settings.
2. Increase in ROI of individual groundwater recovery wells.
3. Recovery of free product or other LNAPL.
4. Remediation of the capillary fringe and smear zone.
5. Simultaneous remediation of soil vapors and groundwater.
6. Effective on lower-permeability soil sites.

The limitations to applying MPE are as follows[46]:

1. Greater aboveground treatment requirements as a result of NAPL emulsions and VOC-laden vapors.
2. Initial startup methods and adjustment period may be longer compared with conventional practices.
3. Potentially higher capital costs compared with conventional pumping approaches.
4. Depth limitations to some MPE configurations.

24.6.9 Example Projects

24.6.9.1 MPE at a Service Station MD-A, Maryland

At a service station in Maryland, MPE was conducted using a VE/GE system that consisted of 10 VE wells and 6 GE wells. The sites were located on a coastal plain, and the soil consisted of sandy silts and clays. The average flow rates were standard 16.7 m^3/h (9.8 scfm) in the VE wells and 0.82 L/min (0.24 gpm) for the GE wells. The concentration of MTBE in groundwater was reduced from 27,027 to 32 μg/L over 3.5 years of system operation. The cleanup was reported as completed; however, a cleanup goal was not provided.[50]

24.6.9.2 MPE at Sparks Solvent/Fuel Site, Sparks, Nevada

Since 1995, the sparks solvent/fuel site located in Sparks, Nevada, a remediation system consisting of MPE, air sparging, and SVE, has been operational. The treatment system consists of 29 MPE wells, an oil–water separator, and a fluidized bed bioreactor, with an influent flow rate of 23.3 L/s (370 gpm) and a retention time of 8 min. Vapors are sent through a condenser, followed by a thermal oxidizer, before its release to the atmosphere. Condensate is sent back through the oil–water separator. Performance data, available for the first 650 days of site operation, showed a reduction in MTBE concentration across the bioreactor from 2400 to 55 μg/L. No data were provided for reduction of MTBE concentrations in the aquifer.[51]

24.7 *IN SITU* BIOREMEDIATION

24.7.1 BIOREMEDIATION PROCESS

Bioremediation is a process by which microorganisms, fungi, and plants metabolize pollutant chemicals.[52,53] It has been used to treat oxygenates in soil and groundwater both *in situ* and *ex situ*. Generally, an engineered bioremediation system stimulates the biodegradation of contaminants through the introduction of electron acceptors (typically oxygen), electron donors (substrates or food sources), nutrients, or microbes[54] that are acclimated to the contaminated soil or groundwater. These amendments are either introduced to the subsurface *in situ* or are added to extracted groundwater or excavated soil. A description of the various types of amendments is provided below.[55]

1. *Electron acceptors*—Oxygen is the most common electron acceptor used to promote biodegradation and is added in different ways including in sparged air, through injection of a solid or liquid that generates oxygen or through *in situ* electrochemical generation. Other electron acceptors, including nitrate, sulfate, and iron (III) compounds, may be added to support anaerobic biodegradation.
2. *Electron donors*—In direct biodegradation pathways, the contaminant acts as the electron donor or substrate. However, during cometabolic degradation, a different electron donor is metabolized, resulting in the consequential oxidation of the contaminant. In some contaminated plumes, other electron donors, such as other constituents of gasoline, may also be present. In cases where they are not, and cometabolic degradation pathways are desired, electron donors may be added.
3. *Nutrients*—Nutrients, such as nitrogen and phosphorus and other trace elements, are necessary for cell growth because they are key biological building blocks.[52,53] Addition of nutrients as a supplement helps ensure that concentrations of nutrients do not become a limiting factor for bioremediation.
4. *Bioaugmentation*—Bioaugmentation involves the addition of supplemental microbes to the subsurface where organisms able to degrade specific contaminants are deficient. Microbes may be grown from populations already present at a site or "seeded" from cultures grown in aboveground reactors or available commercially as cultivated strains of bacteria known to degrade specific contaminants. The application of bioaugmentation technology is highly site-specific and dependent on the microbial ecology and physiology of the subsurface.[56]

This section focuses on engineered *in situ* remediation technologies that use microorganisms to biodegrade pollutant chemicals. *In situ* bioremediation technologies are configured to either directly inject supplements into the contaminated media; to place the supplements in the pathway of groundwater flow; or to extract contaminated groundwater, amend it with supplements, and recirculate the amended groundwater through the contaminated zone.

The design and configuration of *in situ* bioremediation systems vary widely based on site-specific conditions. A treatability study or pilot-scale testing is often performed to determine the type and amount of amendments required to create and maintain the conditions optimal for biodegradation as well as to select the type of engineered system that is most suitable to introduce the amendments to the subsurface.[57] Some of the key considerations for various types of engineered *in situ* remediation systems are summarized below.[56] A discussion of *ex situ* applications of bioremediation, which focuses on biological treatment of extracted groundwater, is included in the section about treatment of extracted groundwater.

24.7.1.1 Direct Injection Wells/Trenches

In a direct injection system, degradation is enhanced through the addition of microbes, nutrients, electron acceptors, or electron donors directly into the aquifer at injection points or directly into the soil. Direct injection technologies include those that employ injection wells or trenches through which supplements are introduced. Some common direct injection technologies use chemical or electrochemical means to increase the level of oxygen in the groundwater, or inject microorganisms that are specifically conditioned to degrading the contaminants of concern. The natural flow of the groundwater is generally not impeded, but is monitored to determine that the degradation of the contaminants and their daughter products is completed within an acceptable distance from the source.

24.7.1.2 Recirculation Systems

A recirculation system extracts contaminated groundwater from the site, adds to or amends the extracted water *ex situ*, and reinjects the "activated" water to the subsurface, generally upgradient of the contaminated zone. As an alternative, extraction and injection are performed at different elevations in a single well, creating vertical circulation. A groundwater recirculation configuration may be used to provide containment of a plume or to allow the addition of amendments in a more controlled environment.

24.7.1.3 Permeable Reactive Barriers

The placement of supplements in the pathway of groundwater flow constitutes a PRB, sometimes referred to as a treatment zone or "biobarrier." With a PRB approach, an active bioremediation zone is created by methods such as backfilling a trench with nutrient-, oxidant-, or reductant-rich materials, or by creating a curtain of active bioremediation zone through direct injection or groundwater recirculation at the toe of a plume. PRBs contain a contaminant plume by treating only groundwater that passes through it.

24.7.2 EFFECTS OF THE PROPERTIES OF MTBE AND OTHER OXYGENATES ON TREATMENT

Early studies on MTBE contamination of groundwater concluded that the compound was either nonbiodegradable or very resistant to biodegradation. However, more recent research has shown that MTBE can be degraded both aerobically and anaerobically, although anaerobic intrinsic degradation rates are relatively slow. The research has found that there are naturally occurring microbes capable of using MTBE as their sole carbon and energy source. Such microorganisms seem to be widespread, but are present natively in low numbers and take time to reach a sufficiently dense population to sustain MTBE degradation. As a result, cometabolic approaches are often considered for MTBE bioremediation, wherein an organic substrate (electron donor) that is readily degraded is added to the subsurface, resulting in the consequential oxidation of MTBE. Because the ability of microorganisms to cometabolically degrade MTBE is consistently found in strains that are predisposed to catabolize structural analogs of MTBE, suitable cosubstrates include simple branched and even nonbranched alkanes such as propane and butane.[58–62]

Although detailed comparative evaluations of the aerobic degradation rates of other fuel oxygenates have not been performed to date, the aerobic biodegradation rates of TAME, ETBE, DIPE, TBA, and TAA were observed to be of the same order of magnitude as the aerobic degradation rate of MTBE in one research study using a mixed culture.[63] Together with the similarity of product chemical structure, these results suggest that the same or similar enzyme systems and pathways are responsible for the biodegradation of these oxygenates and that the bioremediation of fuel oxygenates other than MTBE therefore has similar constraints.[24] Church and Tratnyek[63] proposed a degradation pathway of MTBE and other oxygenates as shown in Figure 24.5.

Successful field-scale applications of engineered bioremediation systems have been limited to the aerobic pathway, as opposed to the anaerobic pathway. The advantages of the aerobic pathway include the following:

1. More energy is derived by microorganisms from the aerobic metabolism of MTBE and other fuel oxygenates; consequently, MTBE degrading cultures grow more quickly under aerobic conditions.
2. There are a number of aerobes that are known to use MTBE as a sole carbon and energy source; anaerobic pathways and the types of microorganisms involved are less well documented.
3. Where the terminal electron acceptor is not present initially in sufficient quantity, addition of oxygen for aerobic bioremediation can be as simple as bubbling air into the aquifer; addition of electron acceptors for anaerobic bioremediation is more complex and can foster concerns regarding the toxicity and fate of the added material.
4. Laboratory studies have provided inconsistent results regarding the degree to which MTBE is biodegraded anaerobically to end products and the extent to which other oxygenates are biodegraded under anaerobic conditions.

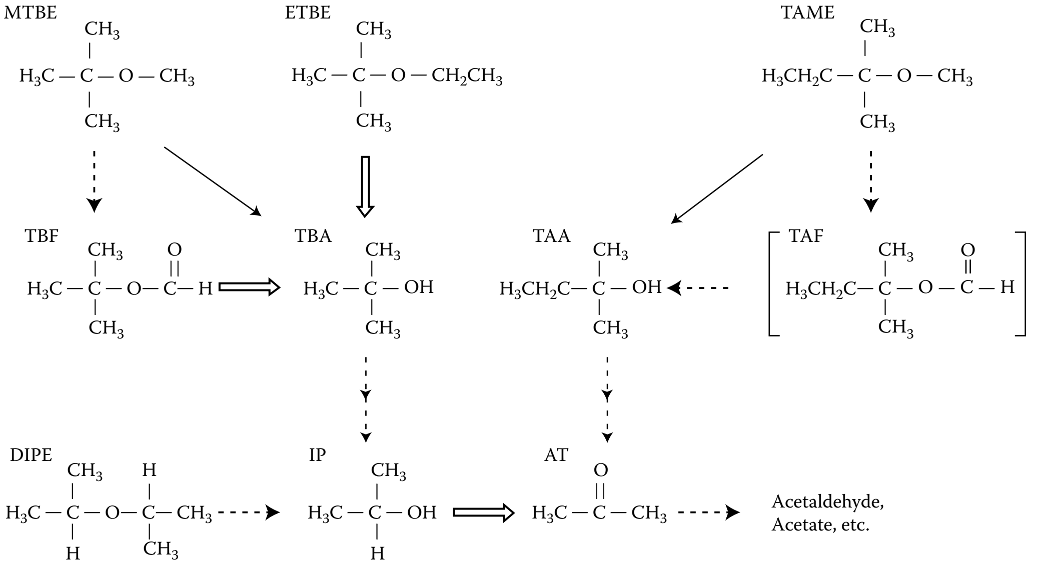


FIGURE 24.5 Proposed degradation pathway of MTBE and other oxygenates. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

TABLE 24.12
MTBE Biodegradation Mechanisms and Products

Zone		Electron Donor	Electron Acceptor	Products of Complete Degradation
Aerobic		MTBE	O_2	CO_2 and H_2O
Anaerobic	Nitrate reducing	MTBE	NO_3^-	N_2, NH_3, CO_2, and H_2O
	Iron reducing	MTBE	Fe^{3+}	Fe^{+2}, CO_2, and H_2O
	Sulfate reducing	MTBE	SO_4^{-2}	H_2S, CO_2, and H_2O
	Methanogenic	MTBE	CO_2	CH_4, CO_2, and H_2O

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

However, the many pathways by which MTBE and other oxygenates may be biodegraded anaerobically have been the subject of recent research and ongoing studies. Table 24.12 highlights the various electron acceptors that are used in anaerobic bioremediation studies and contrasts the products of complete anaerobic degradation with those for aerobic metabolism.

While Table 24.12 lists the products of complete degradation of MTBE, incomplete degradation of MTBE and other oxygenates may also occur under certain conditions. Of specific note, TBA has been shown to be a degradation intermediate that may persist under anaerobic conditions.[60] In some cases, this can result in MTBE plumes having a concentration of TBA in excess of the concentration of MTBE.[58] A paper published by Schmidt et al.[64] provides further information about the role of TBA in microbial biodegradation. Therefore, application of bioremediation approaches to MTBE and other oxygenates often have considered the complete pathway to end products and the possible stall of the bioremediation process at intermediates along that pathway.

24.7.3 APPLICATION OF BIOREMEDIATION TO TREATMENT OF OXYGENATES

Bioremediation is applied to MTBE and other oxygenates in systems that range in complexity from not being engineered at all (natural biodegradation) to systems that are completely engineered, including the addition of conditioned microorganisms (bioaugmentation) and of nutrients as well as cosubstrates and electron acceptors (biostimulation). Further, these systems can be based on aerobic or anaerobic pathways, or a sequential combination of these pathways.

The rate at which natural biodegradation of MTBE and other oxygenates will occur at a site is affected by a number of site conditions, including groundwater chemistry, presence of other contaminants, and number of native microbes capable of degrading MTBE or other oxygenates. Whether the contaminated zone is aerobic or anaerobic (nitrate reducing, iron reducing, sulfate reducing, or methanogenic), and other chemical parameters (e.g., pH, alkalinity, and inorganic content) will determine what types of microbes may be able to grow and what type of biodegradation pathway may be followed. Figure 24.6 depicts the oxidative zones that may be present in a plume at a petroleum-contaminated site and illustrates how each of the anaerobic and aerobic pathways listed in Table 24.12 may be part of the natural biodegradation process.

Multiple microbes that are capable of biodegrading oxygenates have been identified at sites contaminated with MTBE and other oxygenates. Whether such microbes are present at a specific site will affect the viability of natural biodegradation without the need for bioaugmentation. Where these microbes are present, natural biodegradation or limited biostimulation, such as air sparging to increase oxygen levels, may be effective in reducing the concentrations of MTBE and other oxygenates. However, other conditions must be conducive to support significant natural biodegradation.

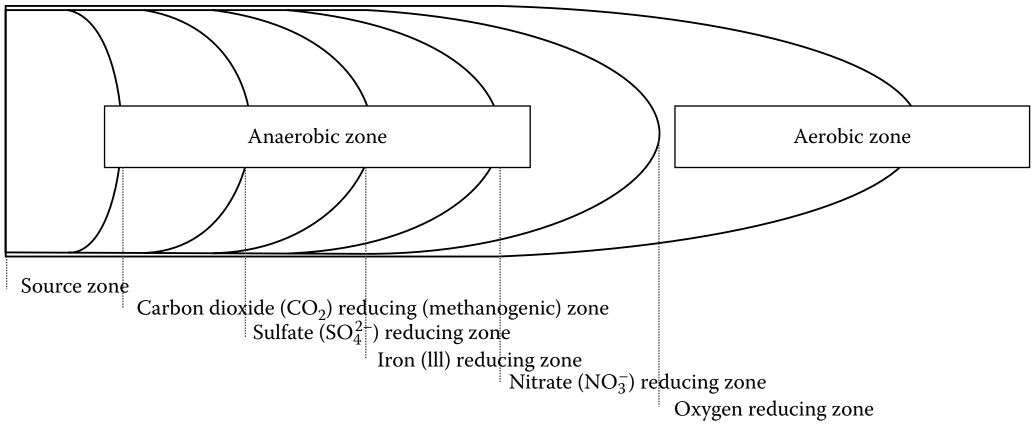


FIGURE 24.6 Typical zones downgradient of petroleum contaminant. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

Typically, only those sites that have aerobic conditions in the contaminated zone because of shallow water tables and high rates of groundwater recharge have achieved significant natural biodegradation of MTBE and other oxygenates.[65]

In some cases, the presence of other contaminants, such as benzene, has been shown to facilitate the natural biodegradation of MTBE and other oxygenates through cometabolism. However, contaminants such as BTEX may also inhibit the biodegradation of oxygenates through the depletion of electron acceptors or nutrients, or may be preferentially used because of the relatively slow growth of oxygenate-degrading microorganisms.[24,66] In addition, sites contaminated with alcohols such as ethanol may also inhibit the biodegradation of ether-based oxygenates such as MTBE through the depletion of electron acceptors or nutrients.[67]

Fully engineered systems for the bioremediation of oxygenates typically incorporate both biostimulation and bioaugmentation to accelerate the biodegradation process. Most commonly, these systems are based on the aerobic pathway so that the biostimulation component includes the addition of oxygen, through air/oxygen sparging or addition of oxygen-releasing chemicals, as well as the addition of nutrients. The addition of oxygen through one of these means can be used to make the entire contaminant zone aerobic and thereby provide more uniform conditions for accelerated biodegradation. Maintaining high oxygen levels is especially important to effective aerobic biodegradation in that oxygenate-degrading organisms have been shown in research studies to require a higher concentration of oxygen. The bioaugmentation component is achieved by adding microbial cultures that are conditioned to degrade oxygenates either by being grown on these contaminants or by culturing isolated species that have the required enzymes. Bioaugmentation is often critical to the success of an engineered bioremediation system in that microorganisms capable of degrading oxygenates may not be present natively and are slow growers.[55,68]

The use of anaerobic pathways may have engineering advantages under certain conditions, such as in treating oxygenate contamination in deep aquifers or source zones. Recent research and field studies have focused on the various anaerobic pathways for the biodegradation of MTBE and other fuel oxygenates.[60] However, the results of these studies in terms of oxygenate degradation efficiency have been variable and no single anaerobic pathway has demonstrated consistent success for degrading oxygenates to end products, even in the laboratory environment.[69] Therefore, site-specific treatability studies and pilot testing are generally performed if bioremediation using anaerobic pathways is to be considered at a site.

Engineered systems may also incorporate the addition of a cosubstrate to help establish an active microbial community and thereby accelerate the biodegradation of oxygenates. Hydrocarbon gases, such as propane and butane, are one type of cosubstrate that has been used in field applications due to the simplicity of injecting and diffusing a hydrocarbon gas.[62] Some proprietary technologies are based on the use of specific cosubstrates and strains of microbes.

24.7.4 TYPES OF PROJECTS USED IN BIOREMEDIATION TREATMENT OF OXYGENATES

From the 323 MTBE projects in U.S. EPA's MTBE Treatment Profiles dataset, 73 projects were identified where MTBE was treated using engineered bioremediation systems, either alone or in conjunction with another technology. Information on the treatment of other oxygenates during these 73 projects is limited, with a total of 12 of the 73 projects reporting TBA as a cocontaminant. Sixty-two of the 73 bioremediation projects employed either *in situ* or *ex situ* bioremediation alone. However, 11 of the projects supplemented bioremediation treatment with air sparging, SVE, or pump-and-treat. Of the 40 projects specifying the type of MTBE biodegradation mechanism employed, 37 projects reported using the aerobic pathway, one project reported using cometabolic pathways, one project reported using a combination of aerobic and anaerobic pathways, and one project reported using a combination of aerobic and cometabolic pathways. Short summaries of three of these projects, *In Situ* Bioremediation at Port Hueneme, Oxnard, California; *In Situ* Bioremediation at Sunoco Service Station, Massachusetts; and *In Situ* Bioremediation at South Beach Marina, Hilton Head, South Carolina, are included at the end of this section.

24.7.5 PERFORMANCE OF *IN SITU* BIOREMEDIATION IN TREATMENT OF OXYGENATES

Tables 24.13 and 24.14 summarize performance data for the 35 completed and 38 ongoing *in situ* bioremediation projects. The concentration of MTBE in groundwater prior to treatment was as high as 870,000 μg/L and as low as 10 μg/L. The data show that bioremediation (either alone or in combination with other technologies) has been employed to remediate MTBE in groundwater and soil to concentrations <50 μg/L and has achieved MTBE concentration reductions >99%. The median project duration for the 20 completed sites ranged from 6 months to 1 year.

In addition to the performance data reported for MTBE, eight of the 12 projects in the dataset that reported treating TBA using bioremediation also provided performance data. All of these eight sites provided TBA concentration prior to bioremediation treatment (the highest initial concentration was 90,000 μg/L) and two provided TBA concentrations following treatment (both achieved <5 μg/L).

TABLE 24.13
Completed *In Situ* Bioremediation Projects Performance for 35 Projects

Technologies	Number of Projects	Initial MTBE Concentration (μg/L)			Final MTBE Concentration (μg/L)			Median Project Duration (months)
		Minimum	Median	Maximum	Minimum	Median	Maximum	
In situ bioremediation only	25	5	2800	100,000	1	35	33,000	6
In situ bioremediation with air sparging and SVE	6	4151	10,800	44,400	NR	NR	NR	12

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

NR = Information not provided.

TABLE 24.14
Ongoing *In Situ* Bioremediation Projects Performance for MTBE at 38 Sites

MTBE Concentration Range	Number of Projects Reporting Initial MTBE Concentrations	Number of Projects Reporting Posttreatment MTBE Concentrations
Greater than 100,000 μg/L	1	0
Greater than or equal to 10,000 μg/L but less than 100,000 μg/L	12	1
Greater than or equal to 1000 μg/L but less than 10,000 μg/L	11	3
Greater than or equal to 100 μg/L but less than 1000 μg/L	4	3
Greater than or equal to 50 μg/L but less than 100 μg/L	0	1
Less than 50 μg/L	5	5

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

Because of the heightened interest in bioremediation of TBA, additional information was obtained about several of these sites. These data, provided in the online database, show that several sites were able to reduce the concentration of TBA, sometimes to less than its site-specific cleanup level. For example, at several sites in Texas, including Turtle Bayou Easement Area and Rural Area Disposal Area, *in situ* bioremediation was used in conjunction with other technologies such as SVE, and *in situ* thermal desorption. At these sites, the concentrations of TBA were reduced to less than its cleanup goal, with concentrations after treatment ranging from 100 to 1000 μg/L. At the Naval Base Ventura County, Port Hueneme, California, *in situ* bioremediation was used in a biobarrier configuration, and the concentration of TBA was reduced from >1000 to <5 μg/L.

24.7.6 COSTS OF *IN SITU* BIOREMEDIATION TREATMENT OF OXYGENATES

Project cost data were reported for 28 of the 73 bioremediation projects in the dataset; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that the reported costs incorporate different components, such as treatment, monitoring, design, oversight, and health and safety. Most (21 projects) of the reported costs were for ongoing projects and represent either a partial actual cost or an estimated total project cost.

The median reported total cost for all bioremediation projects was approximately USD125,000, with most projects having a total cost between USD50,000 and USD350,000. The total cost for all 28 projects reporting this information ranged from USD4000 to USD5,200,000 per project, depending on scale, type of engineered application, and site conditions. For example, at the Port Hueneme site, a 152.5 m (500 ft) wide biobarrier was constructed in a shallow sand aquifer and had an installation cost of USD435,000, with first year operation and maintenance (O&M) costs of USD75,000. At a site in South Carolina, 11.36 m^3 (3000 gallons) of a liquid microbial solution was injected through 40 monitoring and 15 injection points, for a total cost of USD63,500.

Because the area, volume, or mass treated was not consistently available for the 28 bioremediation projects, no unit costs were estimated. The cost per volume of subsurface treated was reported in one literature source[33] as ranging from approximately USD222 to USD432/m^3 (USD170–USD330/yd^3) for *in situ* bioremediation in general. This source also reported unit costs for *ex situ* bioremediation ranging from USD15.7 (USD12) to more than USD1300/m^3 (USD1000/yd^3) treated. These results suggest that the cost for bioremediation is highly variable and depends on site-specific conditions and remedial goals.[1,70] Overall, the cost of bioremediation is generally considered to be better than the average for applicable groundwater remediation technologies.[34]

24.7.7 FACTORS THAT AFFECT THE PERFORMANCE AND COST OF OXYGENATE TREATMENT USING *IN SITU* BIOREMEDIATION

When oxygenates are present and must be remediated at a site, bioremediation, either alone or in combination with other technologies, may be a suitable remediation approach. Although both ether- and alcohol-based oxygenates are susceptible to biodegradation, the site conditions will determine whether bioremediation is an appropriate technology for a given site Key factors that affect the performance and cost of bioremediation include[1,71]

1. Concentration, mass, and distribution of VOCs in the soil and groundwater
2. Geology
3. Moisture content
4. Mineral content
5. pH
6. Temperature
7. Concentrations of terminal electron receptors and nutrients
8. Presence of appropriate microbes in the subsurface
9. Cleanup goals
10. Requirements for site cleanup.

These factors affect the design of the bioremediation system, the biodegradation pathways that can be employed, and the amendments that must be added to enhance bioremediation.[34,40]

Bioremediation is generally considered to be more suitable for the dissolved phase in groundwater plumes or low concentrations in soil rather than grossly contaminated source areas where free product may be present. Other technologies that incorporate free product removal, such as MPE and pump-and-treat, are generally considered more applicable to source areas. Therefore, source areas are typically treated through removal or another technology prior to the application of bioremediation. Because of the above factors, the design of a bioremediation system is typically based on significant site analysis and bench- and pilot-scale testing rather than the application of packaged treatment systems.

24.7.8 ADVANTAGES AND LIMITATIONS

The advantages of applying bioremediation are as follows[40,57]:

1. Application involves equipment that is widely available and relatively easy to install.
2. *In situ* systems create minimal disruption and/or disturbance to ongoing site activities.
3. Time required for subsurface remediation using aerobic bioremediation may be shorter than the time required for pump-and-treat.
4. Bioremediation is generally recognized as being less costly than other remedial options (e.g., pump-and-treat or chemical oxidation).
5. It can be combined with other technologies (e.g., bioventing and SVE) to enhance site remediation.
6. In many cases, it does not produce waste products that require disposal.

The limitations to applying bioremediation are as follows[40,57]:

1. Injection wells and/or infiltration galleries may become plugged by microbial growth or mineral precipitation.
2. Oxygenate-degrading microorganisms are typically slow growing and may not be present natively at all sites; pilot or treatability studies may be needed to confirm the applicability of bioremediation at a specific site.
3. Bioremediation of source zones may take substantial time due to the presence of free product and lack of immediate bioavailability.
4. Bioremediation difficult to implement in low-permeability aquifers (hydraulic conductivity $<10^{-4}$ cm/s).
5. Reinjection wells or infiltration galleries may require permits or may be prohibited. Some states require permits for air injection.
6. It may require long-term monitoring and maintenance for biobarrier-type applications.
7. Effective remediation may only occur in more permeable layers or channels within an quifer.

24.7.9 EXAMPLE PROJECTS

24.7.9.1 *In Situ* Bioremediation at Port Hueneme, Oxnard, California

A full-scale cleanup has been in progress using *in situ* bioremediation to treat MTBE, BTEX, and TBA in groundwater at the Naval Base Ventura County, Port Hueneme in Oxnard, California. Geology at the site consists of a shallow sand aquifer bounded on the bottom by a clay aquitard, through which groundwater flows at an average velocity of 0.3 m/d (1 ft/d). At a depth of 3–6 m (10–20 ft) below ground surface, the 1500 in. by 150 m (5000 by 500 ft) dissolved MTBE plume mixes with a smaller the BTEX plume that originates from sands contaminated with residual NAPL.

The *in situ* bioremediation system consists of a 150 m (500 ft)-wide “biobarrier,” which acts as a passive flow-through system and was installed just downgradient of the NAPL plume. Contaminated groundwater containing dissolved MTBE, TBA, and BTEX travels through the biobarrier and is injected with various combinations of oxygen, air, and conditioned microorganisms. Oxygen gas and bioaugmented sections are located in the central core of the dissolved contaminant plume and air injections are used on the edge of the plume. Operation of the system began in the fall of 2000. Initial MTBE, BTEX, and TBA concentrations in the groundwater plume were >10,000 μg/L in the center of the plume.

In 2002, after 18 months, contaminant concentrations were reduced to <5 μg/L in monitoring wells downgradient of the biobarrier and extending across the length of the biobarrier. No significant differences in performance were observed for the differently operated sections of the barrier. Dissolved oxygen increased from a preinjection concentration of less than 1 mg/L to 10–35 mg/L throughout the treatment zone, thereby increasing the potential for aerobic biodegradation to occur. In addition, the increased dissolved oxygen levels upgradient of the treatment zone due to dispersion of the injected gas appear to cause upgradient reductions in MTBE and benzene concentrations. Peripheral monitoring wells have not shown an increase in contaminant concentrations, indicating that groundwater is flowing through and not around the biobarrier.

The biobarrier system includes 252 gas injection wells, 174 monitoring wells, 25 satellite gas storage tanks, 154 solenoid valves, a 6.8 m^3/h (240 ft^3/h)-capacity oxygen generator, automated timer circuits, and associated piping and electrical lines. The total installation cost of this equipment was USD435,000; initial year (2001) O&M costs were USD75,000 and are expected to continue for a service life of 40 years. A preliminary cost comparison with an existing pump-and-treat system at this site suggests savings of more than USD34 million over the project life. The state regulatory agency recently approved continued use of this biobarrier and installation of a second biobarrier (at the toe of the plume) as the final remedy for the MTBE plume.[72,73]

24.7.9.2 *In Situ* Bioremediation at Sunoco Service Station, Massachusetts

A full-scale cleanup was performed using *in situ* bioremediation to treat MTBE and BTEX at a service station in Massachusetts. Soil at the site consists of a layer of sand and gravel underlain by peat, silt, and clay. The *in situ* bioremediation system consisted of 12 injection wells and two butane injection panels used to stimulate cometabolic aerobic biodegradation of the contaminants in groundwater. The system was operated between October 2000 and January 2001. MTBE concentrations were reduced from 370 to 12 μg/L and BTEX contamination in groundwater was reduced by approximately two orders of magnitude during the 4-month period.[74]

24.7.9.3 *In Situ* Bioremediation at South Beach Marina, Hilton Head, South Carolina

A full-scale cleanup was performed using *in situ* bioremediation to treat MTBE, BTEX, and naphthalene in groundwater at a service station with leaking underground fuel storage tanks. At this site, groundwater is 1.32–2.11 m (4.32–6.92 ft) below the ground surface, with an average hydraulic gradient of 0.078 m/m (0.078 ft/ft) and with a calculated velocity of 1.96 m/yr (6.42 ft/yr). No confining units were identified at the site.

The *in situ* bioremediation application at this site included injection of a liquid microbial solution into the subsurface through monitoring and injection wells. This solution includes microbes (*Pseudomonas*, *Bacillus*, and *Corynebacterium*), oxygen, emulsifier, surfactant, and nutrients. Five injections were conducted. Over 11.3 m^3 (3000 gallons) was injected from February 1999 to September 2000 into approximately 40 wells and 15 Geoprobe injection points. As of September 2000, MTBE levels decreased by 96% (3310–146 μg/L), while benzene decreased by 83% (2571–435 μg/L), toluene by 66% (24,330–8300 μg/L), and naphthalene by 84% (5377–853 μg/L); xylene levels increased and were above preoperational level as of September 2000. The system will continue to be operated until all target levels have been met. The total cost for the cleanup of this site is USD63,500.[34]

24.8 *IN SITU* CHEMICAL OXIDATION

24.8.1 ISCO Process

ISCO is a technology in which an oxidant, and other amendments as necessary, is introduced into contaminated media to react with site contaminants such as MTBE, other fuel oxygenates, and other organic compounds, converting them to innocuous products, such as carbon dioxide and water. Typically, hydrogen peroxide (H_2O_2), ozone (O_3), or permanganate (MnO_4^-) oxidants have been used to treat MTBE in soil and groundwater. Persulfate ($S_2O_8^=$) compounds have also been used as chemical oxidants for treating MTBE. All of these chemicals react, either directly or through the generation of highly reactive free radicals, such as OH• and H•, or SO_4^-•, with organic compounds such as MTBE to break hydrocarbon bonds and form degradation products such as alcohols, carbon dioxide, and water. In some applications, different oxidants may be used in combination, such as H_2O_2/O_3, or in conjunction with catalysts, such as H_2O_2 in the presence of ferrous iron (Fenton's chemistry or reagent), to enhance oxidation through the generation of free radicals. Depending on site conditions, oxidants may be introduced to the contaminated area using a variety of engineered approaches, including groundwater well injection, groundwater well recirculation, lance injection (jetting), PRBs, deep soil mixing, or soil fracturing.[75]

24.8.2 Effect of the Properties of MTBE and Other Oxygenates on Treatment

As with other organic and some inorganic contaminants, MTBE and other oxygenates are susceptible to degradation through oxidation reactions. If a sufficient amount and strength of oxidant and enough time are provided, all of the ether- and alcohol-based fuel oxygenates can be mineralized to carbon dioxide and water. For example, the following equations show the stoichiometric mineralization of some of the common oxygenates through oxidation using hydrogen peroxide:

ETBE, TAME, DIPE: $C_6H_{14}O + 18H_2O_2 \rightarrow 6CO_2 + 25H_2O$
MTBE: $C_5H_{12}O + 15H_2O_2 \rightarrow 5CO_2 + 21H_2O$
TBA: $C_4H_{10}O + 12H_2O_2 \rightarrow 4CO_2 + 17H_2O$
Ethanol: $C_2H_6O + 6H_2O_2 \rightarrow 2CO_2 + 9H_2O$
Methanol: $CH_3O + 5/2H_2O_2 \rightarrow CO_2 + 4H_2O$

Analogous equations can be derived for mineralization using other oxidants. However, the oxidation of MTBE or other oxygenates to carbon and water is a multistep, multipath process in which each step has different equilibrium and kinetic factors that govern the extent and rate that each reaction can take place. Not all oxidants have proven successful in the mineralization of MTBE, leaving by-products such as tert-butyl formate (TBF) and TBA. The full spectrum of possible reaction intermediates and governing criteria have not been determined for MTBE and the other oxygenates. However, in general, the greater the number of carbon atoms in the oxygenate, the greater the stoichiometric proportion of oxidant that will be required (under the same conditions) to fully oxidize it. For example, based on the previous equations, the complete mineralization of 1 lb of ETBE, MTBE, TBA, ethanol, and methanol would require 6.0, 5.7, 5.5, 4.4, and 1.22 kg (2.7 lb) of hydrogen peroxide, respectively.[76]

While the above comparison (or similar comparisons for other oxidants) of the amount of oxidant required for different oxidants may hold under controlled laboratory conditions, the actual amount and type of oxidant that is necessary for the treatment of MTBE or other oxygenates at a given site will depend on numerous factors beyond the amount of contaminant present including

1. The amount and types of other contaminants (such as other petroleum constituents) that will also consume oxidant.
2. The chemical composition of the soil and groundwater, specifically the amount of natural organic matter (NOM) and other reduced species, such as iron (II) or manganese (II); often analyzed as the chemical oxygen demand (COD) of the soil, or the soil oxidant demand.
3. The pH, alkalinity, and temperature of the treatment area; these conditions will affect equilibrium and kinetic constants defining the extent and rate that each oxidation step can take place.
4. The potential for biodegradation of site contaminants or oxidation products.
5. Hydraulic and geologic parameters, such as hydraulic conductivity, hydraulic gradient, and permeability, that will affect the migration and dissolution of the oxidant once it is introduced to the subsurface.

Because these factors can vary from site to site, typically, field analyses of these parameters and bench- and pilot-scale studies are conducted to determine the type and amount of oxidant required for a specific application.

24.8.3 Application of ISCO to Treatment of Oxygenates

During ISCO, oxidants and any necessary amendments are introduced to the treatment area with one or more of the available delivery approaches. Pilot-scale testing is often used to determine the type of amendment and delivery system used at a given site. Some of the key considerations for the common oxidants and delivery approaches are summarized below.

24.8.3.1 Oxidants/Amendments

Hydrogen Peroxide (H_2O_2)—Hydrogen peroxide has been used alone or in combination with other chemicals (such as using ferrous iron as a catalyst to generate free radicals through Fenton's chemistry) or with ultraviolet (UV) light. When used alone, hydrogen peroxide is typically injected as a concentrated solution (35–50%), which decomposes violently when contacting groundwater, generating heat and high volumes of gas. When using Fenton's chemistry, the pH of the treatment area is typically maintained at acidic ($pH < 4$) conditions and a more dilute hydrogen peroxide solution is used. Hydrogen peroxide and iron catalysts are typically injected separately, such as through specific ports in an injection lance, or through injection wells, because free radicals tend to react rapidly and can dissociate if generated prior to injection. Excess hydrogen peroxide that is not used in degrading organic compounds will rapidly degrade to water and oxygen.[77]

Ozone (O_3)—Ozone is a highly reactive chemical that has been used to treat organic compounds in *ex situ* groundwater and drinking water treatment systems.[78] It can also be used to treat MTBE in an ozone–air sparging system. This system injects ozone through tubing to a microporous sparge point designed to generate very small bubbles ("microbubbles," approximately 50 μm in diameter), which have a high surface-to-volume ratio. Organic contaminants in groundwater, such as MTBE, volatilize into ozone bubbles and are oxidized. Ozone that is not consumed degrades to oxygen. Ozone is often used in combination with other oxidants, such as hydrogen peroxide, to enhance oxidation through the generation of free radicals. If bromine is present in the treatment area, bromate generation, which can occur during ozonation, is typically monitored during treatment.

Permanganate (MnO_4^-)—Permanganate is often employed in the form of solid or a solution of potassium or sodium permanganate for groundwater treatment.[79–81] It has a smaller oxidizing potential than ozone and hydrogen peroxide using Fenton's chemistry, resulting in the relatively slower oxidation of MTBE and other oxygenates. However, permanganate has a longer half-life compared with the stronger oxidants, and persists in the environment for a longer time. The end product of permanganate oxidation is manganese dioxide, which, depending on the groundwater pH, can precipitate into the formation. Excessive precipitation may reduce soil permeability.

Other Oxidants—Combinations of the above oxidants and other oxidants such as persulfate compounds are also being used to treat MTBE and other oxygenates. These and other combinations and other oxidants are being developed to maximize the generation of highly oxidizing free radicals, increase oxidant persistence, or otherwise enhance *in situ* oxidation.

24.8.3.2 Delivery Approaches

Groundwater well injection—Oxidants may be introduced to the treatment zone through existing or new groundwater monitoring wells as a liquid, gas, or solid. This method relies on the natural migration of oxidants from the well into the formation. Injection wells need to be adequately spaced to allow for oxidant delivery to the entire treatment area.

Groundwater recirculation—A groundwater recirculation system may be used to extract groundwater from within or at the downgradient edge of the contaminated area, introduce oxidants and amendments aboveground, and reinject the groundwater upgradient of the treatment area. This approach can be used to increase the flow-through of oxidant through the treatment area, as well as to achieve downgradient containment of a contaminated groundwater plume.

Lance injection, jetting, and fracturing—Use of a high-pressure lance can create microfractures in soils that increase soil permeability and allow for direct injection of oxidants and amendments into a desired treatment area without the need for an existing or new groundwater well.

Soil mixing—For lower-permeability soils, soil mixing using tilling for shallow soil or an auger for deeper soil can be used to introduce oxidants to a treatment area.

PRB—Oxidants can be injected into the treatment zone of a PRB to oxidize the groundwater that flows through it. This approach can be used as a containment approach for a contaminated groundwater plume. Also, a PRB could be placed upgradient or within a treatment area allowing the oxidized groundwater leaving the PRB to flow through the treatment area.

There are also technologies that use electrical or other forms of energy to generate oxidizing and reducing radicals in aqueous solution and thereby destroy contaminants such as MTBE and other oxygenates. These technologies include ultrasound and electron beam (E-beam) treatment, and are primarily used in *ex situ* applications. Recently, however, ultrasound treatment has been proposed as a potential *in situ* application by incorporating ultrasonic transducers into a robotic self-powered mining head.[82]

Additional information relevant to the application of ISCO at sites in general or contaminated with MTBE and other oxygenates is available in the following Refs. [75,82–86].

24.8.4 TYPES OF PROJECTS USED IN ISCO TREATMENT OF OXYGENATES

From the 323 MTBE projects in U.S. EPA's MTBE Treatment Profiles dataset, 21 projects were identified where MTBE was treated using ISCO. No ISCO projects reported treating other oxygenates. Four of the projects used ozone and 17 used hydrogen peroxide, either alone or with Fenton's chemistry.

Most of the 21 ISCO projects were performed at full scale (17 projects) at the time that their profiles were compiled. Eight of the 21 projects were identified as completed, and the remaining 13 as ongoing. In addition, while most[14] of the projects used ISCO alone, seven projects supplemented ISCO with air sparging, pump-and-treat, SVE, or MPE.

24.8.5 PERFORMANCE OF ISCO IN TREATMENT OF OXYGENATES

Tables 24.15 and 24.16 summarize performance data for the eight completed and 13 ongoing ISCO projects. The data presented in these tables show that ISCO (either alone or in combination with other technologies) has been used to remediate MTBE in groundwater from concentrations

TABLE 24.15
Completed ISCO Projects—Performance for Eight Projects

Technologies	Site Name And Location	Scale	Initial MTBE Concentration (μg/L)	Final MTBE Concentration (μg/L)	Median Project Duration (months)
ISCO only	Former maintenance and repair garage, NY—H, West Chester, NY	Pilot	451	171	12
	Spill site (Long Island, NY), Long Island, NY	Pilot	6300	79	2
	Service station, PA—D, Warminster, PA	Full	50,000	6.6	14
	Service station, NJ—E, North Haledon, NJ	Full	403,000	1430	2
	Garage, NJ—F, Island Heights, NJ	Full	55	4	14
	Warehousing Facility in Union County, NJ	Full	6400	70	NR
ISCO with SVE	Former Service Station, PA—A, Bucks County, PA	Full	475,000	68,400	18
ISCO with pump-and-treat	North Texas Service Station, TX	Full	17,000	31	9

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

TABLE 24.16
Ongoing ISCO Projects—Performance for 13 Sites

MTBE Concentration Range	Number of Projects Reporting Initial MTBE Concentrations	Number of Projects with Last Reported MTBE Concentrations
Greater than 100,000 μg/L	0	0
Greater than or equal to 10,000 μg/L but less than 100,000 μg/L	1	0
Greater than or equal to 1000 μg/L but less than 10,000 μg/L	3	2
Greater than or equal to 100 μg/L but less than 1000 μg/L	6	2
Greater than or equal to 50 μg/L but less than 100 μg/L	0	1
Less than 50 μg/L	2	6

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

>10,000 μg/L to <50 μg/L and has achieved MTBE concentration reductions >99%. Because the dataset included relatively few completed projects with performance data, Table 24.15 provides a summary of specific projects instead of a summary of minimum, median, and maximum concentrations. The median project duration for the 19 completed sites ranged from 9 to 18 months.

24.8.6 COSTS OF ISCO TREATMENT OF MTBE

The total project cost was reported for one of the 21 ISCO projects identified above. The completed Former Service Station, Pennsylvania, project that used ISCO with SVE, reported a total project cost of USD146,000. This cost was broken down further into USD90,000 of capital cost and USD56,000 of operation and maintenance cost. Because the area, volume, or mass treated was not available for this project, no unit cost was calculated.

There is little additional information in the literature about the costs of using ISCO for the treatment of MTBE and other oxygenates, or for other contaminants. The cost per volume of subsurface treated was reported in one literature source as ranging from USD68 to USD405/m^3 (USD52–USD310/yd^3) in general.[75] The cost of ISCO is generally considered to be the average of the costs for remediation technologies for treatment of contaminated groundwater.[34]

24.8.7 FACTORS THAT AFFECT THE PERFORMANCE AND COST OF OXYGENATE TREATMENT USING ISCO

When MTBE or other oxygenates are present and must be remediated at a site, ISCO, either alone or in combination with other technologies, may be a suitable remediation approach. Although both ether- and alcohol-based oxygenates are susceptible to chemical oxidation, the chemical, hydraulic, and geologic conditions of a given site will determine whether ISCO is a feasible option for treatment. For example, ISCO may not be economically feasible for sites with high concentrations of NOM or other constituents that may consume large amounts of oxidant. In addition, sites with low subsurface permeability may require more complex approaches, such as fracturing or soil mixing, to deliver the necessary oxidant to the treatment zone, potentially increasing costs. Other site characteristics, such as pH, alkalinity, and temperature will also affect system design and impact cost and performance. For example, for oxidants that have specific pH requirements, pretreatment of the aquifer with an acid solution to lower the pH is typically considered. In addition, off-gas generated by the chemical reactions in ISCO may require capture and treatment.[76]

In addition to the technology-specific factors described above, additional factors may also affect the performance and cost of an ISCO system. These factors include the concentration, mass, and distribution of contaminants in the groundwater; subsurface geology and hydrogeology; cleanup goals; and requirements for site cleanup. For example, heterogeneity within the subsurface may result in preferential pathways that prevent the injected oxidant from reaching the entire treatment area. Because of the above factors, the design of an ISCO system is typically based on pilot-scale testing rather than generic design equations.

24.8.8 ADVANTAGES AND LIMITATIONS

The advantages of applying ISCO are as follows[34,40]:

1. It has the potential to be used to target hot spots that may not be amenable to bioremediation.
2. It has the potential to achieve cleanup goals in a relatively short amount of time (several months to a year).
3. Depth of application is only limited to the delivery approach used.

The limitations to applying ISCO are as follows[34,40]:

1. Relatively large amounts of oxidant may be needed for treatment of large masses of contaminant (the oxidant does not target only the contaminants of concern).
2. ISCO may have low contact between the oxidant and the contaminant in heterogeneous media or in areas with low permeability.
3. Special precautions may need to be taken to protect worker health and safety during operation (because of the use of strongly oxidizing chemicals); also concentrated oxidant injection can result in violent subsurface reactions.
4. Chemical reactions may form toxic by-products (such as bromate during ozone oxidation) in the groundwater.
5. Off-gas may require capture and treatment.

24.8.9 EXAMPLE PROJECTS

24.8.9.1 Ozone Sparging at Former Service Station, Bucks County, Pennsylvania

At a former service station located in Bucks County, Pennsylvania, remediation needed to be completed within 9 months to facilitate the sale of the property. The cleanup approach used ozone sparging, pump-and-treat, MPE, and SVE to treat MTBE. Free product was removed prior to performing ozone sparging. The sparging system consisted of multiple, nested sparge wells in a treatment area of 54.9 m by 45.8 m (180 ft by 150 ft), and used an ozone dosage of 1.13 kg (2.5 lb/d) at standard 3.4 m^3/h (2 scfm) over a 4-month period. MTBE concentrations in groundwater were reduced from 17,000 to 31 μg/L, which was below the cleanup level of 2900 μg/L. The total cost reported for treatment was USD146,000, consisting of USD90,000 for capital and USD56,000 for O&M.[31]

24.8.9.2 Fenton's Chemistry at Warehousing Facility in Union City, New Jersey

The groundwater at an operating warehousing facility in Union, New Jersey was contaminated with MTBE (concentrations up to 6400 μg/L), TBA, and BTEX. Soil at the site consists of soft red shales interbedded with harder sandstones and minor amounts of conglomerate. After completing a pilot study, hydrogen peroxide and catalysts were injected at six points during three treatment cycles over a 3-month period in mid-1996 (each cycle consisted of 15 days with injection followed by 15 days without injection). MTBE concentrations in groundwater were reduced to <5 μg/L, which was below the cleanup level of 70 μg/L. Rebound was evaluated 4 months after the treatment was completed; results remained below the cleanup level. There was no current cost data provided for this site.[31]

24.9 GROUNDWATER PUMP-AND-TREAT AND DRINKING WATER TREATMENT

24.9.1 Groundwater Extraction for Pump-and-Treat and Drinking Water Treatment

Groundwater pump-and-treat involves the extraction of groundwater from a contaminant plume and the treatment of extracted water using one or more aboveground technologies. Drinking water treatment systems where the extracted water is contaminated with fuel oxygenates involve many of the same activities as groundwater pump-and-treat. In general, the methods for extraction of the groundwater are not linked to or limited by the aboveground (*ex situ*) treatment technologies. This section focuses on groundwater extraction, while the following section focuses on aboveground treatment of the extracted groundwater, for both pump-and-treat and for drinking water treatment.

The groundwater extraction component typically consists of multiple wells and/or trenches for the extraction of groundwater and includes differential control of extraction rates from individual wells to optimize operation. Most groundwater extraction systems incorporate extraction wells that are installed within the contaminant plume downgradient from the source. These extraction wells are designed and controlled to act as a barrier to additional downgradient movement of the contaminant plume and, over a long period of time, to extract contaminant mass. Due to the water solubility of MTBE and other oxygenates, and the associated occurrence of significant quantities of contaminant mass in the dissolved phase, such groundwater extraction systems have specific application to the remediation of plumes incorporating oxygenate contamination.

24.9.2 Effect of the Properties of MTBE and Other Oxygenates on Groundwater Extraction

The properties of MTBE and other oxygenates are relevant to both the extraction and treatment components of pump-and-treat. The properties of fuel oxygenates, specifically their relatively high aqueous solubility and low tendency to partition to organic matter, affect how they migrate with groundwater. As a result, oxygenates tend to become dissolved in and migrate with groundwater more readily than other petroleum contaminants such as BTEX. One consequence of this tendency that is beneficial to pump-and-treat remediation is that oxygenates are also more readily extracted with groundwater than other contaminants.

24.9.3 Application of Pump-and-Treat to Treatment of Oxygenates

A pump-and-treat system consists of an extraction and a treatment component. Groundwater is typically extracted through vertical groundwater recovery wells although, in the last decade or so, horizontal wells and trenches have also been employed. Variables in the design of a typical system include[87]

1. Types of extraction systems to be used.
2. Number and location of extraction points.
3. Design of extraction points (e.g., diameter, depth, and well screen interval).
4. Type of pumping apparatus to employ (e.g., aboveground vacuum, submersible, and pneumatic).
5. Design of a distribution system to transport extracted groundwater to the aboveground treatment system (e.g., aboveground versus underground piping or possible need for double-walled piping at RCRA-regulated sites).

For the most part, the above considerations are not affected by the specific contaminants present at the site, but by site characteristics, such as plume distribution, hydrogeologic characteristics, and aboveground obstacles (such as buildings or active roadways). Typical extraction system construction materials, such as polyvinyl chloride (PVC) piping and stainless steel pumps, are appropriate for fuel oxygenates at typical contaminated groundwater concentrations. Groundwater extraction system optimization approaches at sites contaminated with MTBE and other oxygenates are similar to those used at other sites, such as the use of phased construction, adaptive management of pumping rates, periodic modeling of the well arrays, and pulsed pumping.[88]

A conventional pump-and-treat extraction system is typically designed to recover only groundwater. Integrated or separate systems have also been used to capture free product or contaminated vapor concurrently with groundwater. More detailed information relevant to the application of pump-and-treat at sites contaminated with MTBE and other oxygenates and in general is available in the literature.[88–90]

24.9.4 TYPES OF PROJECTS USED IN PUMP-AND-TREAT FOR TREATMENT OF OXYGENATES

From the 323 projects in U.S. EPA's MTBE Treatment Profiles dataset, 85 projects were identified where MTBE in groundwater was remediated using pump-and-treat along with 15 additional projects that treated MTBE in drinking water (collectively referred to as pump-and-treat projects). Information on the treatment of other oxygenates was reported for 20 of these 100 projects: 16 projects reported TBA, 6 projects reported TAME, 2 projects reported ethanol, and 1 project reported DIPE as a contaminant in addition to MTBE.

Most of the 100 pump-and-treat projects were full scale (84 projects) and were ongoing (78 projects) at the time that its profile was published. In addition, while most (54%) of the projects used pump-and-treat alone, almost half supplemented pump-and-treat with air sparging, SVE, or other technologies, such as phytoremediation, bioremediation, or ISCO.

24.9.5 PERFORMANCE OF PUMP-AND-TREAT IN TREATMENT OF OXYGENATES

For the 100 pump-and-treat projects in the dataset, initial concentrations in groundwater were as high as 475,000 μg/L (North Texas Service Station, Texas). Concentrations after treatment were as low as nondetectable (the typical reporting limit for MTBE is 5 μg/L). Tables 24.17 through 24.20 summarize the available MTBE and TBA performance data for pump-and-treat projects.

TABLE 24.17
MTBE Performance Summary for 21 Completed Pump-and-Treat Projects

Technology(ies)	Number of Projects	Initial MTBE Concentration (μg/L)			Final MTBE Concentration (μg/L)			Median Project Duration (months)
		Minimum	Median	Maximum	Minimum	Median	Maximum	
Pump-and-treat only (groundwater)	8	96	1800	8000	2	24	68	27
Pump-and-treat with air sparging and SVE	5	3	10	390	2	3	4.8	50
Pump-and-treat with other technologies	4	1200	11,000	475,000	18	2070	68,400	40

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

TABLE 24.18

MTBE Performance Summary for 62 Ongoing Pump-and-Treat Projects

MTBE Concentration Range	Number of Projects Reporting Initial MTBE Concentrations	Number of Projects with Last Reported MTBE Concentrations
Greater than 100,000 μg/L	4	1
Greater than or equal to 10,000 μg/L but less than 100,000 μg/L	11	2
Greater than or equal to 1000 μg/L but less than 10,000 μg/L	14	5
Greater than or equal to 100 μg/L but less than 1000 μg/L	11	3
Greater than or equal to 50 μg/L but less than 100 μg/L	3	2
Less than 50 μg/L	10	13

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

The data presented in Table 24.17 for 21 completed pump-and-treat projects (either alone or in combination with other technologies) show that MTBE concentration reductions in groundwater of >99% have been achieved in several projects. The median project duration for the 21 completed sites ranged from 1.5 to 5.5 years.

Treatment performance data for ongoing projects are shown in Tables 24.18 and 24.19, for pump-and-treat and drinking water treatment projects, respectively. Both types of projects treated groundwater with relatively high initial MTBE concentrations (>100,000 μg/L). The available data show that 10 of 11 drinking water treatment projects achieved treated MTBE concentrations of <50 μg/L, while the results for pump-and-treat were more widely distributed.

Table 24.20 provides a summary of treatment performance data for nine pump-and-treat projects that provided performance data for TBA. Initial TBA concentrations were as high as 17,000 μg/L,

TABLE 24.19

MTBE Performance Summary for 12 Ongoing Drinking Water Treatment Systems

MTBE Concentration Range	Number of Projects Reporting Initial MTBE Concentrations	Number of Projects with Last Reported MTBE Concentrations
Greater than 100,000 μg/L	3	0
Greater than or equal to 10,000 μg/L but less than 100,000 μg/L	2	0
Greater than or equal to 1000 μg/L but less than 10,000 μg/L	5	0
Greater than or equal to 100 μg/L but less than 1000 μg/L	1	1
Greater than or equal to 50 μg/L but less than 100 μg/L	0	0
Less than 50 μg/L	1	10

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

TABLE 24.20
TBA Performance Data for Nine Pump-and-Treat Projects

Concentration Range	Number of Projects Reporting Initial Concentrations	Number of Projects with Last Reported Concentrations
Greater than 100,000 μg/L	0	0
Greater than or equal to 10,000 μg/L but less than 100,000 μg/L	1	0
Greater than or equal to 1000 μg/L but less than 10,000 μg/L	4	1
Greater than or equal to 100 μg/L but less than 1000 μg/L	4	0
Greater than or equal to 50 μg/L but less than 100 μg/L	0	0
Less than 50 μg/L	1	7

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

with most after-treatment concentrations <50 μg/L. Due to the additional interest in TBA, a review of data for the 390 projects in the database as of April 2004 showed a total of 15 pump-and-treat projects reporting performance data for TBA. Most of these projects reported using the HiPOx process for the treatment of extracted groundwater, with additional projects using GAC treatment.

24.9.6 COSTS OF PUMP-AND-TREAT FOR TREATMENT OF MTBE

Project cost data were reported for 43 of the 100 pump-and-treat projects in the dataset; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that these costs incorporate different components, such as treatment, monitoring, design, oversight, and health and safety. Table 24.21

TABLE 24.21
Cost Summary for 43 Pump-and-Treat and Drinking Water Treatment Projects (2004 USD)[a]

Technologies	Number of Projects	Total Cost Range (USD)		Median Total Reported Cost (USD)
		Minimum	Maximum	
Pump-and-treat only	15	71,900	1,120,000	500,000
Pump-and-treat with air sparging and SVE	9	96,400	567,000	327,000
Pump-and-treat with air sparging	1	672,000	672,000	672,000
Pump-and-treat with SVE	7	160,000	624,000	339,000
Pump-and-treat with other technologies	1	65,000	65,000	65,000
Drinking water treatment	10	119,000	4,000,000	245,000

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

[a] 2009 USD = 1.11 × 2004 USD.

summarizes the cost information from these 43 projects, broken down by type of other technologies used in conjunction with pump-and-treat.

Another source reported the unit costs of pump-and-treat (based on only capital cost) as <USD5.28/m^3/yr (USD20/1000 gallons/yr) for projects treating >75,700 m^3/yr (20 MG/yr) of groundwater, and unit costs (based on O&M cost) as <1.32 m^3/yr (USD5/1000 gallons/yr) for projects treating >75,700 m^3/yr (20 MG/yr) of groundwater.[87] These unit costs represent treatment costs for the use of pump-and-treat in general, and are not specific to the treatment of MTBE and other oxygenates. In another source, the cost of pump-and-treat is generally considered to be worse than the average of the costs for remediation technologies for treatment of contaminated groundwater.[34]

24.9.7 Factors That Affect the Performance and Cost of Oxygenate Treatment Using Pump-and-Treat

Because of the high water solubility of oxygenates, groundwater extraction may be effective in removing a significant mass of these contaminants. Key factors that affect the performance and cost of the extraction component of a pump-and-treat system include

1. The depth and accessibility of the plume; site hydrogeologic characteristics, such as aquifer permeability.
2. The hydraulic conductivity and flow gradient.
3. Remedial goals for the site.
4. The presence or prior removal of the contaminant source.

If groundwater contamination is deep underground or is beneath areas (such as buildings and rail lines) where conventional vertical wells cannot be placed, innovative drilling techniques or more powerful extraction pumps may be required. Alternatively, shallow and accessible groundwater may be easily extracted using simple collection trenches. Hydrogeologic characteristics will define the number, design, and spacing of extraction points, with tighter formations typically requiring more extraction points for a given area. Groundwater flow characteristics and the number and spacing of wells will be the basis for determining the flow rate of groundwater that needs to be extracted to achieve the desired capture zone. Cleanup goals are also a factor. On-site containment goals may require only pumping from the downgradient edge of a plume, whereas a goal of complete aquifer restoration may require more well points pumping at a higher extraction rates.

One of the most significant factors that affect cost and performance is whether the contaminant source area at a site is present. If a contaminant source area is allowed to continue to contribute to the groundwater plume, groundwater extraction may be required for much longer periods of time than if the contaminant source is removed or treated prior to beginning groundwater pump-and-treat. Because they are relatively water soluble, oxygenates tend to dissolve in groundwater rather than form NAPL. When they do form NAPL, they float rather than sink, and thus form an LNAPL. Thus, removal or treatment of MTBE and other oxygenate source areas can be more straightforward than for other contaminants such as chlorinated solvents.

24.9.8 Advantages and Limitations

The advantages of applying pump-and-treat are as follows[34,40]:

1. The properties of MTBE (high water solubility and low organic/water partition coefficient) make it amenable to groundwater extraction.
2. Pump-and-treat can be used to remediate an aquifer or to provide for hydraulic containment.

The limitations to applying pump-and-treat are as follows[34,40]:

1. Long-term operation may be required to achieve remediation goals for large plumes, complex hydrogeologies, or if an active source remains in place.
2. The cost of constructing, operating, and maintaining treatment systems is considered to be relatively high.
3. Biofouling or mineral precipitation in extraction wells or treatment processes can reduce system performance.

24.9.9 EXAMPLE PROJECTS

The following two project descriptions incorporate examples of completed, full-scale applications of pump-and-treat technology to MTBE-contaminated sites.

24.9.9.1 Pump-and-Treat at Christy Station, North Windham, Maine

MTBE was detected in groundwater at Christy Station, located in North Windham, Maine, soon after the fuel station was constructed in 1997. Between May and June 1998, a full-scale cleanup was performed using a pump-and-treat system that consisted of two extraction wells operating at a combined 3 gpm. The extracted groundwater was treated using shallow tray aeration followed by GAC, and the treated groundwater was disposed off-site. Initial concentrations of MTBE in groundwater were as high as 6000 μg/L, but MTBE concentrations stabilized at 300 μg/L with the operation of the pump-and-treat system. The goal was to reduce MTBE in the aquifer to concentrations <500 μg/L. Following aeration, MTBE in the extracted groundwater was reduced to concentrations ranging from 10 to 30 μg/L, and following GAC adsorption, MTBE was reduced to concentrations of <2 μg/L. A performance standard for extracted groundwater was not identified. The cost assessment for the remediation was USD200,000, the capital cost for the pump-and-treat system was USD60,000, and the O&M cost was USD11,000 for 1 month of operation.[91]

24.9.9.2 Pump-and-Treat and SVE at Service Station NH-B, Somersworth, New Hampshire

During inventory measurements in September 1996, a gasoline station in New Hampshire, referred to as Service Station NH-B, detected a release of 7950 L (2100 gallons) of gasoline. Soil at the site consists of 1.22–2.44 m (4–8 ft) of sandy fill overlying 0.61–3.97 m (2–13 ft) of glacial till, with bedrock occurring at 3.04–4.58 m (10–15 ft) below the ground surface. The depth of the groundwater ranges from 1.52 to 4.58 m (5–15 ft) below the ground surface. The site is characterized by fractured bedrock and a hydraulic gradient of 30 m/1000 m (30 ft/1000 ft). Remedial activities included the removal of three USTs: 782 T (860 tons) of contaminated soil, 102 m^3 (27,000 gal) of groundwater containing 71.7 kg (158 lb) of hydrocarbons, and 454 L (120 gal) of LNAPL. A pump-and-treat system consisting of seven recovery wells screened to bedrock and operating at a total flow rate of 7.5 gpm was implemented. The extracted groundwater was treated using oil/water separation, filtration, and air stripping. The air stripper contained a 7 horse power (HP) blower that operated at 1000 scfm. Maximum concentrations in the influent to the air stripper were 1,670,000 μg/L of MTBE and 439,000 μg/L of BTEX. SVE was conducted using 11 vertical wells and 4 horizontal wells, and a 11.2 kW (15 HP) blower operated at standard 8.5 m^3/min (300 scfm) and 89–127 mm (3.5–5 in) of mercury. No vapor treatment was performed. As of January 2000, the pump-and-treat system had removed 1950 kg (4300 lb) of hydrocarbons and SVE had removed (2976 lb) of hydrocarbons. Enhanced bioremediation is currently performed at the site. The current total remediation cost for this site is USD590,000.[31]

24.10 TREATMENT OF EXTRACTED GROUNDWATER USED IN PUMP-AND-TREAT AND DRINKING WATER TREATMENT SYSTEMS

24.10.1 Ground Treatment of Extracted Groundwater

The aboveground (*ex situ*) treatment technologies used for extracted groundwater are applied both in pump-and-treat systems and drinking water treatment systems. In general, the methods for extraction of groundwater are not linked to or limited by the type of aboveground treatment technologies. This section focuses on aboveground treatment of extracted groundwater, for both pump-and-treat and drinking water treatment, while the previous section focuses on groundwater extraction. This section also includes specific examples of treatment applications used in pump-and-treat and drinking water treatment systems.

The general types of aboveground technologies that have been used for treating extracted groundwater that is contaminated with MTBE and other oxygenates include the following[90]:

1. *Air Stripping*—Processes in which contaminants are volatilized from water to air in an engineered system, such as a packed tower[92]; treatment of the resulting contaminated vapor phase may also be required.
2. *Adsorption*—Processes in which contaminants are adsorbed from water onto a medium, such as GAC or resin, as driven by equilibrium forces.[93,94]
3. *Chemical Oxidation*—Processes in which contaminants are sequentially oxidized to less toxic products through the introduction of chemical oxidants[79] or the creation of oxidizing conditions through other means, such as using UV radiation, electrical stimulation, or cavitation.
4. *Biotreatment*—Processes in which contaminants are biodegraded in an engineered system, such as an attached growth[95,96] or an activated sludge bioreactor.[97]

24.10.2 Effect of the Properties of MTBE and Other Oxygenates on Treatment

The properties of MTBE and other oxygenates affect their relative treatability in extracted water using different technologies. Air stripping, adsorption, oxidation, and biotreatment technologies are technically capable of and have been used to treat water contaminated with some or all of the fuel oxygenates. However, the properties of oxygenates versus other fuel contaminants such as BTEX, and the different properties of ether-based versus alcohol-based oxygenates, are important factors to consider when selecting and designing an aboveground treatment system. The effect of fuel oxygenates properties on treatment using each of the commonly used technologies is briefly discussed below.

24.10.2.1 Air Stripping

Similar to air sparging, air stripping relies on the volatilization of contaminants from the aqueous to the vapor phase. The property that shows the extent to which this transfer can take place during air sparging is the Henry's law constant, which represents the extent to which a contaminant will partition between the dissolved state and the vapor state under equilibrium conditions.[92] A contaminant with a greater Henry's law constant is more readily stripped from water during air stripping than one with a lesser Henry's law constant. The discussion related to the effect of the properties of fuel oxygenates on air sparging is also applicable to air stripping. As discussed in that section, all common fuel oxygenates (with the possible exception of DIPE) are less readily stripped than BTEX (based on their Henry's law constants). Because of this, air stripping systems designed to treat oxygenates often are designed to allow for more air/water contact time than a system designed to treat BTEX constituents at the same concentrations. This is typically accomplished by the use of a larger stripping tower or packing material with a higher specific surface area. As an illustration, based on their ranges of Henry's law constants, ether-based oxygenates would require 5–10 times more air contact than BTEX to volatilize the same concentration of contaminant. Because of this, an air stripping system designed to treat BTEX may not be capable of adequately addressing ether-based oxygenates. Alcohol-based oxygenates are even more difficult, and in some cases impractical, to strip from groundwater.

The properties of oxygenates may also affect the applicability and design of a system to treat the contaminated vapor effluent resulting from air stripping, if one is required.

24.10.2.2 Adsorption

In adsorption processes, contaminated water is contacted with a solid adsorption medium, such as GAC or resin. Based on their equilibrium properties relative to the specific adsorption medium, contaminants will partition from the water to the solid until the system reaches equilibrium.[93] The maximum concentration of a given contaminant that can be adsorbed is dependent on

1. The type of adsorption medium used.
2. The specific contaminant and its concentration.
3. Concentrations of other substances in the water that may competitively adsorb.
4. Parameters such as temperature.

Although the actual treatability of a contaminated water stream is dependent on all of these parameters, the relative treatability of MTBE and other oxygenates can be estimated based on their relative tendency to partition from water to an organic matrix. One common measure of this tendency is the organic carbon-based partition coefficient. Generally, contaminants with lower partition coefficients are less amenable to treatment using GAC or resin adsorption. Figure 24.7 shows the ranges of partition coefficients for ether- and alcohol-based coefficients and BTEX.

As shown in Figure 24.7, the average partition coefficients for ether- and alcohol-based oxygenates are much lower than for BTEX. Based on this, it would be expected that adsorption systems

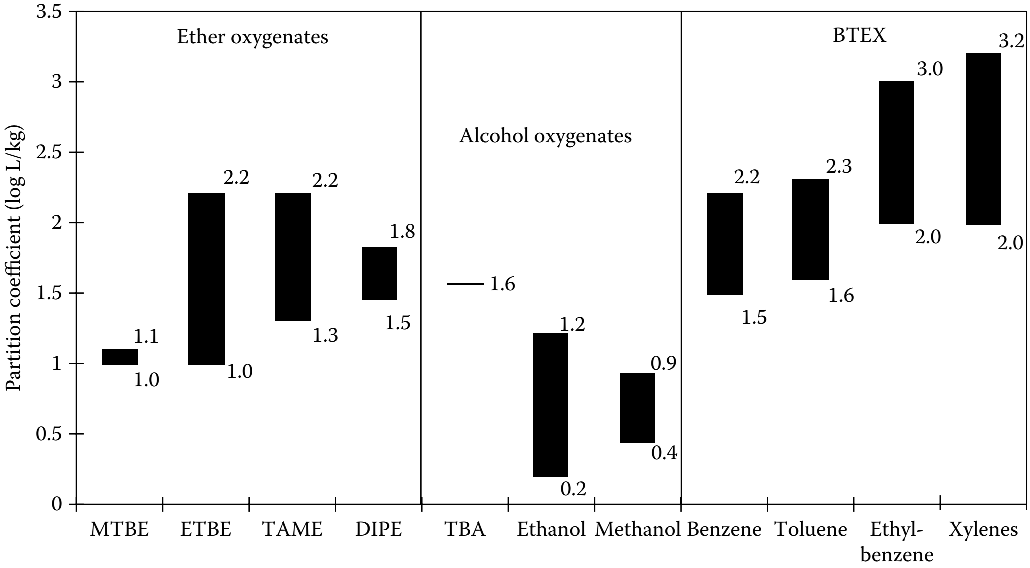


FIGURE 24.7 Relative ranges of partition coefficients for fuel oxygenates and BTEX. (Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.)

designed only to treat BTEX may not be able to effectively address ether-based oxygenates, and that the lower molecular weight alcohol-based oxygenates would not be amenable to adsorption.

24.10.2.3 Chemical Oxidation

MTBE and other oxygenates are susceptible to degradation through oxidation reactions. If a sufficient amount and strength of oxidant and enough time are provided, all ether- and alcohol-based fuel oxygenates can be destroyed via chemical oxidation. However, the amount and type of oxidant that is necessary for the treatment of MTBE or other oxygenates at a given site will depend on numerous factors beyond the amount of contaminant present.

There are also technologies that use electrical or other forms of energy to generate oxidizing and reducing radicals in aqueous solution and thereby destroy contaminants such as MTBE and other oxygenates. These technologies include E-beams and ultrasound. High-energy E-beams induce radiolysis (radiation-driven splitting) of water to form oxidizing hydroxyl radicals (OH•) as well as reducing hydrated electrons (e^-_{aq}) and hydrogen (H•). Ultrasound technology relies on the breakdown of water molecules into oxidizing and reducing free radicals (OH• and H•) under the intense heat and pressures generated during ultrasound-induced cavitation. Both of these technologies have been demonstrated, on the pilot scale, in application to groundwater contaminated with MTBE.[83]

24.10.2.4 Biotreatment

MTBE and other oxygenates are susceptible to biodegradation. For *in situ* biological treatment, the primary focus is on creating conditions that are conducive (sufficient electron acceptors, nutrients, microbes, and cometabolite) to stimulate biodegradation. With aboveground biotreatment, the creation of these conditions is simpler because the treatment is occurring in a defined, controlled, and accessible system. However, the relative biodegradability of different contaminants, such as ether- and alcohol-based oxygenates, is an important consideration in the selection and design of a biotreatment component for a pump-and-treat system.

24.10.3 TECHNOLOGIES USED FOR ABOVEGROUND TREATMENT OF OXYGENATES

One or more aboveground technologies are typically used to treat extracted groundwater before reinjection or discharge to surface water or the sewer. Multiple technologies, or treatment trains, are commonly used at sites contaminated with MTBE and other oxygenates (e.g., air stripping followed by GAC polishing). A significant amount of literature has been dedicated to the design of aboveground treatment systems. Some of the key considerations relevant to treatment of MTBE and other oxygenates in extracted groundwater are summarized below.[90]

24.10.3.1 Air Stripping

1. A typical volumetric ratio of air to water for the effective treatment of MTBE is at least 150–200 parts air to one part water, greater than that required to solely remove BTEX.
2. Most states require the capture and treatment of air stripper off-gas. Typical off-gas treatment technologies that are applicable to MTBE and other oxygenates are adsorption, thermal treatment, and biotreatment.

24.10.3.2 Adsorption

1. Because of their water solubility and low partition coefficients, MTBE and other oxygenates are difficult to adsorb on GAC. Other, more preferentially adsorbed, contaminants in groundwater may also reduce the capacity of GAC to remove MTBE and other oxygenates. In some cases, the more absorbable contaminants may even displace MTBE or other

oxygenates that are already adsorbed. In addition, natural groundwater constituents, such as iron, manganese, or organic carbon, may also consume adsorption capacity. Because of this, two or more GAC beds are often used in series so that contaminant breakthrough can be monitored in the first bed without risking the discharge of contaminants into the effluent.

2. Certain types of adsorption media have been shown to preferentially adsorb certain contaminants. For example, research has shown that, in some cases, coconut shell-based GAC removes MTBE better than typical coal-based GAC. In addition, synthetic resins have been developed to preferentially adsorb some oxygenates, such as TBA, that are less absorbable by GAC. Often, adsorption processes also take advantage of the biodegradability of MTBE and other oxygenates by promoting bacterial growth on the adsorption.

24.10.3.3 Chemical Oxidation

1. For the *ex situ* treatment of groundwater contaminated with MTBE or other oxygenates using chemical oxidation, most systems rely on processes that generate hydroxyl radicals, which are capable of completely oxidizing organic material to primarily carbon dioxide and water. Approaches that have been used to generate hydroxyl radicals for the oxidation of MTBE and other oxygenates include the following:

   - Combination of hydrogen peroxide and UV light.
   - Combination of hydrogen peroxide and ferrous iron (Fenton's chemistry).
   - Combination of ozone and UV light.
   - Combination of ozone and hydrogen peroxide (such as in the HiPOx system).
   - Ultrasonic cavitation (using high-energy ultrasonic vibrations to generate high temperatures and pressures).
   - E-beam (using high-energy electrons to split water molecules into free radicals).

2. The incomplete oxidation of MTBE and other oxygenates may result in the generation of undesirable intermediate products, such as TBF, TBA, and acetone. The design (oxidant dosage and contact time) should be adequate to achieve complete oxidation or additional treatment processes, such as GAC, may be used to address residual contamination.
3. The presence of other oxidant-consuming constituents in the feed water, such as iron, natural organic carbon, carbonates, bromide, and other contaminants, may require pretreatment of the feed stream, additional oxidant dosage, or more contact time to adequately destroy the MTBE and other oxygenates.

24.10.3.4 Biotreatment

1. Biological treatment systems that incorporate mechanisms to retain sufficient biomass are generally applicable to groundwater containing lower concentrations of contaminants. These systems typically consider the limited supply of carbonaceous material (food) to sustain a viable population of degrading microbes. Attached growth bioreactors, and suspended growth bioreactors that incorporate membrane-based biomass separation systems,[98] are generally appropriate for these applications.
2. Because the biological degradation rate of MTBE has been observed to be slower than for other common contaminants, such as BTEX, MTBE will typically be the rate-limiting contaminant that determines the necessary hydraulic retention time for a mixed contaminant system, since it will typically be the slowest to degrade.
3. Due to the difficulties involved in maintaining an adequate microbial mass applied to low concentrations of MTBE or other oxygenates in groundwater, treatability studies are often performed to confirm that extracted groundwater can be adequately treated in a bioreactor.

Recently, some efforts have been made to combine treatment technologies that employ adsorption and biological treatment. Biological treatment technologies that use naturally occurring microorganisms have successfully treated MTBE-contaminated groundwater. However, these microorganisms do not grow efficiently on MTBE, and thus require a microbial retention mechanism. GAC serves as an attachment medium that immobilizes microbes.[93] Other retention mechanisms include permeable barrier membranes and PRBs. GAC is often promoted for its capability for absorbing on environmental pollutants. However, in the presence of BTEX, the tendency of MTBE and TBA to adsorb on carbon is lowered. Consequently, GAC may not offer substantial adsorption capacity for MTBE or TBA.

More detailed information relevant to the application of aboveground treatment at sites contaminated with fuel oxygenates and in general is available in the literature.[88–90]

24.10.4 TYPES OF PROJECTS THAT USED ABOVEGROUND TREATMENT OF EXTRACTED GROUNDWATER

From the 323 projects in the MTBE Treatment Profiles Website dataset, 85 projects were identified where MTBE in groundwater was remediated using pump-and-treat along with 15 additional projects that treated MTBE in drinking water (collectively referred to as pump-and-treat projects). Seventy of these projects reported the type of aboveground treatment used, as shown in Table 24.22. The projects in the dataset used adsorption most frequently, either alone or in combination with other technologies. Nine of the 39 projects that used adsorption reported information about the type of adsorption media that was used in the treatment system. Bituminous carbon was used for four projects; coconut shell carbon for two projects; and organoclay carbon, resin, or biologically enhanced GAC for one project each. Air stripping (21 projects) and oxidation (22 projects) were also used frequently. Three of the air stripping projects reported that catalytic oxidation was used for off-gas treatment. No other projects reported information about off-gas treatment. Two of the air stripping projects reported air-to-water ratios; they were 150:1 and 200:1. Most[21] of the oxidation projects reported the type of oxidation that was employed. Hydrogen peroxide/ozone was used for 16 projects; hydrogen peroxide/UV was used for three projects; hydrogen peroxide alone and ultrasonic cavitation were used for one project each.

As an example of aboveground treatment, a site in Mission Viejo, California had an operating DPE system withdrawing soil vapor and groundwater for treatment with oxidation and bioreaction,

TABLE 24.22
Aboveground Treatment Technologies Used at 70 Groundwater Pump-and-Treat Remediation and Drinking Water Treatment Projects

Aboveground Treatment Technology Employed	Number of Pump-and-Treat Projects	Number of Drinking Water Treatment Projects	Total Number of Projects
Air stripping only	8	3	11
Air stripping with adsorption	9	1	10
Adsorption only	18	8	26
Adsorption with oxidation	1	2	3
Oxidation only	19	0	19
Biotreatment only	1	0	1
Total	56	14	70

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

respectively. Initially, the major contaminant was TBA, with a lesser concern about MTBE. However, as the formation dried out and more porosity developed, the concentrations of BTEX were found to be increasing. Site consultants considered that if the BTEX exceeded the TBA/MTBE concentration for a long time period, then the biomass would prefer the BTEX and would lose its ability to consume TBA/MTBE. To address this concern, a "sacrificial" carbon canister containing 200 lb of coconut carbon was installed ahead of the bioreactor to remove the BTEX while allowing the TBA/MTBE to pass through and be remediated in the bioreactor. While feeding approximately 5.7 L/min (1.5 gpm) of a stream containing approximately equal concentrations of TBA/MTBE and BTEX, the stream exiting the carbon canister showed breakthrough for TBA in 2 days, the first time a sample was taken. The TBA entering and leaving the carbon canister showed no decrease in concentration after the first week. The BTEX took about 45 days to breakthrough.[99]

24.10.5 PERFORMANCE OF TECHNOLOGIES IN ABOVEGROUND TREATMENT OF OXYGENATES

Of the projects in the database, four completed projects using pump-and-treat provided performance data for initial and final MTBE concentrations. Median concentrations were 27,000 μg/L for before treatment and <1 μg/L for after treatment. The median project duration for these projects was 14 months. Note that these treatment performance figures are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website.

24.10.6 COSTS OF PUMP-AND-TREAT FOR TREATMENT OF MTBE

Project cost data were reported for 12 pump-and-treat projects in the dataset based on type of aboveground treatment used; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that these costs incorporate different components, such as treatment, monitoring, design, oversight, and health and safety. Table 24.23 summarizes the cost information from these 12 projects, broken down according to the type of aboveground treatment technologies used.

Table 24.24 summarizes ranges of projected unit costs[90] for the treatment of different flow rates—3.78, 37.8, and 378 L/s (60, 600, and 6000 gpm) of MTBE-contaminated water using air stripping, oxidation, and adsorption technologies. These results show that air stripping is less costly than either adsorption or oxidation, and that there are economies of scale with treatment of relatively larger quantities of water.

TABLE 24.23

Cost Summary for Pump-and-Treat by Aboveground Treatment Technologies (2000 USD)[a]

Aboveground Treatment Technologies	Number of Projects	Total Cost Range (USD) Minimum	Total Cost Range (USD) Maximum	Median Total Reported Cost (USD)
Air stripping only	6	74,000	1,200,000	545,000
Air stripping with adsorption	3	216,000	1,180,000	339,000
Adsorption only	3	160,000	624,000	180,000
Total	12	450,000	3,000,000	1,060,000

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

[a] 2009 USD = 1.22 × 2000 USD.

TABLE 24.24
Estimated Range of Unit Costs for Aboveground Treatment Technologies (2000 USD)[a]

Technology Category	USD/3.78 m³ Treated (3.78 L/s system)		USD/3.78 m³ Treated (37.8 L/s system)		USD/3.78 m³ Treated (378 L/s system)	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Air stripping	1.66	3.20	0.30	1.09	0.13	0.64
Adsorption	2.30	4.61	0.77	2.37	0.30	2.22
Oxidation	2.18	4.11	0.57	2.08	0.32	1.59

Source: Adapted from U.S. EPA, *Technologies for Treating MTBE and Other Fuel Oxygenates*, EPA 542-R-04–009, United States Environmental Protection Agency, Washington, DC, May 2004.

[a] 2009 USD = 1.22 × 2000 USD.

24.10.7 FACTORS THAT AFFECT THE PERFORMANCE AND COST OF ABOVEGROUND TREATMENT OF OXYGENATES

Once water contaminated with MTBE or other oxygenates has been extracted, the relative tendency to remain in the aqueous phase can make aboveground treatment more complicated than the treatment of other contaminants, such as BTEX. Key factors that may affect the cost and performance of aboveground treatment include

1. The concentrations of oxygenates and other contaminants.
2. Extracted groundwater flow rates.
3. Other groundwater chemistry parameters that may interfere with treatment, such as natural organic carbon, iron, manganese, hardness, alkalinity, and pH.
4. Effluent water and off-gas discharge standards.

These factors may influence the specific aboveground treatment technology that is selected, the possible need for multiple aboveground treatment processes (treatment trains), and the need for pretreatment of groundwater or posttreatment of off-gas. Also, as with the extraction component, the presence of an active source area may result in the need for long-term operation of aboveground treatment systems.

24.10.8 TREATABILITY AND LIMITATIONS

The treatability of MTBE and other oxygenates using aboveground treatment is as follows[1]:

1. In general, aboveground treatment systems can be more readily controlled and monitored to optimize the removal of MTBE and other oxygenates than *in situ* treatment systems.
2. *Air stripping*—Treatment of ether-based oxygenates may require greater air-to-water ratios than treating only BTEX; treatment of alcohol-based oxygenates may be impractical.
3. *Adsorption*—Ether-based oxygenates are less readily removed than BTEX using GAC and some alcohol-based oxygenates may not be adsorbable at all; synthetic resins that more selectively remove fuel oxygenates are available.
4. *Chemical oxidation*—Fuel oxygenates can be destroyed using hydroxyl radical oxidation; the oxidant dosage and contact time are based more on overall oxidant demand of extracted groundwater than on types of oxygenate contaminants.
5. *Biotreatment*—Fuel oxygenates can be biodegraded given adequate retention time in a bioreactor with a sufficient mass of conditioned microbes.

The limitations to applying aboveground treatment are as follows[34,40]:

1. The cost of constructing, operating, and maintaining treatment systems is considered to be relatively high.
2. Biofouling or mineral precipitation in extraction wells or treatment processes can reduce system performance.

24.10.9 EXAMPLE PROJECTS

The following two project descriptions relate to demonstrations of innovative *ex situ* treatment systems for groundwater contaminated with MTBE and other oxygenates.

24.10.9.1 Biodegradation of MTBE in a High Biomass Retention Reactor

Demonstration study at Pascoag, Rhode Island: a pilot-scale specialized Biomass Concentrator Reactor (BCR), an activated sludge-type bioreactor that uses a membrane-based biomass separation system, was tested for the aerobic biodegradation of MTBE. The BCR design encompasses an aeration chamber housing a high surface area porous polyethylene membrane system that retains all of the biomass within the aeration chamber. Its simple operation and low maintenance requirements may render it economically more feasible than other water treatment technologies. The water flux through the membrane relies completely on gravity. The system includes 30 membrane compartments, with each one removable for cleaning.

The BCR was used in a demonstration at a Pascoag, Rhode Island abandoned gasoline station where substantial amounts of gasoline had leaked into the groundwater, contaminating it with MTBE, TBA, TAME, TAA, DIPE, TBF, acetone, methanol, ethanol, and BTEX. The objective of the study was to demonstrate the effectiveness of the BCR in treating MTBE, other oxygenates, and BTEX to near or below detectable limits. The BCR was operated at the Pascoag site for nearly 6.5 months up to 18.9 L/min (5 gpm). Average influent concentrations of VOCs were MTBE, 6500 μg/L; TBA, 69 μg/L; TAME, 1130 μg/L; TAA, 130 μg/L; DIPE, 36 μg/L; TBF, 29 μg/L; acetone, 480 μg/L; methanol, 300 mg/L; and the sum of BTEX, 3700 mg/L. Effluent concentrations were very low despite continual flow interruptions from the source wells. Over the entire project, including flow interruptions and non-steady-state flow conditions, MTBE in the effluent averaged near 9 μg/L (<5 μg/L during 5 gpm steady-state flow conditions without flow interruptions); TBA, 0.5 μg/L; TAME, 1.4 μg/L; TAA, 0.06 μg/L; DIPE, 0.05 μg/L; TBF, 0.02 μg/L; acetone, 6.6 μg/L; methanol, 2 μg/L; and sum of BTEX, 1.3 μg/L. Nonpurgeable organic carbon (NPOC) was reduced by close to 50%.[100]

24.10.9.2 Demonstration of the HiPOx Oxidation Technology for the Treatment of MTBE-Contaminated Groundwater

The HiPOx technology is an advanced oxidation process that incorporates high-precision delivery of ozone and hydrogen peroxide to chemically destroy organic contaminants while minimizing bromate formation. The MTBE-contaminated groundwater (initial MTBE concentration of 748 μg/L) from the Ventura County Naval Base in Port Hueneme, California was used to evaluate this technology. Due to extremely high concentrations of bromide in the feed water (1.3 mg/L) and the desire to limit bromate formation, a pilot-scale system was operated with 630 ozone injector ports in series, as part of U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program.

The HiPOx process achieved >99.9% reduction in MTBE concentration and easily met the treatment goal of reducing the concentration of MTBE to below 5 μg/L. However, significant concentrations of MTBE degradation intermediates and oxidation by-products were present in the final effluent. TBA was produced early during the chemical oxidation process. Its concentration was diminished by further oxidation, reaching below its regulatory limit of 12 μg/L in two of the three runs. Acetone was generated and a sizable percentage was left unoxidized in the final effluent (>100 μg/L). Bromate concentrations in the effluent exceeded the drinking water standard of 10 μg/L for all three runs.

A model calculation showed that the HiPOx system may have been fully successful in limiting bromate formation under the chosen oxidant doses if the influent bromide concentration was 0.56 mg/L or less. Since a bromide concentration of 0.56 mg/L is still extremely high for a drinking water source, the HiPOx system appears to hold promise for destroying MTBE and its oxidative by-product TBA while controlling bromate formation, even in waters that have high bromide concentrations.[101]

24.10.9.3 Application of High-Energy E-Beam to the Treatment of MTBE-Contaminated Groundwater

A demonstration of the high-energy electron beam (E-beam) technology applied to groundwater contaminated with MTBE and with BTEX was conducted at the Naval Base Ventura County, Port Hueneme, California, as part of U.S. EPA's SITE program. The E-beam technology destroys organic contaminants in groundwater through irradiation with a beam of high-energy electrons; the oxidizing radicals that are generated by the E-beam react with and destroy organic contaminants, including MTBE and its breakdown products.

Results of two weeks of steady-state operation at an E-beam dose of 1200 krads indicated that MTBE and BTEX concentrations in the effluent were reduced by >99.9% from influent concentrations that averaged over 1700 μg/L MTBE and 2800 μg/L BTEX. Further, the treatment goals for the demonstration, which were based on drinking water regulatory criteria, were met for all contaminants except TBA, a degradation product of MTBE. Dose experiments indicated that TBA was not consistently reduced to below the treatment goal of 12 μg/L although the results indicated that TBA by-product formation decreased as the dose increased. Acetone and formaldehyde were the two most prevalent organic by-products that were formed by E-beam treatment, with mean effluent concentrations during the two-week steady-state testing of 160 and 125 μg/L, respectively. Bromate was not formed during E-beam treatment.

An economic analysis of the E-beam treatment system indicated that the primary costs are for the E-beam equipment and for electrical energy. The estimated cost ranged from over USD10.6/m^3 (USD40/1000 gallons) for a small-scale remedial application to about USD0.26/m^3 (USD1/1000 gallons) for a larger-scale drinking water application.[102]

24.11 PHYTOREMEDIATION, PRBs, AND THERMAL TREATMENT

24.11.1 Other Technologies Used in Treatment of MTBE and Other Oxygenates

In addition to the technologies discussed earlier in this chapter, three additional technologies (phytoremediation, PRBs, and thermal treatment) have also been used to treat MTBE and other oxygenates in soil and groundwater. Phytoremediation is a category of treatment technologies that employs plants (or in some cases fungi) to conduct remediation. Treatment during phytoremediation can be accomplished through one or more natural processes, including enhanced bioremediation in the rhizosphere (plant root zone), phytostabilization of contaminants by organic plant material, plant uptake, plant metabolism, and phytovolatilization (volatilization through plant leaves).[103] PRBs are subsurface barriers that remediate groundwater as it passes through an engineered treatment zone. For the treatment of MTBE and other oxygenates, treatment zones that use bioremediation processes are most common.[104] Thermal treatment is a generic term that applies to technologies that use heat to mobilize, extract, or destroy contaminants either *in situ* or *ex situ*. While these technologies were applied less frequently, they may represent viable treatment options at some sites contaminated with MTBE and other oxygenates.

24.11.2 PHYTOREMEDIATION TREATMENT OF OXYGENATES

Phytoremediation, as it applies to MTBE and other oxygenates, is a relatively new remedial approach and many of the removal and degradation pathways are currently being studied. However, it is known that phytoremediation relies on multiple processes to accomplish the removal of contaminants from shallow groundwater. Each of these processes is affected by different chemical properties as well as site-specific conditions. The biodegradability of oxygenates affects their treatment in the rhizosphere, where the conditions support an abundance of metabolically active bacteria and fungi that may enhance contaminant degradation. The relatively high solubility and low organic partition coefficients of oxygenates generally limits significant removal through phytostabilization, but facilitates removal through root uptake. In addition, volatility and Henry's constants may affect the removal through phytovolatilization.[105]

The manner in which phytoremediation can be applied to treat MTBE and other fuel oxygenates is highly variable, based on the site conditions, specific contaminants to be treated, cleanup goals, and other factors. Information relevant to the application of phytoremediation at sites contaminated with MTBE and other oxygenates is available in the literature.[105–109]

From the 323 MTBE treatment profiles, eight projects were identified where MTBE was treated using phytoremediation. These projects used various approaches, including hybrid poplar trees, Monterey pine, oak, eucalyptus, and engineered wetlands.

24.11.3 PRB TREATMENT OF OXYGENATES

A PRB is a treatment system configuration with treatment zones that can employ any of a number of treatment technologies, such as *in situ* bioremediation or ISCO. Depending on which treatment technology is employed, the properties of MTBE and other oxygenates as they apply to that specific technology will affect the treatment differently.

Information relevant to the application of PRBs at sites contaminated with MTBE and other oxygenates is available in Refs. [110–114].

Although no projects in the dataset were identified explicitly to be using PRBs, several projects discussed under other technologies involved these types of components. For example, several bioremediation projects, such as at Port Hueneme, were performed using a PRB configuration.

No total project cost data were reported for any of the projects in the dataset that employed PRB treatment technology. However, additional information in the literature indicates the application of PRBs for the treatment of other contaminants. A U.S. EPA case study in 2000 showed a range of total costs for 16 PRB projects ranging from USD43,000 to USD1,900,000 with a median total cost of USD680,000.[50]

24.11.4 *IN SITU* THERMAL TREATMENT OF OXYGENATES

Thermal treatment can be used to mobilize or destroy MTBE and other oxygenates from soil either *in situ* or *ex situ*, similar to other petroleum contaminants. Volatilization from soil is affected by vapor pressure, with a higher vapor pressure making volatilization occur more readily. In general, alcohol-based oxygenates have lower vapor pressures than ether-based oxygenates, but the vapor pressures of both are comparable with or greater than other petroleum contaminants such as benzene. Similar to other organic contaminants, MTBE and other oxygenates may also be susceptible to thermal destruction at high temperatures.

Information relevant to the application of *in situ* thermal treatment at sites contaminated with MTBE and other oxygenates is available in a U.S. EPA report.[115]

While no projects in the dataset were identified explicitly as using *in situ* thermal treatment, several projects discussed under other technologies involved these types of components. For example, one site in Texas discussed under bioremediation (Rural Area Disposal Area, Liberty, Texas) used a combination of technologies that included an *in situ* thermal treatment component.

24.11.5 ADVANTAGES AND LIMITATIONS

The advantages of applying other treatment technologies are as follows[1]:

1. Phytoremediation or PRBs may be a cost-effective alternative for remediating or containing relatively low-concentration, shallow, and widespread groundwater plumes.
2. Thermal treatment technologies tend to remove oxygenates along with other petroleum contaminants (such as petroleum hydrocarbons) that are more typically treated using this technology.

The limitations to applying other treatment technologies are as follows[1]:

1. The processes that effectively treat MTBE and other oxygenates during phytoremediation are still being studied.
2. Phytoremediation may be less applicable to higher concentration or deeper groundwater plumes.

24.12 NONTREATMENT REMEDIES

Nontreatment remedies that address oxygenates include excavation, free product recovery, MNA, and ICs. Nontreatment remedies may be appropriate for use either alone or in conjunction with one or more of the other remedies discussed in this chapter.

24.12.1 EXCAVATION

Excavation is the removal of contaminated soil or sludge from a site by using mechanical equipment. It is often used at sites where significant volumes of petroleum products are present in the soils located near the surface and which are likely to be a continuing source of contaminant migration. Commonly, excavation is performed prior to or while implementing other remedies such as groundwater treatment technologies. Similar to free product recovery, excavation is used to remove/control the source of contamination, so that MTBE will not continue to migrate to the vadose zone and groundwater.[34]

Site-specific characteristics, such as the presence of aboveground and belowground obstructions, largely dictate the implementation of excavation. Locations where underground utilities or storage facilities exist may require extensive and time-consuming exploratory excavation and hand-digging. Excavation around or near buildings may require the use of underpinning or sheet piling to stabilize the structure and rerouting of utility lines. Shoring or sloping may be required in sandy soil to maintain trench wall stability. Monitoring for air quality may be required during excavation. When fugitive air emissions exceed air quality standards, there may be limitations imposed on the quantity of soil that can be excavated per day.

Excavation equipment ranges from hand tools, such as pick axes and shovels, to backhoes, front-end loaders, clamshells, and draglines, depending on the amount of soil to be excavated, the total depth of the excavation, moisture content of the soil, and the space allowed at the site for staging of excavated material. Backhoes and front-end loaders are the most commonly used equipment for excavation of relatively shallow (<4.58 m (15 ft) below the ground surface) soils. Excavation rates for these types of units with 0.76 m^3 (1 yd^3) bucket capacities are typically 57.3 m^3/h (75 yd^3/h). Larger bucket capacities can increase this rate to up to 122.3 m^3/h (160 yd^3/h).[116] The maximum excavation rate using hand tools is approximately 0.76 m^3/h/laborer (1 yd^3/h/laborer).

Factors that affect the costs for excavation include the depth of contamination, depth of groundwater (requiring dewatering), and extent of underground infrastructure and/or nearby structures that require shoring. The cost for excavation tends to be higher for areas with deeper contamination, shallower groundwater, and more infrastructures and nearby structures.

24.12.2 Free Product Recovery

Free product recovery is the extraction of separate phase material (primarily petroleum liquids) that is located in the subsurface (in the case of petroleum liquids, at the top of the water table). It is often used at sites where significant volumes of petroleum products have reached the water table, and which are likely to be a continuing source of contaminants migrating to the vadose zone or dissolving in groundwater. Commonly, free product recovery is performed prior to or during implementation of remedies such as groundwater treatment. Similar to excavation, free product recovery is used to remove/control the source of contamination, so that the source will not continue to migrate to the vadose zone or the groundwater.

Note that free product removal is a federal regulatory requirement, under 40 CFR. It requires owners and operators to remove free product to the maximum extent practicable, while continuing other remedial actions.

Technologies typically used to recover free product include skimming equipment in wells, trenches, or excavation pits, and pumping of free product. These approaches have been used with and without depressing the water table to enhance migration of free product to a well or drain. The design of a free product recovery system requires an understanding of the site hydrogeology and characteristics, the types, extent, and distribution of free product in the subsurface, and the engineering aspects of the equipment and installation. Free product recovery is sometimes combined with other technologies to enhance removal of contaminants from the vadose zone or that are dissolved in the groundwater.

U.S. EPA published a guide[117] for state regulators about how to effectively recover free product at leaking USTs. In the guide, U.S. EPA provided scientific and engineering considerations for evaluating technologies for the recovery of free product from the subsurface. The guide discussed the behavior of hydrocarbons in the subsurface, methods for evaluating the recoverability of subsurface hydrocarbons, and recovery systems and equipment.

24.12.3 Monitored Natural Attenuation

U.S. EPA defines MNA as “the reliance on natural processes, within the context of a carefully controlled and monitored site cleanup approach, to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The natural processes include biodegradation, dispersion, dilution, sorption, volatilization, stabilization, and transformation. These processes reduce site risk by transforming contaminants to less toxic forms, reducing contaminant concentrations, and reducing contaminant mobility and bioavailability.” Other terms for natural attenuation in the literature include “intrinsic remediation,” “intrinsic bioremediation,” “passive bioremediation,” “natural recovery,” and “natural assimilation.”[30]

While offering the potential to clean up sites at lower cost, MNA typically would require a longer period of time to achieve remediation objectives, compared with active remediation measures. In addition, it generally requires extensive long-term monitoring data. Other potential limitations of MNA include the potential that the toxicity and/or mobility of transformation products may be greater than for the parent compound (e.g., TBA as a degradation product of MTBE); hydrologic and geochemical conditions amenable to natural attenuation may change over time and could result in renewed mobility of previously stabilized contaminants; and more extensive education and outreach efforts may be required to gain public acceptance of MNA. Information about research on field use of MNA is provided in Ref. [118].

U.S. EPA published a guide about the steps needed to understand the rate and extent to which natural processes are reducing contaminant concentrations.[56] Although this guide is directed at sites contaminated by chlorinated solvents, some of the steps would also have relevance for sites contaminated by oxygenates like MTBE. The guide identifies parameters that are useful in the evaluation of natural attenuation and provides recommendations on how to analyze and interpret the data collected from the site characterization process. It also provides suggestions for integrating MNA into an integrated approach to remediation that includes an active remedy.

Recently, U.S. EPA published a report[119] that provides guidance about the types of monitoring used during MNA remedies.

24.12.4 INSTITUTIONAL CONTROLS

ICs are nonengineered instruments such as administrative and/or legal controls that minimize the potential for human exposure to contamination by limiting land or resource use, and generally are used in conjunction with engineering measures such as treatment or containment. ICs are used during all stages of a cleanup and often involve multiple activities ("layered IC") implemented in parallel or in series. Examples of ICs are[120]

1. Easements
2. Covenants
3. Well drilling prohibitions
4. Zoning restrictions
5. Special building permit requirements (sometimes referred to as deed restrictions).

Often, ICs are considered within the context of long-term plume management and MNA. Typically, after the source of contamination has been addressed (such as through removal or destruction), ICs are used to limit the long-term use of a site and the potential for exposure of residual contaminants to human or environmental receptors. When deciding about appropriate types of ICs, site managers look at the life cycle strengths, weaknesses, and costs for implementation, monitoring, and enforcement, and coordination with state and local governments that have responsibilities for ICs. Additional information about ICs is available in a U.S. EPA guide.[120]

ACRONYMS

AST	Aboveground storage tank
BCR	Biomass concentrator reactor
BTEX	Benzene, toluene, ethylbenzene, and xylene
DIPE	Diisopropyl ether
DL	Detection limit
DPE	Dual-phase extraction
COD	Chemical oxygen demand
ETBE	Ethyl *tert*-butyl ether
GAC	Granular activated carbon
HP	Horse power
IC	Institutional control
ISCO	*In situ* chemical oxidation
LNAPL	Light nonaqueous phase liquid
MNA	Monitored natural attenuation
MPE	Multiphase extraction
MTBE	Methyl *tert*-butyl ether
NAPL	Nonaqueous phase liquid
ND	Nondetect
NOM	Natural organic matter
NPOC	Nonpurgeable organic carbon
ppmv	Parts per million by volume
PRB	Permeable reactive barriers
PVC	Polyvinyl chloride

RCRA	Superfund and Resource Conservation and Recovery Act
RFG	Reformulated gasoline
ROI	Radius of influence
scfm	Standard ft^3/min
SITE	Superfund Innovative Technology Evaluation
SSTL	Site-specific target level
SVE	Soil Vapor extraction
TAA	*tert*-Amyl alcohol
TAEE	*tert*-Amyl ethyl ether
TAME	*tert*-Amyl methyl ether
TBA	*tert*-Butyl alcohol
TPE	Two-phase extraction
US	United States
U.S. EPA	United States Environmental Protection Agency
UST	Underground storage tank
VE/GE	Vapor extraction/groundwater extraction
VOC	Volatile organic compound
ZOI	Zone of influence

APPENDIX

U.S. Army Corps of Engineers Civil Works Construction Yearly Average Cost Index for Utilities[a]

Year	Index	Year	Index
1967	100	1989	383.14
1968	104.83	1990	386.75
1969	112.17	1991	392.35
1970	119.75	1992	399.07
1971	131.73	1993	410.63
1972	141.94	1994	424.91
1973	149.36	1995	439.72
1974	170.45	1996	445.58
1975	190.49	1997	454.99
1976	202.61	1998	459.40
1977	215.84	1999	460.16
1978	235.78	2000	468.05
1979	257.20	2001	472.18
1980	277.60	2002	484.41
1981	302.25	2003	495.72
1982	320.13	2004	506.13
1983	330.82	2005	516.75
1984	341.06	2006	528.12
1985	346.12	2007	539.74
1986	347.33	2008	552.16
1987	353.35	2009	570.38
1988	369.45		

Source: U.S. ACE, Yearly average cost index for utilities, in *Civil Works Construction Cost Index System Manual*, 110-2-1304, U.S. Army Corps of Engineers, Washington, DC, pp. 44, 2004. Available at http://www.nww.usace.army.mil/cost.

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25 Evapotranspiration Landfill Cover

Nazih K. Shammas

CONTENTS

25.1 INTRODUCTION

The technology available for landfill remediation is changing. New remediation methods are becoming available, and some are now being accepted by regulators. The old notion of entombment and preservation of waste is giving way to new concepts for managing wastes that may remove the threat to human health and the environment. Both old and new technology should meet the critical goal of landfill remediation, which is to protect human health and the environment.

Leading new technologies include the landfill as a bioreactor,[1] and the use of natural attenuation processes to enhance effectiveness of remediation at reduced cost by naturally renewable and continuing processes.[2,3]

Alternative final cover systems, such as the innovative evapotranspiration (ET) cover systems, are increasingly being considered for use at waste disposal sites, including municipal solid waste (MSW) and hazardous waste landfills when equivalent performance to conventional final cover systems can be demonstrated. Unlike conventional cover system designs that use materials with low hydraulic permeability (barrier layers) to minimize the downward migration of water from the cover to the waste (percolation), ET cover systems use water balance components to minimize percolation. These cover systems rely on the properties of soil to store water until it is either transpired through vegetation or evaporated from the soil surface.

The ET landfill cover is a complete cover, not a cover component. It offers opportunities for improved performance and lower construction and maintenance cost. In addition, the new cover may be beneficial for use with bioreactor landfills because ET covers can be designed to pass a controlled amount of precipitation through the cover and into the waste.[4]

Design, construction, and use of ET landfill covers are dependent upon the following:

1. Definition of requirements for the cover.
2. Decision that an ET cover meets site cover requirements.

The ET landfill cover design problem includes complex relationships between climate, soil, and vegetation and is best solved with the aid of a computer model.[4–6] ET landfill covers have different design requirements than do conventional covers; therefore, model requirements for design and evaluation differ from conventional practice. This chapter provides the bases of ET cover systems, including general considerations in their design, performance, monitoring, cost, current status, limitations on their use, and project-specific examples. It is intended to provide basic information to site owners and operators, regulators, consulting engineers, and other interested parties about these potential design alternatives. United States Environmental Protection Agency (U.S. EPA) has developed an on-line database that provides information about specific projects using ET covers.[7]

25.2 REQUIREMENTS FOR LANDFILL COVERS

This section is an overview of the requirements and definitions for landfill covers. Additional details are available in Refs. 8–13.

25.2.1 Landfill Remediation Requirements

The application of containment—the presumptive remedy—often requires the design and installation of a landfill cover. Other common components, such as landfill gas management, groundwater treatment or containment, and collection and disposal of leachate, may also be required. Landfill covers may offer several environmental benefits (minimize erosion, prevent occurrence of disease vectors and other nuisances, and meet aesthetic and other end-use purposes), but they are based on three primary goals.[14,15]

1. Minimize infiltration of precipitation into the waste to control potential leaching of contaminants from the waste.
2. Isolate the wastes to prevent direct contact with potential receptors at the surface and to control movement of waste by wind or water.
3. Control landfill gases to minimize risks from toxic or explosive gases that may be generated within the landfill.

Final cover systems are intended to remain in place and maintain their functions for an extended period of time.

In addition, cover systems are also used in the remediation of hazardous waste sites. For example, cover systems may be applied to source areas contaminated at or near the ground surface or at abandoned dumps. In such cases, the cover system may be used alone or in conjunction with other technologies to contain the waste (e.g., slurry walls and groundwater pump and treat systems).

25.2.2 Site-Specific Requirements for Landfill Covers

The site-specific requirements for landfill remediation should be developed before beginning design or selection of cover type. Site-specific requirements depend on numerous site-specific factors, including landfill history; waste type, quantity, and age; climate; geologic setting; local surface water and groundwater use; and regulatory requirements.

After a performance requirement has been established for remediating a particular landfill, any remedial alternative meeting that requirement can be selected and applied. Site-specific requirements are discussed in more detail in Refs. 8 and 13.

25.2.3 Conventional Covers

The dominant feature of covers currently in use is one or more barrier layers that are intended to stop the natural downward movement of water through the profile of the cover. Conventional and barrier-type covers include several layers, including grass for surface cover. These covers typically include one or more barrier layers made of compacted clay, geomembranes, or geosynthetic clay. Barrier-type covers are more completely described in Refs. 9, 13, and 16–19. The Subtitle D cover is a simplified barrier-type cover with a single barrier layer of compacted clay. It is less expensive than other barrier-type covers and is used in dry climates.[20,21]

The design of cover systems is site-specific and depends on the intended function of the final cover—components can range from a single-layer system to a complex multilayer system. To minimize percolation, conventional cover systems use low-permeability barrier layers. These barrier layers are often constructed of compacted clay, geomembranes, geosynthetic clay liners, or combinations of these materials.

Depending on the material type and construction method, the saturated hydraulic conductivities for these barrier layers are typically between 1×10^{-5} and 1×10^{-9} cm/s. In addition, conventional cover systems generally include additional layers, such as surface layers to prevent erosion; protection layers to minimize freeze/thaw damage; internal drainage layers; and gas collection layers.[6,22]

Although barrier layers are sometimes referred to as impermeable, in practice this is seldom true. Suter et al.[23] reviewed failure mechanisms for compacted soil covers in landfills; they concluded that natural, physical, and biological processes can be expected to cause clay barriers to fail in the long term. Melchior[24] reported the results of a German study in a cool, wet climate; he found that clay barriers were already leaking 150–200 mm/yr in the eighth year of operation. Geomembrane barriers are also prone to leak. Board and Laine[25] traced most leaks in geomembranes to holes left by construction. Melchior[24] reported that three composite covers, containing more than one barrier, leaked, on average, between 1 and 4 mm/yr with annual leakage as high as 5.2 mm/yr. Albright and Benson[26] reported that conventional clay-barrier covers at two sites leaked 5.5% and 37% of the precipitation into the waste.

Regulations under the Resource Conservation and Recovery Act (RCRA)[27,28] for the design and construction of final cover systems are based on using a barrier layer (conventional cover system). Under RCRA Subtitle D, the minimum design requirements for final cover systems at MSW landfills depend on the bottom liner system or the natural subsoils, if no liner system is present. The final cover system must have permeability less than that of the bottom liner system (or natural subsoils) or $<1 \times 10^{-5}$ cm/s, whichever is less. This design requirement was established to minimize the "bathtub effect," which occurs when the landfill fills with liquid because the cover system is more permeable than the bottom liner system. This "bathtub effect" greatly increases the potential for generation of leachate. Figure 25.1a shows an example of an RCRA Subtitle D cover at an MSW landfill with a 6-in. (0.15 m) soil erosion layer, a geomembrane, and an 18-in. (0.45 m) barrier layer of soil that is compacted to yield a hydraulic conductivity $\leq 1 \times 10^{-5}$ cm/s.[29]

For hazardous waste landfills, RCRA Subtitle C provides certain performance criteria for final cover systems. While RCRA does not specify minimum design requirements, U.S. EPA has issued guidance for the minimum design of these final cover systems. Figure 25.1b shows an example of an RCRA Subtitle C cover at a hazardous waste landfill.[30]

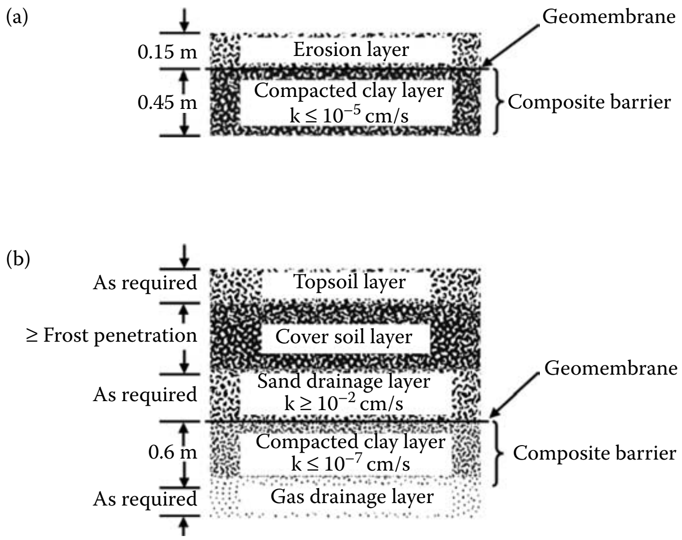

FIGURE 25.1 Examples of final cover systems. (a) MSW landfill and (b) hazardous waste landfill.[15]

The design and construction requirements, as defined in the RCRA regulations, may also be applied under cleanup programs, such as Superfund[31] or state cleanup programs, as part of a remedy for hazardous waste sites such as abandoned dumps. In these instances, the RCRA regulations for conventional covers are usually identified as applicable or relevant and appropriate requirements for the site.

Under RCRA, an alternative design, such as an ET cover, can be proposed in lieu of an RCRA design if it can be demonstrated that the alternative provides equivalent performance with respect to reduction in percolation and other criteria, such as erosion resistance and gas control.

25.2.4 ET Cover Definition

Because of the water-holding properties of soils and the fact that most precipitation returns to the atmosphere via ET, it is possible to devise a landfill cover to meet remediation requirements, and yet contain no barrier layer. The ET cover consists of a layer of soil covered by native grasses; it contains no barrier or “impermeable” layers. The ET cover uses two natural processes to control infiltration: (1) soil provides a water reservoir and (2) natural evaporation from the soil plus plant transpiration (ET) empties the soil water reservoir.[32–38] The ET cover is an inexpensive, practical, and easily maintained biological system that will remain effective during extended periods of time—perhaps centuries—at low cost.

The ET cover contains selected soil and requires correct placement to maintain desirable soil properties. Successful performance by the ET cover requires robust plant growth and good soil properties. It should be designed for the site to ensure that it meets the cover requirements.

25.2.5 ET Cover Concept Verification

The technology that forms the basis for ET landfill covers was developed, tested, and well understood years ago, and field data are available from water balance measurements in both natural and constructed soil layers similar to those required for ET covers. The concept was corroborated in the field by both long- and short-term measurements that were collected during the past century. The long-term measurements established the water balance under grass during time periods from three decades to several centuries in length, and included unusually wet periods, fires, and other natural disasters. These data demonstrate that the ET cover can minimize movement of precipitation through soil covers by using natural forces and the soil’s water-holding capacity.[11]

25.2.6 Requirements for ET Landfill Covers

The ET cover has the following minimum criteria:

1. Support a robust, healthy, vegetative cover.
2. The soil should allow rapid and prolific root growth in all parts of the soil cover.
3. The soil should hold enough water to minimize water movement below the cover during extreme or critical design periods.

In keeping with the requirements for all landfill remediation, the ET cover must meet the requirements for a landfill cover.

The soil and plants employed on the cover are critical to success. A mixture of grasses native to the area is preferred to provide effective water removal from the cover in all years in spite of temporary changes in local conditions. Native grasses have already proven their ability to withstand local climate variations, insects, plant disease, periodic fire, and other factors. A mixture of native grasses assures an active vegetative cover during years when insects, plant disease, or other factors reduce the vigor of one or more species.[11,38]

The soil cover construction process is important because it has the power to assure success or cause poor performance of the cover. The ET cover uses a different mechanism to control water from that of conventional covers; therefore, the design and construction methods also differ. The soil of the cover should provide adequate plant nutrients, plant-available water-holding capacity, aeration, soil strength, and other factors critical to rapid and robust plant growth, including the highly essential root system. Soil strength is particularly important because it limits the rate of plant root growth. Soil strength may be optimized by control of soil density during and after cover soil construction. These and other requirements are discussed by Hauser et al.[11–13]

25.3 DESCRIPTION OF ET COVER SYSTEMS

ET cover systems use one or more vegetated soil layers to retain water until it is either transpired through vegetation or evaporated from the soil surface. These cover systems rely on the water storage capacity of the soil layer, rather than low hydraulic conductivity materials, to minimize percolation. ET cover system designs are based on using the hydrological processes (water balance components) at a site, which include the water storage capacity of the soil, precipitation, surface runoff, ET, and infiltration. The greater the storage capacity and evapotranspirative properties, the lower the potential for percolation through the cover system. ET cover system designs tend to emphasize the following[6,39,40]:

1. Fine-grained soils, such as silts and clayey silts, that have a relatively high water storage capacity.
2. Native vegetation to increase ET.
3. Locally available soils to streamline construction and provide for cost savings.

In addition to being called ET cover systems, these types of covers have also been referred to in the literature as water balance covers, alternative earthen final covers, vegetative landfill covers, soil-plant covers, and store-and-release covers.

Two general types of ET cover systems are

1. Monolithic barriers[41]
2. Capillary barriers.[15]

Monolithic covers, also referred to as monofill covers, use a single vegetated soil layer to retain water until it is either transpired through vegetation or evaporated from the soil surface. A conceptual design of a monolithic cover system is shown in Figure 25.2.

Capillary barrier cover systems consist of a finer-grained soil layer (like that of a monolithic cover system) overlying a coarser-grained material layer, usually sand or gravel, as shown conceptually in Figure 25.3. The differences in the unsaturated hydraulic properties between the two layers minimize percolation into the coarser-grained (lower) layer under unsaturated conditions.

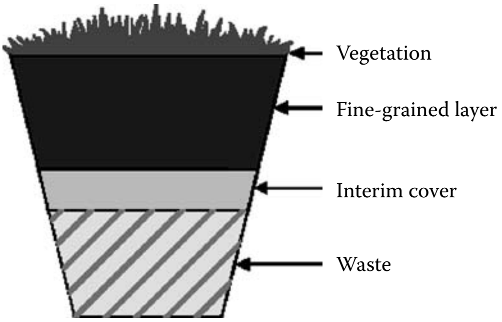

FIGURE 25.2 Conceptual design of a monolithic ET final cover.[15]

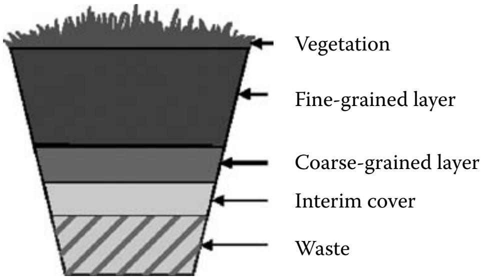

FIGURE 25.3 Conceptual design of a capillary barrier ET final cover.[15]

The finer-grained layer of a capillary barrier cover system has the same function as the monolithic soil layer; that is, it stores water until it is removed from the soil by evaporation or transpiration mechanisms. The coarser-grained layer forms a capillary break at the interface of the two layers, which allows the finer-grained layer to retain more water than a monolithic cover system of equal thickness. Capillary forces hold the water in the finer-grained layer until the soil near the interface approaches saturation. If saturation of the finer-grained layer occurs, the water will move relatively quickly into and through the coarser-grained layer and to the waste below.

In addition to being potentially less costly to construct, ET covers have the potential to provide equal or superior performance compared to conventional cover systems, especially in arid and semiarid environments. In these environments, they may be less prone to deterioration from desiccation, cracking, and freezing/thawing cycles. ET covers also may be able to minimize side slope instability, because they do not contain geomembrane layers, which can cause slippage.[5,42,43]

Capillary barrier ET cover systems may also eliminate the need for a separate biointrusion and/or gas collection layer. The coarser-grained layer can act as a biointrusion layer to resist root penetration and animal intrusion, due to its particle size and low water content. The coarser-grained layer can also act as a gas collection layer, because the soil properties and location within the cover system are comparable with a typical gas collection layer in a conventional cover system.[39,44]

25.4 LIMITATIONS

ET cover systems are generally considered potentially applicable only in areas that have arid or semiarid climates; their application is generally considered limited to the western United States. In addition, site-specific conditions, such as site location and landfill characteristics, may limit the use or effectiveness of ET cover systems. Local climatic conditions, such as amount, distribution, and form of precipitation, including amount of snow pack, can limit the effectiveness of an ET cover at a given site. For example, if a large amount of snow melted when vegetation was dormant, the cover may not have sufficient water storage capacity, and percolation might occur.[6,45]

Further, landfill characteristics, such as production of landfill gases, may limit the use of ET covers. The cover system may not adequately control gas emissions since typical ET cover designs do not have impermeable layers to restrict gas movement. If gas collection is required at the site, it may be necessary to modify the design of the cover to capture and vent the gas generated in the landfill. In addition, landfill gas may limit the effectiveness of an ET cover, because the gases may be toxic to the vegetation.[13,45]

Limited data are available to describe the performance of ET cover systems in terms of minimizing percolation, as well as the covers' ability to minimize erosion, resist biointrusion, and remain effective for an extended period of time. While the principles of ET covers and their corresponding soil properties have been understood for many years, their application as final cover systems for landfills has emerged only within the past 10 years. Limited performance data are available on which to base applicability or equivalency decisions.[39,43,46]

Numerical models are used to predict the performance and assist in the design of final cover systems. The availability of models used to conduct water balance analyses of ET cover systems is currently limited, and the results can be inconsistent. For example, models such as Hydrologic Evaluation of Landfill Performance (HELP) and Unsaturated Soil Water and Heat Flow (UNSAT-H) do not address all of the factors related to ET cover system performance. These models, for instance, do not consider percolation through preferential pathways; may underestimate or overestimate percolation; and have different levels of detail regarding weather, soil, and vegetation. In addition, HELP does not account for physical processes, such as matric potential, that generally govern unsaturated flow in ET covers.[39,42,47]

25.5 DESIGN ISSUES AND REQUIREMENTS

The ET cover cannot be tested at every landfill site; so it is necessary to extrapolate the results from sites of known performance to specific landfill sites. The factors that affect the hydrologic design of ET covers encompass several scientific disciplines and there are numerous interactions between factors. As a consequence, a comprehensive computer model is needed to evaluate the ET cover for a site.[48] The model should effectively incorporate soil, plant, and climate variables, and include their interactions and the resultant effect on hydrology and water balance. An important function of the model is to simulate the variability of performance in response to climate variability and to evaluate cover response to extreme events. Because the expected life of the cover is decades, possibly centuries, the model should be capable of estimating long-term performance. In addition to a complete water balance, the model should be capable of estimating long-term plant biomass production, need for fertilizer, wind and water erosion, and possible loss of primary plant nutrients from the ecosystem.

Model needs are best met by an "engineering design model." In addition to requirements discussed here, an engineering model should require site parameters that can be measured or are available in historical records. Because adequate site-specific data are almost never available, the engineering design model should not require calibration.

The properties of the ET cover and its design are different from those of conventional covers. Because model evaluation should include all of the important elements required in design, this section provides a review of important elements of the ET cover that influence its design and should be evaluated before selecting and using a particular model. The reader may find additional important details in Refs. 4, 8–12, and 42.

Because borrow soils will be mixed and modified during placement, the cover soil for an ET landfill cover, as constructed, will be unique to the site. However, the soil properties may be easily described. The design process requires an evaluation of whether or not the proposed soil and plant system can achieve the goals for the cover. Numerous factors interact to influence ET cover performance. A mathematical model is needed for design that is capable of (1) evaluating the site water balance that is based on the interaction of soil, plant, and climate factors and (2) estimating the performance of an ET landfill cover during extended future time periods.

Future predictions of ET cover performance require a sophisticated model. A suitable model should include the following[14]:

1. Contain a stochastic climate generator capable of simulating daily precipitation and other weather parameters that are similar in amount and statistical variability to historical weather records for the site.
2. Realistically estimate daily plant and soil response to variable generated climate.
3. Realistically estimate daily water balance including deep percolation (PRK).

These requirements are similar to those required for flood flow estimates before designing a bridge or culvert on a roadway. In both cases, the future climate and resulting water balance are unknown, but an estimate of the critical future event and its probability of occurrence are needed to guide the design. These needs can be satisfied for ET landfill cover design or evaluation by a suitable hydrologic computer model.

25.5.1 HYDROLOGIC WATER BALANCE

A major requirement of a landfill cover is to control the amount of precipitation that enters the waste. The amount of water that percolates through the cover and may enter the waste is called PRK. PRK is a part of a much bigger hydrologic system and must be assessed in parallel with the other parts. Therefore, it is necessary to estimate the entire hydrologic water balance for the cover in order to assess its behavior.[49]

Because the quantity of water on or near the earth is believed to be constant, the hydrologic water balance for a landfill cover may be expressed by the statement[14]:

$$\text{Incoming water} = \text{Outgoing water}$$

$$\mathrm{P + I = ET + Q + L + \Delta\ SW + PRK,} \tag{25.1}$$

where P is the precipitation, I is the irrigation, if applied, ET is the evapotranspiration (the actual amount, not potential amount), Q is the surface runoff, L is the lateral flow, ΔSW is the change in soil water (SW) storage, and PRK is the deep percolation (below the cover or root zone).

The site water balance for an ET landfill cover is illustrated in Figure 25.4. The incoming water (P + I) should equal the outgoing water (ET + Q + L + ΔSW + PRK). Where all terms are measured, for example, lysimeter measurements—the difference or lack of balance is an expression of measurement error.

Lateral flow (L) within the soil layer containing plant roots is small for most landfill cover situations and is zero for lysimeters with sidewalls. During the course of a hydrologic year, ΔSW is usually small in comparison to the other terms, but it may be large on a daily basis. A primary focus for the design is PRK below the ET landfill cover as represented by the rearranged equation:

$$\mathrm{PRK = P + I - ET - Q - L - \Delta SW - Error.} \tag{25.2}$$

Here, Error = lack of balance in the measured terms.

PRK is the primary design criterion for landfill covers that are expected to limit and control the amount of precipitation that enters the waste of the landfill. As a result, the primary focus of model

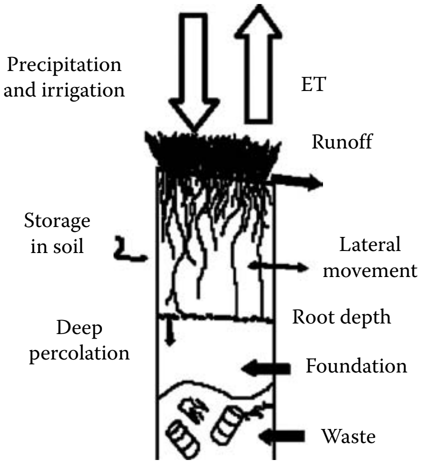

FIGURE 25.4 Water balance terms for an ET landfill cover.[14]

evaluation is the accuracy with which a model estimates PRK. However, the model estimate of PRK is strongly affected by errors in measured inputs P and I, and by errors in estimating ET, Q, and ΔSW. ET is the largest term of the outgoing water balance for almost all sites. Q is often the second-largest term; it is substantial at many, but not all, sites. Therefore, in addition to the accuracy of PRK estimates, it is also important to assess the accuracy of the model estimates of both ET and Q because errors in these estimates contribute directly to the error in PRK.

In a natural system, soil–water content changes in response to water removal by plants, soil evaporation, and gravitational drainage. During and immediately after rainfall or snowmelt, soil–water storage may change rapidly in response to the influx of water from the rain or snowmelt and the removal of water due to drainage by gravitational forces and plant use. While gravitational drainage can be a significant removal mechanism, it is effective for a short time and is near zero most of the time. Soil evaporation is important for one to a few days after precipitation; then it rapidly declines to near-zero amounts. Plant use is the primary mechanism for change in soil–water content and continues for long time periods or until the soil becomes dry.

Because soil–water content strongly affects daily values of ET, Q, and PRK, errors in estimates of change in total soil–water content will be included in errors of the ET, Q, and PRK terms estimated by a model. An appropriate model should continuously estimate the amount of soil–water in storage for all layers within the soil profile. The rate of plant water use and soil evaporation from a particular layer may be large or small depending on several interacting factors. A significant error in the amount of soil–water stored in one of the topsoil layers may have no effect on the value of PRK if lower layers were dry on that day. Errors in estimates of soil–water storage in each individual layer may or may not contribute to errors in PRK, depending on water content of each layer of the entire soil profile and other factors. The principles of water balance analysis are contained in Refs. 50 and 51, and water balance analysis for landfill covers is described in Refs. 9, 16, 42, 49, and 52–54.

25.5.2 CLIMATE

The total amount of precipitation over a year, as well as its form and distribution, determines the total amount of water storage capacity needed for the cover system. The cover may need to accommodate a spring snowmelt event that causes the amount of water at the cover to be relatively high for a short period of time or conditions during cool winter weather with persistent, light precipitation. Storage capacity is particularly important if the event occurs when local vegetation is dormant, yielding less ET.

Regional climate should be the first consideration when evaluating the suitability of an alternative landfill cover for a site. If the regional climate appears to be compatible with the requirements of the alternative cover, then site characteristics should be examined to determine whether the site climate is also suitable. Site and regional climate may differ substantially for sites near mountains, in valleys, in the rain shadow of coastal mountains, or near the coast. The Air Force Center for Environmental Excellence commissioned a generic assessment of the suitability of the ET landfill cover based on regional climate for the continental United States.[4]

An adequate measurement of the climate at a site requires the longest available record and should contain a minimum of 20 years of data. The importance of long records can be illustrated by the annual precipitation from Coshocton, Ohio: While the 35-year average annual precipitation is 37 in., one 5-year period averaged 88% of the overall average (32.6 in.) and another averaged 115% (42.6 in.). Clearly, a short record may not accurately describe the climate at a site and should not be used for design.[14]

Site-specific climatic factors that are important to selection of landfill cover type and to design of ET landfill covers include daily measurements of precipitation, maximum and minimum temperature, relative humidity, total solar radiation, and wind run.[6,45,55] If all of the data are not available, one can make useful—but less accurate—estimates of cover performance using only daily precipitation and maximum and minimum temperature measurements.

Any model used for ET cover design should, at a minimum, be able to utilize daily precipitation and temperature data and preferably should be able to utilize the other important climate factors as well in order to produce the most accurate estimates.

25.5.3 EVAPOTRANSPIRATION

ET is the evaporation of water from the soil surface and by plant transpiration (primarily through the stomata on the plant's leaves). ET should be carefully considered during all stages of design since it will be the largest mechanism of water removal in the water balance for an ET cover. With current knowledge, it is necessary to estimate potential evapotranspiration (PET) first and then using the PET estimate the actual evapotranspiration (AET) for the site.

PET is the maximum ET that can result from a set of climatic conditions. It is limited by the amount of energy available to evaporate water. The equivalent term "reference crop evaporation" is used by research workers who investigate the physics of ET. For the purposes of plant growth and production, PET is defined as the amount of water that would return to the atmosphere if abundant, freely transpiring plant leaves are available, and the water supply to the plants is abundant and unrestricted. The magnitude of PET is useful for preliminary planning to identify the maximum possible performance that might be expected from an ET cover.

Hauser and Gimon[4] estimated the ratio of PET to precipitation for the continental United States; the results are summarized in Figure 25.5. They arbitrarily used a PET ratio of 1.2 or greater to indicate likely success for the ET cover because AET is likely to be less than PET. The ratio of PET to precipitation is >1 for almost all of the continental United States. The ET cover is likely to be appropriate for sites where the ratio is ≥1.2; but it may also be appropriate and should be evaluated for all sites where the ratio is >1.[14]

AET is less than the PET amount except for relatively short time periods during and after rainfall or snowmelt events. When modeling the performance of an ET landfill cover, the estimate of AET is very important. The accuracy with which a model estimates AET is the biggest controlling factor for hydrologic modeling accuracy because (1) AET is the largest term on the right-hand side of Equation 25.1 and (2) water removed from the soil by AET affects or controls the size of the other terms on the right-hand side of Equation 25.1.

Numerous factors control AET and thus control the hydrologic performance of an ET cover. Soil–water content, rate of root growth, and total root mass strongly affect the rate of AET. AET is also affected by whether wet soil is available in surface soil layers, deeper in the profile, or in

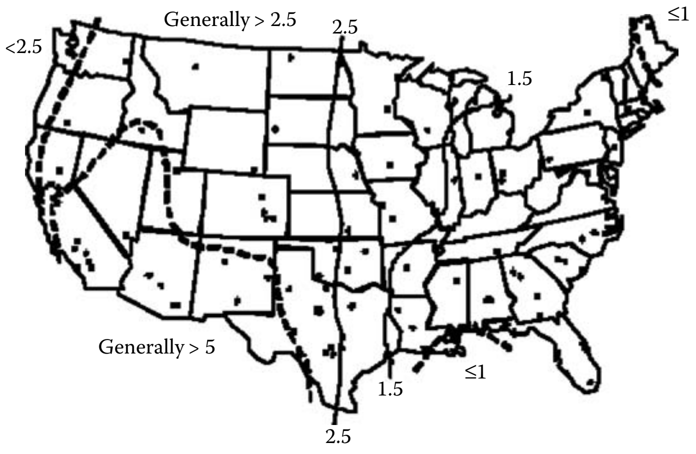

FIGURE 25.5 PET/precipitation ratio.[14]

TABLE 25.1
Factors Affecting Amount and Rate of Surface Runoff from ET Landfill Covers

Soil	Surface	Other Factors
Infiltration rate	Surface crust and tilth	Rainfall intensity
Water content	Plant type (sod or bunch grass, etc.)	Time of occurrence of high intensity
Particle size distribution	Cover density	Storm duration
Frozen soil	Growth rate	Interception by plants
Bulk density	Stage of annual growth cycle	Soil surface depressions
Clay mineralogy	Biomass production	Litter on the soil surface
Macro porosity	Roughness and storage	Land slope

Source: Hauser, V.L. and Gimon, D.M., *Evaluating Evapotranspiration (ET) Landfill Cover Performance Using Hydrologic Models*, Air Force Center for Environmental Excellence (AFCEE), Brooks City-Base, TX, January 2004.

all layers. While root mass and root growth rate strongly affect AET, they are in turn controlled by other factors.

25.5.4 SURFACE RUNOFF

Surface runoff (Q) is the second-largest part of the hydrologic water balance for ET landfill covers at many sites in humid regions. Even at dry sites where surface runoff is small, errors in estimates of Q are important, and especially so if the model estimates significant Q on days with no runoff. Estimates of Q are therefore important to the design process at all sites.

Water leaving the site (Q) reduces the volume that must be stored within the cover. Errors in estimating daily Q will result in erroneous estimates of cover performance as measured by PRK of water below the cover. If the estimated Q is too low, the estimated PRK will be too high and vice versa.

Surface runoff can begin only after (1) rainfall or snowmelt fills storage by plant interception and surface ponding and (2) the rainfall or snowmelt rate exceeds the soil infiltration rate. Excellent sources for technical details include Chow et al.,[50] ASCE Manual 28,[53] and Linsley et al.[56] Factors affecting Q are listed in Table 25.1.

Any model chosen for use in ET cover design should make reasonably accurate estimates of Q. There are several methods used to estimate Q. The ASCE Manual 28[53] discusses 18 engineering design models that compute Q; some of them use infiltration equations to estimate Q. One of the models used the Richards equation to estimate infiltration. One used the Smith and Parlange infiltration equation, and two used an “index.” Two models could use either the soil conservation service (SCS) curve number method or the Green–Ampt infiltration equation. Nine of the models used the SCS curve number method and six used the Green–Ampt infiltration equation. The data shown in ASCE Manual 28[53] indicated that the SCS curve number method and the Green–Ampt infiltration equation are, by far, the most popular methods for estimating surface runoff in engineering design models.

25.5.5 SOIL–WATER STORAGE AND MOVEMENT

ET landfill covers control the precipitation falling on the surface by providing adequate water storage capacity in the soil to contain the infiltrating precipitation. Total (potential) soil–water storage capacity is controlled by soil properties. The storage capacity available at any instant in time is controlled primarily by the balance between infiltration from precipitation and rate of water removal from the soil by ET. The majority of ET is the result of plant transpiration. ET covers perform best when the primary limitation to plant growth is soil–water content, thus assuring rapid soil drying.

The physics of water movement within the soil is important to the design of an ET cover. The modern understanding of water movement in unsaturated soils has been under development for about 150 years, and the development of new concepts continues in the modern era. Henri Darcy[57] provided the earliest known quantitative description of water flow in porous media. Darcy developed an equation for water flow in saturated sand, and modern equations for both saturated and unsaturated flow are based on his early work.

Currently used equations for water flow in unsaturated soil are based on the assumption that soils are similar to a bundle of capillary tubes and that water flow can be approximated by the Hagen–Poiseuille equation.[58] While it is obvious that the pore space in soil is not the same as a bundle of capillary tubes, the concept has proven highly useful and is currently used in mathematical descriptions of water flow in soil.

The Richards equation is widely used in research to estimate water flow in both saturated and unsaturated soils. It is also used in software proposed for use in evaluation of ET landfill covers.

Theoretical estimation of water flow in unsaturated soils is difficult and complex. The derivation of the versions of the Richards equation commonly solved in modern models required several assumptions. In addition, it is difficult to accurately estimate likely field values for unsaturated soil hydraulic conductivity on the scale of a complete ET cover. Nevertheless, the Richards equation provides useful estimates of flow of water within the soil where adequate estimates of soil hydraulic conductivity are available.

Other models successfully employ a simple water routing system. Each layer of soil is assumed to hold all water entering the layer up to the field capacity. When the water content of a soil layer exceeds the field capacity, water drains downward to the next layer at the rate specified by the hydraulic conductivity of the saturated soil in the layer.

25.5.6 DEEP PERCOLATION

Estimates of water movement through the cover (PRK) are of particular concern for ET cover design and evaluation. The performance of ET covers should be estimated for large and critical climatic events expected during the life of the cover. Therefore, a major concern for ET cover performance is the determination of the greatest amount of water that the ET cover soil must store during a defined time period. Critical events causing maximum soil–water storage may result from a single-day storm, a multiple day storm, or other events.

The following example illustrates the concept.[14] Model estimates are available for a landfill located on the western edge of the Central Great Plains; the cover soil was 0.6 m thick and composed of loam soil. Model estimates of soil water in storage for each day of a 100-year simulation period along with estimates of daily values of PRK are available. The estimates revealed that no water should be expected to move through the cover. Figure 25.6 presents the estimates of daily precipitation and daily soil–water content during the wettest year of the 100-year model estimate, and it includes

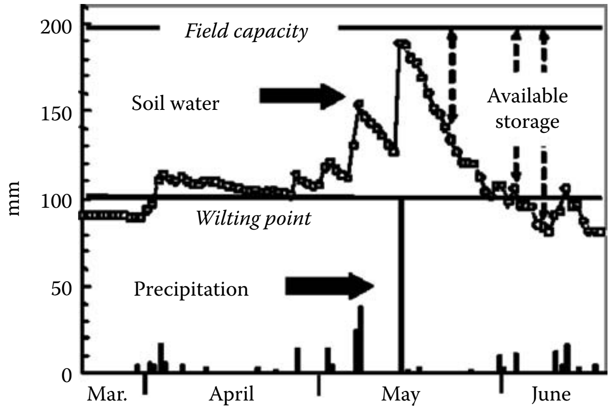

FIGURE 25.6 Critical event.[14]

the greatest single-day storage of soil–water during the 100-year period. In this example, the critical event was the result of several days with precipitation followed by a large, single-day precipitation event. The cover described could successfully control PRK.

Any model used for ET cover design should, at a bare minimum, demonstrate that the design being modeled will adequately control the projected critical event for the site being considered. Preferably, it should also estimate how much excess storage capacity would be available during that critical event so that an appropriate safety factor can be included in the final cover design. Additional details regarding factors that affect PRK may be found in Refs. 11 and 12.

25.5.7 Soil Type

Finer-grained materials such as silts and clayey silts are typically used for monolithic ET cover systems and the top layer of a capillary barrier ET cover system because they contain finer particles and provide a greater storage capacity than sandy soils. Sandy soils are typically used for the bottom layer of the capillary barrier cover system to provide a contrast in unsaturated hydraulic properties between the two layers. Many ET covers are constructed of soils that include clay loam, silty loam, silty sand, clays, and sandy loam.

The storage capacity of the soil varies among different types of soil, and depends on the quantity of fine particles and the bulk density of the soil. Compaction impacts bulk density, which in turn affects the storage capacity of the soil and the growth of roots. One key aspect of construction is minimizing the amount of compaction during placement. Higher bulk densities may reduce the storage capacity of the soil and inhibit growth of roots.[6,59]

25.5.8 Soil Thickness

The thickness of the soil layer(s) depends on the required storage capacity, which is determined by the water balance at the site. The soil layers need to accommodate extreme water conditions, such as snowmelts and summer thunderstorms, or periods of time during which ET rates are low and plants are dormant. Monolithic ET covers have been constructed with soil layers ranging from 2 to 10 ft. Capillary barrier ET covers have been constructed with finer-grained layers ranging from 1.5 to 5 ft, and coarser-grained layers ranging from 0.5 to 2 ft.

25.5.9 Vegetation Types

Vegetation for the cover system is used to promote transpiration and minimize erosion by stabilizing the surface of the cover. Grasses (wheatgrass and clover), shrubs (rabbitbrush and sagebrush), and trees (willow and hybrid poplar) have been used on ET covers.[60,61] A mixture of native plants consisting of warm- and cool-season species is usually planted, because native vegetation is more tolerant than imported vegetation to regional conditions, such as extreme weather and disease. The combination of warm- and cool-season species provides water uptake throughout the entire growing season, which enhances transpiration. In addition, native vegetation is usually planted, because these species are less likely to disturb the natural ecosystem.[43,45]

Understanding important plant requirements is critical for correct selection of materials, design, construction, maintenance, and performance of an ET landfill cover. The success of an ET cover is ensured by optimizing all factors controlling plant growth except for soil–water supply. The goal is to make soil–water content a limiting factor to plant growth several times during each normal growing season.

The plant cover should have potential rooting depth greater than the thickness of the soil cover. Many native species have potential rooting depths of 2 m or more.[14]

Several plant parameters are important to the design of ET landfill covers. Among the most important are parameters describing: rooting depth, leaf-area-index (LAI), temperature requirements, time to maturity, and water requirements. Models that are suitable for use in design of ET covers will utilize these parameters. The quality of the plant model controls the quality of AET estimates.

25.5.10 SOIL AND ORGANIC PROPERTIES

Soil provides the medium in which plants grow; it stores precipitation within the ET cover and provides nutrients for plant growth. Total (potential) soil–water storage capacity is controlled by soil properties. The storage capacity available at any instant in time is controlled primarily by the balance between infiltration from precipitation and rate of water removal from the soil by ET.

The cover design and construction should optimize soil conditions for water use by plants. This is an important tool and can be used to ensure success of the ET cover. Plant growth and water use are controlled by soil and air temperature, precipitation, solar radiation, wind, humidity, disease, and insect attack. Neither design nor construction practice can exert significant control over these factors; but they can be considered during design to assure success.

Other important soil properties of the ET landfill cover may be controlled by adequate design and good construction practices. The properties that govern root and plant growth and are important to design of ET landfill covers include soil density, aeration, pH, and nutrients. For a complete list of soil properties refer to Table 25.2.

Nutrient and salinity levels affect the ability of the soil to support vegetation. The soil layers need to be capable of providing nutrients to promote vegetation growth and maintain the vegetation system. Low nutrient or high salinity levels can be detrimental to vegetation growth, and if present, supplemental nutrients may need to be added to promote vegetation growth. For example, at Fort Carson, Colorado, biosolids were added to a monolithic ET cover to increase organic matter and provide a slow release of nitrogen to enhance vegetation growth. In addition, topsoil promotes growth of vegetation and reduces erosion. For ET covers, the topsoil layer is generally a minimum of 6 in. thick.[62]

After landfill cover completion, the plant cover may be changed but soil modification may be impractical. Therefore, good soil design and correct construction practices are of utmost importance to the success of the ET cover.

The U.S. Department of Agriculture (USDA) soil classification system was developed for use in describing soils in which plants grow.[63–66] The USDA system is now universally accepted within the United States and it should be used to describe soils used in ET landfill covers.

By its very nature, construction of an ET landfill cover modifies the soil used to create the cover. Hence, the construction process offers the opportunity to either (1) place the soil so that it will

TABLE 25.2
Soil Properties That Govern Root and Plant Growth and Are Important to Design of ET Landfill Covers

Basic Soil Properties	Derived or Secondary Soil Properties	Soil Conditions/Factors Affecting Plant Growth
Particle size distribution	Soil strength	Temperature
Bulk density	Water-holding capacity	Water content
Clay mineral type	Field capacity/wilting point	Oxygen in soil air
pH	Hydraulic conductivity	Toxic substances
Total porosity	Fertility	Ammonia
Percentage large pores	Available nutrient supply	CO_2 from decaying organics
Soil salinity	Tilth	Methane
Soil sodium content	Anions/salinity	Bacteria
Humus content	Aeration properties/connection between pores	Fungi

Source: Hauser, V.L. and Gimon, D.M., *Evaluating Evapotranspiration (ET) Landfill Cover Performance Using Hydrologic Models*, Air Force Center for Environmental Excellence (AFCEE), Brooks City-Base, TX, January 2004.

perform better than before it was moved or (2) damage the soil and greatly reduce the opportunity for success in meeting the requirements for the cover. It is important to understand soil properties that control success and how they may be optimized during cover construction. An appropriate model can help the designer understand how changes in the properties of soils available at the site in question will affect the final design of an ET cover.

Agricultural interests have amended existing soil properties to improve productivity; their experience demonstrates the power of knowledge of soil properties and the ability to control them.[14] A primary benefit of these amendment efforts was improvement in soil–water-holding capacity and increased rate of water removal from all soil layers by plants. The benefits of soil modification remain effective for decades. There is opportunity for similar improvements in soil during ET landfill cover design and construction. Control of ET cover soil properties has potential to enhance cover performance and should add little to construction cost.

The water-holding properties of ET cover soils are important to succeed. Soils that hold much water will achieve the desired water control with a thinner layer of soil than those with low water-holding capacity. The water-holding properties should be expressed as volumetric water content in keeping with model requirements and to facilitate understanding of design parameters. Important water-holding properties include the permanent wilting point, field capacity, and plant-available water content.

25.5.11 Control Layer Types

Control layers, such as those used to minimize animal intrusion, promote drainage, and control and collect landfill gas, are often included for conventional cover systems and may also be incorporated into ET cover system designs. For example, a proposed monolithic ET cover at Sandia National Laboratories in New Mexico will have a biointrusion fence with 1/4-in. squares between the topsoil layer and the native soil layer to prevent animals from creating preferential pathways, potentially resulting in percolation. The biointrusion layer, however, will not inhibit root growth to allow for transpiration. At another site, Monticello Uranium Mill Tailings Site in Utah, a capillary barrier ET design has a 12-in. soil/rock admixture as an animal intrusion layer located 44 in. below the surface, directly above the capillary barrier layer.

In addition, a capillary barrier cover demonstration at Sandia National Laboratories has a drainage layer located above the capillary break. A drainage layer consisting of an upper layer of sand and a lower layer of gravel is located directly below the topsoil layer. The sand serves as a filter to prevent topsoil from clogging the drainage layer, while the gravel allows for lateral drainage of water that has infiltrated through the topsoil.[39,67]

In more recent applications, several types of ET cover designs also have incorporated synthetic materials, such as geomembranes, which are used to enhance the function of minimizing water into the waste. For example, the Operating Industries Inc. Landfill in California has incorporated a soil layer with a geosynthetic clay liner in the design. The cover system for this site will reduce surface gas emissions, prevent oxygen intrusion and percolation, and provide for erosion control.[68]

25.5.12 Safety Factor

As with any engineering design, the ET cover should be designed with safety factors because both design and construction introduce uncertainty regarding performance. Some safety factor concerns are similar between ET covers and conventional covers. However, control of water flow into the waste requires new safety factor considerations for the ET cover, including the following:

1. The size of the soil–water reservoir in the cover soil should be adequate to contain extreme or design storm events.
2. The time required to empty the soil–water reservoir is critical to success.

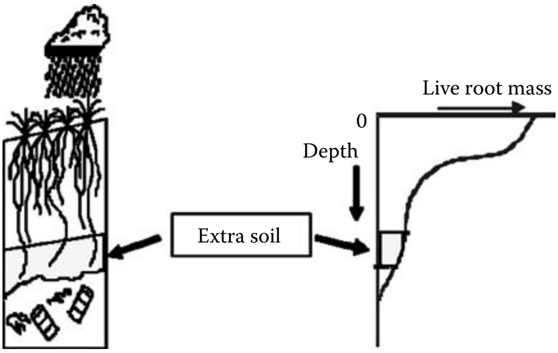

FIGURE 25.7 Root distribution in the cover.

One basis for providing a safety factor is to arbitrarily increase the soil thickness (e.g., build the soil 50% thicker than indicated as adequate by design). However, this intuitive approach may not produce the desired result.

Although the soil's total water-holding capacity is similar for all layers of a uniform soil, the distribution of roots and the rate and amount of water extraction are not. Consider the typical ET cover soil situation in which the soil has uniform properties from top to bottom. The distribution of living plant roots in soil controls the rate of drying of each soil layer. Figure 25.7 illustrates a normal root distribution pattern and an ET cover soil profile. Addition of extra soil to the thickness of the cover, where all soil is uniform, has the effect of adding soil to the bottom of the cover because the plant roots grow from the surface downward. The last increment of soil thickness results in relatively few roots growing in the newly added soil layer, which is effectively on the bottom of the cover. Plants remove water more slowly from deep soil layers than from near-surface soil layers. As a result, during one growing season, plant roots may not remove all plant-available water from the lower layers of the cover if the cover is thick.

As shown in Figure 25.8, an increase in soil thickness from the design thickness (A) by 50% to (B) may result in only a small increase in plant-available water-holding capacity during a single growing season.

A better way to provide a safety factor is to utilize hydrologic factors that are known to affect soil–water use and storage. They may be used in combination with a model to evaluate options and

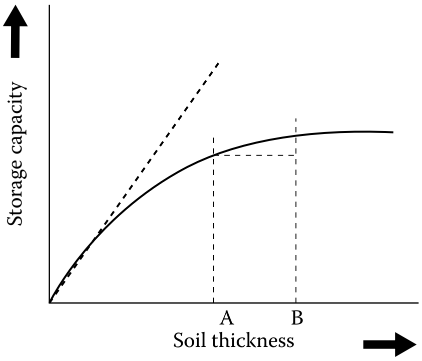

FIGURE 25.8 Effective water storage capacity—one growing season.[14]

select a good course of action. The model should estimate soil–water content for each soil layer on each day of evaluation. It should also maintain a balance of available soil–water storage space. Therefore, the model should indicate available storage for each day along with ET, Q, and PRK. Possible ways to introduce an adequate safety factor include[14]:

1. Base the design on reduced plant-available water-holding capacity (e.g., 10% reduction).
2. Base the design on increased daily precipitation (e.g., 110% of normal precipitation).
3. Increase surface runoff by replacing the second layer of soil—for example, 6–12 in.—with clay soil, or use clay soil for the top 6 in. of the cover; however, maintain the same soil thickness as required for a one-layer soil.
4. Design for either warm- or cool-season plants, but establish both to provide increased annual, total water use.

These possibilities may be used singly or in combination. Use of an appropriate model to simulate the effects of such design changes will enable the designer to add a suitable safety factor to the final design.

25.6 HYDROLOGIC MODELS

ET landfill cover performance is governed by a complex set of interacting processes. Mathematical models may describe individual processes, but because of interactions among processes, these more limited mathematical treatments should be integrated into a single working model. The development of a new computer model suitable for ET landfill cover design would be expensive and require several years of development and testing. An alternative is to evaluate currently available models to determine whether they are suitable for design and analysis of an ET landfill cover.

Engineering design and cover evaluation are best served by a model that incorporates all of the important elements of engineering design that are important to ET covers. Some models are good research or scientific investigation tools, but are not sufficiently complete to serve the practicing design engineer who must consider all aspects of landfill remediation during cover design. In practice, the design engineer must balance the need for high quality, input data against landfill remediation requirements, and available funds. The model should be sufficiently robust to provide reliable answers with less than optimum completeness or accuracy in the input data. It should also be capable of providing guidance to the design engineer regarding the consequences of incomplete input data.

This section describes currently available models and presents important features of each that are pertinent to ET landfill cover design. These models have diverse origins; however, each was intended for use in evaluating the hydrologic cycle and included features that are pertinent to landfill covers. The model developer and/or other reviewers have tested each of these models. The purpose of this evaluation is to determine the level of accuracy and usefulness of a model as it might be applied to ET landfill cover design and evaluation.

25.6.1 IMPORTANT MODEL CHARACTERISTICS

If properly designed, the soil–water reservoir of an ET cover will be only partially filled most of the time. The greatest amount of water that must be stored in the soil will be defined by major or "critical events." The critical event may result from a single storm event or a series of storms. The model used for design or evaluation of an ET landfill cover should be capable of evaluating the cumulative effect of each day's water balance activity and thus identify critical events.

The design process requires estimates of the amount of water stored within the soil mass for each day of the design period. The performance of a completed cover or design may be assessed by estimating the daily, annual, or other sums of PRK, which can be used to determine whether or not the cover will meet design requirements.

Some models require calibration to optimize input parameters; they are best used in a research setting where it is possible to make measurements with which to calibrate the model for a particular site. Appropriate measured hydrologic data are seldom available to calibrate a model for a particular landfill site. Therefore, engineering models used for ET cover design should not require calibration.

The way in which models estimate PET and AET values, plant growth, root growth and distribution, and other parameters can have profound effects on the accuracy of model estimates for ET landfill cover design. For example[14]:

1. There are several possible methods for estimating PET, the largest hydrologic term. Using the wrong method may introduce large errors in each part of the water balance analysis.
2. The density of soil may control the presence, absence, or density of roots found in a particular soil layer. The density of plant roots in a soil layer determines how much water plants can remove from the layer and its rate of removal. Soil compaction, in addition to inhibiting root growth, reduces soil–water-holding capacity. A model that does not consider the effect of soil density on water balance may produce significant errors in water balance estimates.

25.6.2 ENVIRONMENTAL POLICY INTEGRATED CLIMATE MODEL

Development of the Environmental Policy Integrated Climate (EPIC) model and its predecessor, the Erosion Productivity Impact Calculator, began in the early 1980s.[69,70] The first version of EPIC was intended to evaluate the effects of wind and water erosion on plant growth and food production. More recent versions also evaluate factors important to other environmental issues. EPIC is a one-dimensional model; however, it can estimate lateral flow in soil layers at depth. All versions of EPIC estimate surface runoff, PET, AET, soil–water storage, and PRK below the root zone—these complete the hydrologic water balance for an ET landfill cover.

More than 200 engineers and scientists participated in the development of EPIC and more than 50 publications describe testing and use of the model.[70] EPIC is in use by the Natural Resource and Conservation Service; the Agricultural Research Service of the USDA; Iowa State; Texas A&M; Washington State; in Australia; Syria; Jordan; Canada; Germany; Taiwan; and other countries and universities around the world.

EPIC uses a daily time step to simulate climate, hydrology, soil temperature, nutrient cycling, tillage, plant management, and growth. It can estimate soil erosion, pesticide and nutrient movement by water or sediment, and field-scale costs and returns. The EPIC model has been revised and improved several times. From the beginning, the hydrologic submodel was an essential and central part of EPIC because (1) the soil–water available for plant use is a limiting factor to plant growth, (2) surface runoff and soil erosion by water are directly related, and (3) PRK removes nutrients and other chemicals from the soil profile, which will affect plant growth.

EPIC is designed to simulate relevant biophysical processes simultaneously and realistically, using readily available input data and accepted methods. It is capable of simulating plant and soil response for hundreds of years, and it is applicable to a wide range of soils, climates, and plants. EPIC also simulates soil erosion and soil chemical and physical property changes over centuries. The time limit for simulation of hydrologic parameters is restricted only by the availability of high-quality climate input data.

EPIC contains 10 major submodels or components:

1. Climate
2. Hydrology

3. Soil erosion by wind or water
4. Soil temperature
5. Tillage
6. Plant growth
7. Crop and soil management
8. Nutrient cycling
9. Pesticide fate
10. Economics.

Output from the soil erosion, pesticide fate, and economics submodels may not be needed for ET landfill cover evaluation and design; they can be disregarded without affecting other components of the model estimate.

The EPIC model is a comprehensive model that has been extensively tested for water balance estimates in dry and wet climates, including sites with significant accumulation of snow in winter.[14]

An important issue is the reliability of the model over the entire United States. EPIC was tested for accuracy in estimating ET and Q by many investigators on data gathered from the United States and other countries. Numerous tests of the model are described by Sharpley and Williams[70] and by others. Model tests by others are summarized below; in each of these evaluations, EPIC produced accurate estimates of ET and Q.

Estimates of water movement through the cover (PRK) are of particular concern for ET cover design and evaluation. Meisinger et al.[71] demonstrated that EPIC estimated PRK with good accuracy when compared with measurements from high-quality lysimeters at Coshocton, Ohio. Chung et al.[72] evaluated the performance of the EPIC model for two watersheds in southwestern Iowa and found that it estimated seepage flow well. Chung et al.[73] evaluated EPIC against field measured drainage tile outflow in Minnesota and found that the model predicted annual drainage losses of similar magnitude to those measured, and replicated the effects of cropping systems on nitrogen fate in the environment.

In addition to a complete water balance, EPIC estimates plant biomass production, fertilizer use, wind and water erosion, loss of nitrogen and phosphorus from the soil, and the effect of nutrient loss from the soil on plant growth.

25.6.3 HELP Model

The HELP model[74,75] is widely used and accepted for the design of conventional, barrier-type landfill covers. The U.S. Army Engineer Waterways Experiment Station in Vicksburg, Mississippi developed the HELP model for the U.S. EPA. Work began prior to 1982 as evidenced by the early publication of a draft report documenting hydrologic simulation modeling.[76] Recent versions of the HELP model are described in Schroeder et al.[74,75]

Numerous workers tested the HELP model, and it is in general use throughout the United States by regulators, design engineers, and others for planning and evaluating barrier-type landfill covers.

The HELP model is a quasi-two-dimensional hydrologic model of water movement over, into, through, and out of landfills. It places primary emphasis on the properties and function of barrier and drainage layers located above and below the waste; such layers are typically used in barrier-type landfill covers. HELP uses climate, soil, and design data to estimate landfill hydrologic performance as expressed by surface storage, snowmelt, runoff, infiltration, ET, vegetative growth, soil moisture storage, lateral subsurface drainage, leachate recirculation, unsaturated vertical drainage, and leakage through soil, geomembrane, or composite liners. It is capable of modeling landfill systems that include various combinations of vegetation: cover soils, waste cells, lateral-drain layers, low-permeability barrier soils, and synthetic geomembrane layers for up to 100 years. The model was developed to estimate a water balance for landfills, cover systems, and solid waste disposal and containment facilities, emphasizing water percolation through the waste and performance of the landfill bottom liner. HELP provides estimates of surface runoff, ET, and drainage through the surface cover soil—these complete the hydrologic water balance for an ET landfill cover.

The primary purpose of the HELP model is to provide water balance data with which to compare design alternatives for conventional barrier-type covers installed on landfills with bottom liners. It provides a tool for both designers and permit writers and is applicable to open, partially closed, or fully closed sites.

HELP does not address the effects of soil density on plant growth and the water balance. Although the HELP model was designed to evaluate barrier-type covers, it has not met expectations for the evaluation of vegetative covers. Benson and Pliska[77] and Khire et al.[78] evaluated the performance of the HELP model on two sites (Atlanta, Georgia, and East Wenatchee, Washington). During a 3-year period, the HELP model predicted 4.4 times more PRK than was measured at Atlanta (a wet site) and half the measured amount in Washington (a dry site). At both sites, HELP produced large errors in estimates of PRK.

25.6.4 UNSAT-H (VERSION 3.0) MODEL

Version 3.0 of UNSAT-H was developed under the sponsorship of the U.S. Department of Energy (DOE) from the UNSAT model beginning in 1979. The early work was documented by publication of version 1.0 of UNSAT-H,[79] and the most recent version (3.0) was described by Fayer.[80] The UNSAT-H model has been tested for the arid parts of Washington State, a few other arid sites, and at least one location with a wet climate.[80]

Fayer[80] states that the UNSAT-H model was developed to "assess the water dynamics of arid sites and, in particular, estimate recharge fluxes for scenarios pertinent to waste disposal facilities." It addresses soil–water infiltration, redistribution, evaporation, plant transpiration, deep drainage, and soil heat flow as one-dimensional processes. The UNSAT-H model simulates water flow using the Richards equation, water vapor diffusion using Fick's law, and sensible heat flow using the Fourier equation.

UNSAT-H sets infiltration equal to the precipitation rate unless the surface soil becomes saturated. It does not simulate the soil crust that develops on the soil surface; however, the user may describe a constant soil crust as a thin surface soil layer. It "does not simulate runoff explicitly"[80]; however, it assigns excess precipitation that does not infiltrate into the soil as surface runoff.

UNSAT-H uses the Richards equation, Fick's law, and the Fourier equation to estimate the flow of soil–water, vapor, and heat. This may be the strongest part of the model because these are the most rigorous, currently known, theoretical methods for estimating these parameters.

The UNSAT-H model estimates evaporation from the soil in two ways. In the isothermal mode, the user must supply PET data for each day or daily climate data from which the model calculates PET by the Penman method. In the thermal mode, the model estimates evaporation from the difference in vapor density in the atmosphere and in the surface soil layer.

UNSAT-H simulates plant transpiration with a PET concept. The model partitions plants' removal of soil–water between soil layers based on (1) distribution of plant roots within the soil profile for "cheatgrass" (an invading and weedy grass species found in dry regions of Washington State) or (2) the user may supply other functions. The user must enter soil–water parameters that describe the limits for plant extraction of water from each layer of soil. The model also uses the same daily value pattern for the LAI for each year.

The UNSAT-H model user must specify an averaging scheme for the internodal hydraulic and vapor conductivity terms used in soil water calculations. The user must also specify the model node spacing within the soil mass, which may require adjustment by iterative solutions to arrive at a satisfactory numerical analysis. In order to find the correct averaging scheme and node spacing, several "calibration" runs may be required to find systems that will work. These decisions are most appropriately made by a person with training in advanced soil physics and modeling.

UNSAT-H does not address the effects of soil density on plant growth and water balance. Disadvantages caused by the computational methods used to estimate soil water flow include the following: (1) the model requires the user to choose from several submodels to solve the Richards equation; this choice should be made by a person with training in advanced soil physics and (2) the model requires the input of several soil parameters that are difficult to estimate for the completed cover soil.

25.6.5 HYDRUS

The HYDRUS computer model was developed by the Agricultural Research Service of the USDA to estimate water flow in unsaturated soils that support plant growth[81] It was developed as a one-dimensional model, and then modified to allow solution of two-dimensional problems.[82] HYDRUS employs the Richards equation to solve water flow in unsaturated soil; however, it uses different solution methods from those used in UNSAT-H. It also requires extensive data input. The available windows version simplifies data entry and model operation.

25.6.6 MODEL COMPARISONS

Table 25.3 compares the characteristics of these four models.[14] UNSAT-H and HYDRUS are the most widely known Richards equation models that use modern soil physics principles to estimate water movement within the soil profile. HELP and EPIC are widely known engineering models.

25.6.6.1 HYDRUS and UNSAT-H

Examination of Table 25.3 and the comments above clearly demonstrate that both HYDRUS and UNSAT-H are likely to produce very good estimates of water movement within the soil profile. However, they do not estimate snowmelt, model mixed plant communities, directly estimate surface runoff, or consider the effect of soil density on root growth and water use.[14]

Both of them require at least limited model calibration. They do not stochastically estimate daily climate data for model evaluations or long-term changes in plant nutrient status and the resulting changes in plant growth and water balance. HYDRUS and UNSAT-H would be very useful and accurate if used in research; however, they are difficult to use in engineering design of ET landfill covers and provide incomplete estimates of performance.

25.6.6.2 HELP and EPIC

Both HELP and EPIC satisfy the basic requirements for engineering design models. Limitations to HELP include difficulty in modeling mixed plant communities, and using the LAI as the primary plant input to AET estimates. Both models are limited by their use of water storage routing to estimate water movement within the soil–water profile rather than modern soil physics principles. However, it is good to note that the water routing algorithms are based on modern concepts of soil physics.[14]

Both HELP and EPIC are complete engineering design models and the user can obtain the data required to run either of them. The funds available were insufficient for evaluating more than two models on two data sets. Because our goal was to evaluate models that will be useful in ET landfill cover design and evaluation, we evaluated HELP and EPIC.

25.6.6.3 Model Evaluation

The purpose of model evaluation efforts is to determine if an existing model is adequate for design or evaluation of ET landfill covers and to identify its strengths and weaknesses. This purpose is

TABLE 25.3
Comparison of Model Characteristics

Characteristic	EPIC	HELP	UNSAT-H	HYDRUS
Stochastic climate generator (daily values)	Y1	Y	N[a]	N
Daily water balance estimates				
PET (number of options)	Y (4)	Y (1)	Y (1)	Y
AET	Y	LAI[b]	Y	Y
Surface runoff (number of methods)	Y (2)	Y (1)	D[c]	D[c]
PRK	Y	Y	Y	Y
Daily soil water balance	Y	Y	Y	Y
Snowmelt	Y	Y	N	N
Soil erosion by wind or water (number of methods)	Y (4)	N	N	N
Soil density effect on root growth and water use	Y	N	N	N
Soil water flow	Routing[d]	Routing[d]	Richards[e]	Richards[e]
Uses potential plant rooting depth	Y	Y	Y	Y
Model estimates actual root growth	Y	N	N	N
Long-term estimates of plant nutrient availability and effect on water use by plants	Y	N	N	N
Mixed plant community	Y	UI[f]	N	N
Model calibration required?	N	N	Y[g]	Y[g]

Source: Hauser, V.L. and Gimon, D.M., *Evaluating Evapotranspiration (ET) Landfill Cover Performance Using Hydrologic Models*, Air Force Center for Environmental Excellence (AFCEE), Brooks City-Base, TX, January 2004.

[a] Y = yes, N = no.

[b] Based on LAI and "evaporative depth."

[c] D = difference between precipitation and infiltration rate (not directly estimated).

[d] Water storage routing.

[e] Richards equation, vapor flow, etc.

[f] Requires independent user estimates for input data.

[g] Requires repeated runs to establish site-specific time step and grid mesh size, which allow model convergence to a solution.

different from the one of model validation. Model validation includes detailed proof of mathematical functions, computer code representation of the real world, and similar issues.

Evaluation should be carried out on models that have previously been validated and tested, because the development of a new model suitable for the design task would be expensive and time consuming. This evaluation includes the following areas of concern for each model chosen[14]:

1. Accuracy of model estimates of ET, surface runoff, and PRK.
2. Plant parameter inputs, their use within the model, and appropriateness for the design problem.
3. Soil parameter inputs, their use within the model, and appropriateness of estimates that affect plant growth, and water use and storage.
4. Climate parameter inputs or generation.
5. Completeness of the hydrologic system evaluation.
6. Model output and satisfaction of design needs.
7. Level of support required from other models or other sources.
8. Model characteristics that may affect accuracy and completeness of ET cover design and/or evaluation.

25.7 PERFORMANCE AND MONITORING

Protection of groundwater quality is a primary performance goal for all waste containment systems, including final cover systems. The potential adverse impact on groundwater quality results from the release of leachate generated in landfills or other waste disposal units such as surface impoundments. The rate of leachate generation (and potential impact on groundwater) can be minimized by keeping liquids out of a landfill or contaminated source area of a remediation site. As a result, the function of minimizing percolation becomes a key performance criterion for a final cover system.[22]

Monitoring the performance of ET cover systems has generally focused on evaluating the ability of these designs to minimize water drainage into the waste. Percolation performance is typically reported as a flux rate (inches or millimeters of water that have migrated downward through the base of the cover in a period of time, generally considered as 1 year). Percolation monitoring for ET cover systems is measured directly using monitoring systems such as lysimeters or estimated indirectly using soil moisture measurements and calculating a flux rate. A more detailed summary of the advantages and disadvantages of both approaches can be found in Benson and others.[22,83]

Percolation monitoring can also be evaluated indirectly by using leachate collection and removal systems. For landfills underlain with these systems, the amount and composition of leachate generated can be used as an indicator of the performance of a cover system (the higher the percolation, the more leachate that will be generated).[22]

Although the ability to minimize percolation is a performance criterion for final cover systems, limited data are available about percolation performance for final cover systems for both conventional and alternative designs. Most of the recent data on flux rates have been generated by two federal research programs, the Alternative Landfill Cover Demonstration (ALCD)[84] and the Alternative Cover Assessment Program (ACAP). From these programs, flux rate performance data are available for 14 sites with demonstration-scale ET cover systems.[5,39,85]

In addition, previous studies have been conducted that monitored the performance of ET covers. Selected studies include the following: integrated test plot experiment in Los Alamos, New Mexico, which monitored both types of ET covers from 1984 to 1987[86]; Hill Air Force Base alternative cover study in Utah, which evaluated three different covers (RCRA Subtitle D, monolithic ET, and capillary barrier ET) over a 4-year period[87]; and Hanford field lysimeter test facility in Richland, Washington, DC, which monitored ET covers for 6 years.[88]

25.7.1 MONITORING SYSTEMS

Lysimeters are installed underneath a cover system, typically as geomembrane liners backfilled with a drainage layer and shaped to collect water percolation. Water collected in the lysimeter is directed toward a monitoring point and measured using a variety of devices (e.g., tipping bucket and pressure tranducers). Lysimeters have been used in the ALCD and ACAP programs for collecting performance data for ET cover systems.[89]

Soil moisture monitoring can be used to determine moisture content at discrete locations in cover systems and to evaluate changes over time in horizontal or vertical gradients. Soil moisture is measured using methods to determine relative humidity, soil matrix potential, and resistance. Table 25.4 presents examples of nondestructive techniques that have been used to assess soil moisture content of ET cover systems. A high soil moisture value indicates that the water content of the cover system is approaching its storage capacity, thereby increasing the potential for percolation. Soil moisture is especially important for capillary barrier ET cover systems; when the finer-grained layer becomes saturated, the capillary barrier can fail resulting in water percolating through the highly permeable layer to the waste below.[15]

Maintaining the effectiveness of the cover system for an extended period of time is another important performance criterion for ET covers as well as conventional covers. Short- and long-term

TABLE 25.4
Examples of Nondestructive Soil Moisture Monitoring Methods

Method	Description	Instrumentation
Tensiometer	Measures the matric potential of a given soil, which is converted to soil moisture content	Commonly consists of a porous ceramic cup connected to a pressure-measuring device through a rigid plastic tube
Psychrometer	Measures relative humidity (soil moisture) within a soil	Generally consists of a thermocouple, a reference electrode, a heat sink, a porous ceramic bulb or wire mesh screen, and a recorder
Electrical resistance blocks	Measures resistance resulting from a gradient between the sensor and the soil; higher resistance indicates lower soil moisture	Consists of electrodes embedded in a gypsum, nylon, or fiberglass porous material
Neutron attenuation	Emits high-energy neutrons into the soil that collide with hydrogen atoms associated with soil water and counts the number of pulses, which is correlated to moisture content	Consists of a probe inserted into access boreholes with aluminum or polyvinyl chloride casing
Time domain reflectometry	Sends pulses through a cable and observes the reflected waveform, which is correlated to soil moisture	Consists of a cable tester (or specifically designed commercial time domain reflectrometry unit), coaxial cable, and a stainless steel probe

Source: U.S. EPA, *Evapotranspiration Landfill Cover Systems Fact Sheet*, EPA 542-F-03-015, U.S. Environmental Protection Agency, Washington, DC, September 2003.

performance monitoring of a final cover system includes settlement effects, gas emissions, erosion or slope failure, and other factors.

25.7.2 NUMERICAL MODELS

While there are limitations to numerical models, as previously described, they have been used to predict cover performance and assist in the design of ET cover systems. Numerical models have been used to compare the expected performance of ET cover systems with conventional cover systems. By entering multiple parameters and evaluating the design of cover systems, designs can be modified until specific performance results are achieved. The numerical model HELP is the most widely used water balance model for landfill cover design. UNSAT-H and HYDRUS-2D are two other numerical models that have been used frequently for the design of ET covers. HELP and UNSAT-H are in the public domain, while HYDRUS-2D is available from the International Ground Water Modeling Center in Golden, Colorado.[39,78]

Recent studies have compared available numerical models and found that cover design depends on site-specific factors, such as climate and cover type, and that no single model is adequate to accurately predict the performance of all ET covers. Several of the studies identified are intercode comparisons for simulating water balance of surficial sediments in semiarid regions, which compared results of seven numerical models for nonvegetated, engineered covers in semiarid regions; water balance measurements and computer simulations of landfill covers, which evaluated ALCD cover performance and predicted results from HELP and UNSAT-H; and field hydrology and model predictions for final covers in the ACAP, which compared performance results with those predicted by HELP and UNSAT-H.[39,90,91]

25.8 COST

Limited cost data are available for the construction and operation and maintenance (O&M) of ET cover systems. The available construction cost data indicate that these cover systems have the potential to be less expensive to construct than conventional cover systems. Factors affecting the cost of construction include availability of materials, ease of installation, and project scale. Locally available soils, which are usually less costly than imported clay soils, are typically used for ET cover systems. In addition, the use of local materials generally minimizes transportation costs.[39,45]

While the construction cost for an ET cover is expected to be less than that for a conventional cover, uncertainty exists about the costs for O&M after construction. Several factors affecting the O&M cost include frequency and level of maintenance (e.g., irrigation and nutrient addition), and activities needed to address erosion and biointrusion. In addition, when comparing the costs for ET and conventional covers, it is important to consider the types of components for each cover and their intended function. For example, it would generally not be appropriate to compare the costs for a conventional cover with a gas collection layer to an ET cover with no such layer. Additional information about the costs for specific ET cover systems is provided in project profiles, discussed in Section 25.9.

25.9 TECHNOLOGY STATUS

A searchable on-line database has been developed by U.S. EPA with information about ET cover systems.[92] As of September 2003, the database contained 56 projects with monolithic ET cover systems and 21 projects with capillary barrier ET cover systems; these systems have been proposed, tested, or installed at 64 sites located throughout the United States. Some sites have multiple projects, and some projects have multiple covers and/or cover types.

The database provides project profiles that include site background information (e.g., site type, climate, and precipitation), project information (e.g., purpose, scale, and status), cover information (e.g., design, vegetation, and installation), performance and cost information, points of contact, and references. Table 25.5 provides a summary of key information from the database for 34 recent projects with monolithic ET or capillary barrier ET covers.[15]

25.10 EXAMPLES OF ET COVERS

25.10.1 Example 1: Monolithic ET Cover at Lopez Canyon Sanitary Landfill, Los Angeles, California

Site type: MSW landfill.

Scale: Full scale.

Cover design: The ET cover was installed in 1999 and consists of a 3-ft silty sand/clayey sand layer, which overlies a 2-ft foundation layer. The cover soil was placed in 18-in. lifts and compacted to 95% with a permeability of $<3 \times 10^{-5}$ cm/s. Native vegetation was planted, including artemesia, salvia, lupines, sugar bush, poppy, and grasses.

Regulatory status: In 1998, Lopez Canyon Sanitary Landfill received conditional approval for an ET cover, which required a minimum of 2 years of field performance data to validate the model used for the design. An analysis was conducted and provided the basis for final regulatory approval of the ET cover. The cover was fully approved in October 2002 by the California Regional Water Quality Control Board—Los Angeles Region.

Performance data: Two moisture monitoring systems were installed, one at Disposal Area A and one at Disposal Area AB plus in May and November 1999, respectively. Each monitoring system has two stacks of time domain reflectometry probes that measure soil moisture at 24-in. intervals to a maximum depth of 78 in., and a station for collecting weather data. Based on nearly 3 years of data, there is generally <5% change in the relative volumetric

TABLE 25.5
Selected Sites Using or Recently Demonstrating ET Covers

Site Name and Location	Site Type	Status of Project	Date Installed
Monolithic ET Covers—Full-Scale Projects			
Barton County Landfill, Great Bend, KS	MSW landfill	Installation	NA
Coyote Canyon Landfill, Sornis, CA	MSW landfill	Operational	April 1994
Duvall Custodial Landfill, Duvall, WA	MSW landfill	Operational	1999
Fort Carson, Colorado Springs, CO	MSW landfill	Operational	October 2000
Hastings Groundwater Contamination Superfund Site, Hastings, ME	MSW landfill	Design	NA
Horseshoe Bend Landfill, Lawrenceburg, TN	Industrial waste landfill	Operational	1998
Idaho National Engineering and Environmental Laboratory Superfund Site, Idaho Falls, ID	Radioactive waste site	Proposed	NA
Industrial Excess Landfill, Superfund Site, OH	Industrial waste landfill	Proposed	NA
Johnson County Landfill, Shawnee, KS	MSW landfill	Installation	NA
Lakeside Reclamation Landfill, Beaverton, OR	Construction debris	Operational	1990
Lopez Canyon Sanitary Landfill, Los Angeles, CA	MSW landfill	Operational	1999
Marine Corps Logistics Base Superfund Site, GA	MSW and hazardous waste landfill	Proposed	NA
Municipal Waste Landfill at Kirtland Air Force Base, NM	MSW landfill	Operational	2002
Operating Industries Inc. Landfill Superfund Site, CA	MSW landfill	Operational	May 2000
Pantex Plant, Amarillo, TX	Construction debris	Operational	2000
Capillary Barrier ET Covers—Full-Scale Projects			
Gaffey Street Sanitary Landfill, Wilmington, CA	MSW landfill	Installation	NA
Hanford Superfund Site, Richland, WA	Radioactive waste site	Operational	1994
McPherson County Landfill, McPherson, KS	MSW landfill	Operational	2002
Monolithic ET Covers—Demonstration Projects			
Altamont Landfill, Livermore, CA (ACAP project)	Nonhazardous waste site	Operational	November 2000
Bluestem Landfill #2, Marion, IA (ACAP project)	MSW landfill	Operational	October 2000
Finley Buttes Regional Landfill, OR (ACAP project)	MSW landfill	Operational	November 2000
Green II Landfill, Logan, OH (ACAP project)	MSW and hazardous waste landfill	Operational	2000
Kiefer Landfill, Sloughhouse, CA (ACAP project)	Nonhazardous waste site	Operational	July 1999
Marine Corps Logistics Base, Albany, GA (ACAP project)	MSW and hazardous waste landfill	Operational	March 2000
Milliken Landfill, San Bernadino County, CA (ACAP project)	MSW landfill	Operational	1997
Monterey Peninsula Landfill, Marina, CA (ACAP project)	Nonhazardous waste site	Operational	May 2000
Rocky Mountain Arsenal Superfund Site, Denver, CO	Hazardous waste site	Complete	April 1998
Sandia National Laboratories, MM (ALCD project)	Nonhazardous waste site	Operational	1996
Capillary Barrier ET Covers—Demonstration Projects			
Douglas County Landfill, Bennington, NE (ACAP project)	MSW landfill	Operational	August 2000
Hill Air Force Base, Ogden, UT	Hazardous waste landfill	Operational	1994
Lake County Landfill, Poison, MT (ACAP project)	MSW landfill	Operational	November 1999
Lewis and Clark County Landfill, MT (ACAP project)	Nonhazardous waste site	Operational	November 1999
Sandia National Laboratories, NM (ALCD project)	Nonhazardous waste site	Operational	1996
Uranium Mill Tailings Repository, UT (ACAP project)	Hazardous waste landfill	Operational	July 2000

Source: U.S. EPA, *Evapotranspiration Landfill Cover Systems Fact Sheet*, EPA 542-F-03-015, U.S. Environmental Protection Agency, Washington, DC, September 2003.

ACAP: Alternative Cover Assessment Program, a program supported by U.S. EPA; ALCD: Alternative Landfill Cover Demonstration, a program supported by U.S. DOE; NA: Not applicable.

moisture content at the bottom of the cover compared to a nearly 90% change near the surface. This implies that most of the water infiltrating the cover is being removed via ET and is not reaching the bottom of the cover.

Modeling: The numerical model UNSAT-H was used to predict the annual and cumulative percolation through the cover. The model was calibrated with 12 months of soil moisture content and weather data. Following calibration, UNSAT-H predicted a cumulative percolation of 50 cm for the ET cover and 95 cm for a conventional cover over a 10-year period. The model predicted an annual percolation of approximately 0 cm for both covers during the first year. During years 3–10 of the simulation, the model predicted less annual percolation for the ET cover than for the conventional cover.

Maintenance activities: During the first 18 months, irrigation was conducted to help establish the vegetation. Once or twice a year, brush is cleared to comply with Fire Department regulations. Prior to the rainy season, an inspection is conducted to check and clear debris basins and deck inlets. No mowing activities or fertilizer applications have been conducted or are planned.

Cost: Costs were estimated at $4.5 million, which includes soil importation, revegetation, quality control and assurance, construction management, and installation and operation of moisture monitoring systems.

Sources: U.S. EPA,[92] City of Los Angeles,[93] and Hadj-Hamou and Kavazanjian.[94]

25.10.2 Exercise 2: Capillary Barrier ET Cover at Lake County Landfill, Polson, Montana

Site type: MSW landfill.

Scale: Field demonstration under ACAP.

Cover designs: The capillary barrier test section was installed in November 1999. From the surface downward, it is composed of 6 in. of topsoil, 18 in. of moderately compacted silt, and 24 in. of sandy gravel. The cover was seeded in March 2000 with a mixture of grasses, forbs, and shrubs, including bluegrass, wheatgrass, alfalfa, and prickly rose shrubs. A conventional composite cover test section was also constructed at the site.

Performance data: Percolation is being measured with a lysimeter connected to flow monitoring systems, soil moisture is being measured with water content reflectometers, and soil matric potential and soil temperature are being monitored with heat dissipation units. From November 1999 to July 2002, the capillary barrier cover system had a cumulative percolation of 0.5 mm. Total precipitation was 837 mm over the 32-month period. Additional field data were collected through 2005.

Modeling: Numerical modeling was conducted using HYDRUS 2-D, which simulated the wettest year on record over the simulation period of 10 years. The model predicted approximately 0.6 mm of percolation during the first year, and 0.1 mm per year for the remaining 9 years.

Sources: Benson et al.,[5] Bolen et al.,[67] and U.S. EPA.[92]

25.10.3 Example 3: ALCD

The U.S. DOE has sponsored the ALCD, which is a large-scale field test of two conventional designs (RCRA Subtitle C and Subtitle D) and four alternative landfill covers (monolithic ET cover, capillary barrier ET cover, geosynthetic clay liner cover, and anisotropic—layered capillary barrier—ET cover). The test was conducted at Sandia National Laboratories, located on Kirtland Air Force Base in Albuquerque, New Mexico.[84] The ALCD has collected information on the construction, cost, and performance that are needed to compare alternative cover designs with conventional covers. The

TABLE 25.6
Total Percolation and Precipitation Data for ALCD

	1997 (May 1 to December 31)		1998		1999		2000		2001		2002 (January 1 to June 25)	
	Precip. (mm)	Perc. (mm)	Precip. (mm)	Perc. (mm)	Precip. (mm)	Perc. (mm)	Precip. (mm)	Perc. (mm)	Precip. (mm)	Perc. (mm)	Precip. (mm)	Perc. (mm)
Monolithic ET	267.00	0.08	291.98	0.22	225.23	0.01	299.92	0.00	254.01	0.00	144.32	0.00
Capillary barrier ET	267.00	0.54	291.98	0.41	225.23	0.00	299.92	0.00	254.01	0.00	144.32	0.00
Anisotropic (layered capillary barrier) ET	267.00	0.05	291.98	0.07	225.23	0.14	299.92	0.00	254.01	0.00	144.32	0.00
Geosynthetic clay liner	267.00	0.51	291.98	0.19	225.23	2.15	299.92	0.00	254.01	0.02	144.32	0.00
Subtitle C	267.00	0.04	291.98	0.15	225.23	0.02	299.92	0.00	254.01	0.00	144.32	0.00
Subtitle D	267.00	3.56	291.98	2.48	225.23	1.56	299.92	0.00	254.01	0.00	144.32	0.74

Source: U.S. EPA, *Evapotranspiration Landfill Cover Systems Fact Sheet*, EPA 542-F-03-015, U.S. Environmental Protection Agency, Washington, DC, September 2003.

RCRA covers were constructed in 1995, and the ET covers were constructed in 1996. All of the covers are 43 ft wide by 328 ft long and were seeded with native vegetation. The purpose of the project is to use the performance data to help demonstrate equivalency and refine numerical models to more accurately predict cover system performance.[39]

The ALCD has collected data on percolation using lysimeters and soil moisture to monitor cover performance. Total precipitation (precip.) and percolation (perc.) volumes based on 5 years of data are provided in Table 25.6. The ET covers generally have less percolation than the Subtitle D cover for each year shown. More information on the ALCD cover performance can be found in Dwyer.[39]

25.10.4 EXAMPLE 4: ACAP

U.S. EPA is conducting the ACAP to evaluate the performance of alternative landfill covers. ACAP began in 1998, and cover performance is currently being evaluated at 13 sites. The sites are located in eight states from California to Ohio, and include a variety of landfill types, such as MSW, construction and demolition waste, and hazardous waste landfills. At eight sites, conventional and ET covers are being tested side by side. At the remaining five sites, only ET covers are being tested.

The alternative covers typically were constructed with local soils and native vegetation. At two facilities, however, hybrid poplar trees were used as vegetation. At 11 sites, percolation performance is being evaluated by lysimeters. At the other two sites, performance is being evaluated indirectly by monitoring leachate production. Soil moisture is also being evaluated at all 13 sites. Table 25.7 shows an example of the field data for precipitation (precip.) and percolation (perc.) volumes at three of the sites. A summary of field cover performance for all 13 sites through July 2002 is provided in Albright and Benson.[26] More information about ACAP is available on the Desert Research Institute website.[95]

TABLE 25.7
Total Percolation and Precipitation Data for ACAP

			Year 1 2000–2001		Year 2 2001–2002		Year 3 2002–2003	
Site	**Cover Design**	**Start Date**	**Precipitation (mm)**	**Percolation (mm)**	**Precipitation (mm)**	**Percolation (mm)**	**Precipitation (mm)**	**Percolation (mm)**
Altamont, CA (semiarid)	Monolithic ET	11/00	225	Negligible	300	1.5		
	Composite/compacted clay	11/00	225	Negligible	300	Negligible		
Polson, MT (semiarid)	Capillary barrier ET	11/99	300	0.05	300	0.05	250	0.45
	Composite/compacted clay	11/99	300	0.50	300	0.50	250	0.50
Omaha, NE (humid)	Capillary barrier ET (thick)	10/00	600	55	200	Negligible		
	Capillary barrier ET (thin)	10/00	600	100	200	Negligible		
	Composite/compacted clay	10/00	600	5	200	Negligible		

Source: U.S. EPA, *Evapotranspiration Landfill Cover Systems Fact Sheet*, EPA 542-F-03-015, U.S. Environmental Protection Agency, Washington, DC, September 2003.

ACRONYMS

ACAP	Alternative Cover Assessment Program
AET	Actual evapotranspiration
AFLC	Alternative Final Landfill Covers
ALCD	Alternative Landfill Cover Demonstration
DOE	Department of Energy
EPIC	Environmental Policy Integrated Climate
ET	Evapotranspiration
HELP	Hydrologic Evaluation of Landfill Performance
LAI	Leaf-area-index
NA	Not applicable
PET	Potential evapotranspiration
PRK	Deep percolation
RCRA	Resource Conservation and Recovery Act
UNSAT-H	Unsaturated Soil Water and Heat Flow
USDA	United States Department of Agriculture
U.S. DOE	United States Department of Energy
U.S. EPA	United States Environmental Protection Agency

NOMENCLATURE

ΔSW	Change in soil water (SW) storage
Error	lack of balance in the measured terms
ET	Evapotranspiration (the actual amount, not potential amount)
I	Irrigation (if applied)
L	Lateral flow
Q	Surface runoff
P	Precipitation
PRK	Deep percolation (below cover or root zone)

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26 Hazardous Waste Landfill

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CONTENTS

26.1 OVERVIEW OF REGULATIONS FOR HAZARDOUS WASTE LANDFILLS

In the United States, hazardous wastes are regulated under the Resource Conservation and Recovery Act (RCRA),[1] including the Hazardous and Solid Waste Amendments (HSWA) to RCRA.[2] Specific U.S. EPA regulations for waste containment systems at RCRA Subtitle C landfills, surface impoundments, and waste piles are published in 40 CFR 264.[3] These regulations require hazardous waste landfills to have two independent liners with a leak detection system (LDS) between them and a leachate collection and removal system (LCRS) above the primary (or top) liner. The purpose of the LDS is to allow monitoring of the primary liner (i.e., to identify whether, and to what extent, leakage is occurring through the primary liner) and to provide a mechanism for removing liquids that enter this system. A double-liner system with an LDS is a hallmark of hazardous waste landfill regulations in the United States.[4]

For hazardous waste landfills and surface impoundments, U.S. EPA and Congress have set forth performance objectives of preventing hazardous constituent migration out of a unit through the end of postclosure care (or ~30–50 years). The approach U.S. EPA has developed to meet those performance objectives is called the Liquids Management Strategy. The goal of the strategy is to minimize leachate generation through both operational practices and the final cover design, and to maximize leachate collection and removal through use of the lining system and LCRS.[5]

U.S. EPA has issued regulations and guidance primarily focusing on double liners and LCRSs.[6,7] Several *Federal Register* notices and guidance documents have been published by U.S. EPA in this area.[8–11] U.S. EPA also issued final regulations for double liners and for LDSs, including construction quality assurance (CQA) and response action plans.[12–14]

26.1.1 Double Liners and LCRSs

Figure 26.1 is a simplified schematic diagram of a hazardous waste landfill, showing the geometry and placement of double liners and LCRSs in a landfill.[15] In a double-lined landfill, there are two liners and two LCRSs. The primary LCRS is located above the top liner and the secondary LCRS is located between the two liners. In this diagram, the top liner is a geomembrane (GM) liner, also called flexible membrane liner (FML), and the bottom liner is a composite liner system consisting of an FML overlying compacted low-permeability soil (or compacted clay).

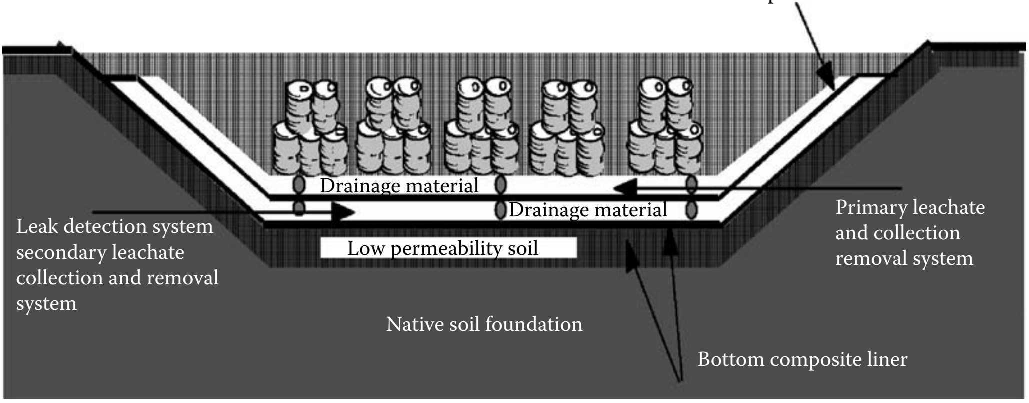


FIGURE 26.1 Schematic of a double-liner and leachate collection system for a hazardous landfill. (Adapted from U.S. EPA, *Training Module: Introduction to Land Disposal Units*, EPA530-K-05-014, U.S. Environmental Protection Agency, Washington, DC, September 2005.)

26.1.1.1 Guidance for Double Liners

The U.S. EPA guidance[6] discusses three types of liners: FMLs, compacted clay liners (CCLs), and composite liner systems (an FML overlying a compacted low-permeability soil layer). Material specifications in the guidance for FMLs and CCLs are briefly reviewed below, along with regulations regarding all three liner systems.

The minimum thickness specification for an FML top liner covered with a layer of soil is 0.75 mm; for an FML without a soil cover layer, the specification is 1.14 mm. An FML in a composite bottom liner system must be at least 0.75 mm thick. Even though these FML thicknesses meet U.S. EPA specifications, 0.75 mm is not a suitable thickness for all FML materials. In fact, most FML materials installed at landfills are in the range of 1.50–2.50 mm in thickness. Other key factors affecting the selection of FML materials include chemical compatibility with waste leachate, aging and durability characteristics, stress and strain characteristics, ease of installation, and water vapor/chemical permeation.

For compacted, low-permeability soil liners, the U.S. EPA draft guidance recommends natural soil materials, such as clays and silts. However, soils amended or blended with different additives (e.g., lime, cement, bentonite clays, and borrow clays) may also meet the current selection criteria of low hydraulic conductivity, or permeability, and sufficient thickness to prevent hazardous constituent migration out of the landfill unit. Therefore, U.S. EPA does not exclude compacted soil liners that contain these amendments. Additional factors affecting the design and construction of CCLs include plasticity index (PI), Atterburg limits, grain sizes, clay mineralogy, and attenuation properties.

26.1.1.2 Federal Regulations for Double Liners

Figure 26.2 shows cross sections of three double-liner designs that have been used to meet regulations. The double-liner design on the left side of the figure meets the minimum technological requirements (MTR) as codified in 1985.[8] The center and right-hand designs meet the MTR as proposed by U.S. EPA.[9,12] The older regulations for MTR called for a double-liner system consisting of an FML top liner and a compacted clay bottom liner that is 3 ft (90 cm) thick with a maximum saturated hydraulic conductivity of no more than 1×10^{-7} (cm/s). The proposed rule on double liners[9,12] gave two design options for MTR landfills: one similar to the older MTR design (differing

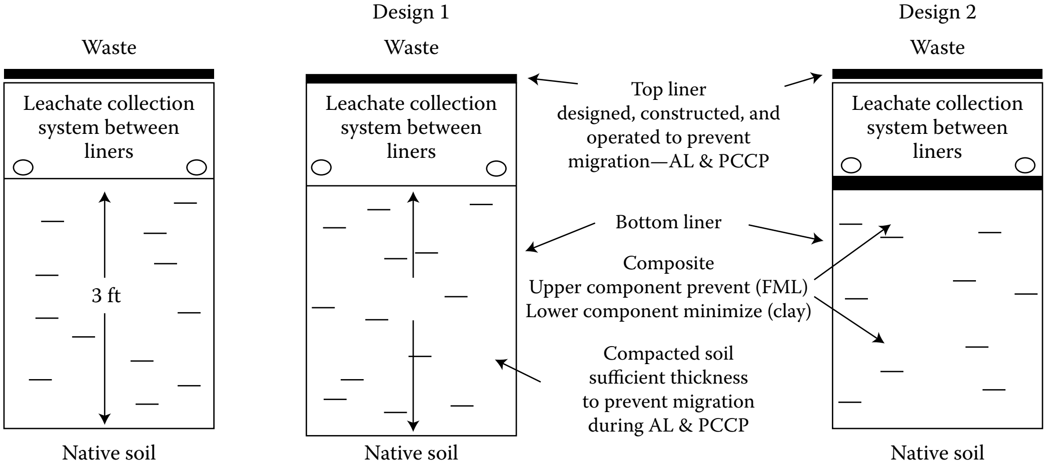


FIGURE 26.2 Double-liner designs. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

only in that the CCL must be sufficiently thick to prevent hazardous constituent migration), and the other calling for an FML top liner and a composite bottom liner.[3]

U.S. EPA's rationale for the requirement of composite bottom liner option in the final double-liner rule is based on the relative permeability of the two liner systems.[13] The results of numerical simulations performed by U.S. EPA,[10] which compared the performance of a composite bottom liner to that of a compacted soil bottom liner under various top liner leakage scenarios, showed that liquids passing through defects in the top FML enter the secondary LCRS above the bottom liners. The hydraulic conductivities of bottom liner systems greatly affect the amount of liquids detected, collected, and removed by the secondary LCRS.

U.S. EPA compared the compacted soil and composite bottom liner systems in terms of theoretical leak detection sensitivity, or the minimal leak rate that can be detected, collected, and effectively removed in the secondary LCRS. The theoretical leak detection sensitivity is <1 gallon/acre/day for a composite liner having an intact FML component. This leak detection sensitivity value reflects water vapor transmission rates for FMLs with no defects. In contrast, with well-constructed clay bottom liners (10^{-7} cm/s permeability), liquids entering the secondary LCRS may go undetected and migrate into the bottom liner until the leak rates approach 100 gallons/acre/day. With a slightly more permeable compacted clay bottom liner with 10^{-6} cm/s permeability, the secondary LCRS may not detect, collect, or remove the liquid flowing from a leak in the top liner until leak rates are very serious (on the order of 1000 gallons/acre/day J).

Figure 26.3 compares theoretical leachate collection efficiencies for landfills having compacted soil bottom liners with those having composite bottom liners. Leachate collection efficiency

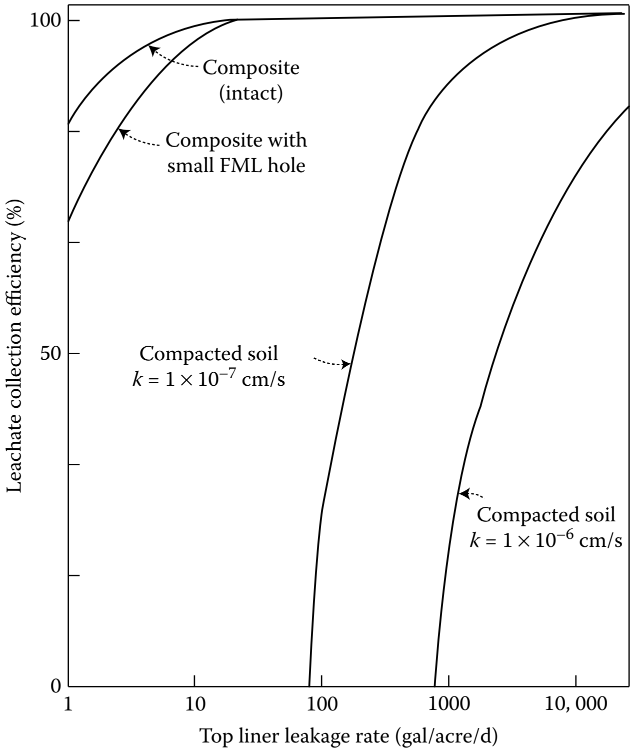


FIGURE 26.3 Comparison of leachate collection efficiencies for compacted soil and composite bottom liners. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

is the amount of liquid collected and removed in the secondary leachate collection system divided by the total amount entering into the secondary LCRS through a breach in the top liner. For low leakage rates, the leachate collection efficiency of a landfill with a composite bottom liner system, even a composite system with tears or small defects in the FML, is very high (above 95% for leak rates in the range of 1–10 gallons/acre/day). In comparison, landfills with compacted clay bottom liners have 0% leachate collection efficiency for low leak rates and only 50% efficiency for leak rates of ~100 gallons/acre/day. These results demonstrate that leachate collection efficiency of the secondary LCRS improves significantly simply by installing an FML over the compacted clay bottom liner.

U.S. EPA also determined the total quantity of liquids entering the two bottom liner systems over a 10-year time span with a constant top liner leak rate of 50 gallons/acre/day. A composite bottom liner with an intact FML accumulates around 70 gal/acre, primarily through water vapor transmission. Even with a 10-ft tear, which would constitute a worst-case leakage scenario, a composite liner system will allow 47,000–50,000 gallons/acre to enter that bottom liner over a 10-year time span. Compacted soil liners meeting the 10^{-7} cm/s permeability standard will allow significant quantities of liquids into the bottom liner, and potentially out of the unit over time, on the order of hundreds of thousands of gal/acre.[5]

The numerical results indicate superior performance of composite liner systems over CCLs in preventing hazardous constituent migration out of the unit and maximizing leachate collection and removal. Consequently, owners of new units subject to the double-liner requirement of HSWA are now installing composite bottom liners or double composite liner systems.[3]

26.1.1.3 Guidance for LCRSs

Double-lined landfills have both primary and secondary LCRSs. The design of the secondary LCRS in the landfill receives particular attention in U.S. EPA's leak detection requirements.[3]

The components of an LCRS include the drainage layer, filters, cushions, sumps, and pipes and appurtenances. Of these components, the drainage layer receives the most attention in the guidance and regulations. The drainage layer can consist of either granular or synthetic material. If granular, it must be either clean sand or gravel with very little fines content in order to facilitate the rapid collection and removal of the liquids that accumulate above the top liner and between the two liners. This minimizes hydraulic head on both liner systems.

According to the guidance, the main selection criteria for granular drainage materials are high hydraulic conductivity and low capillary tension, or suction forces. For typical drainage layer materials, permeabilities range between 10^{-3} and 1 cm/s. A silty sand drainage layer with significant fines content will have a lower permeability (i.e., 10^{-3} cm/s) and significant capillary tension. At the upper end of the scale, drainage layers consisting of clean gravel can achieve permeability on the order of 1–100 cm/s. In this upper range of permeability, capillary tension is negligible. Therefore clean sands and gravels are preferred over silty sands.

There is a high correlation between permeability and capillary rise (the elevation height of liquids retained by granular particles within the drainage layer by surface tension under unsaturated conditions). At 10^{-3} cm/s, there is a significant capillary rise (~1 m) whereas at the upper end of the permeability scale (1 cm/s), the capillary rise is only on the order of 3 cm. Reduction in fines content therefore, significantly reduces capillary rise while increasing the hydraulic conductivity. Increasing hydraulic conductivity, in turn, results in rapid collection and removal of liquids.

Synthetic drainage materials have been introduced to the waste management industry. Unlike granular materials, synthetic drainage materials come in various forms and thicknesses[5]:

- Nets (4–7 mm)
- Needle-punched nonwoven geotextiles (2–5 mm)

- Mats (10–20 mm)
- Corrugated, waffled, or alveolate plates (10–20 mm).

Construction materials also vary. The most common synthetic materials are polypropylene (PP), polyester (PET), or polyethylene (PE). Because synthetic drainage layers are much thinner (<1 in.) than granular drainage layers (1 ft) and have similar design liquids capacity, their use in a landfill results in increased space for waste storage and disposal. This advantage translates into increased revenues for the owner/operator of a landfill.

The main selection criteria for synthetic drainage materials are high hydraulic transmissivities, or in-plane flow rates, and chemical compatibility with the waste leachate. Discussion of the chemical compatibility of synthetic liners and drainage layers is given in a later section.

Hydraulic transmissivity refers to the value of the thickness times the hydraulic conductivity for that drainage layer. Over the lifetime of a facility, the actual hydraulic transmissivities of synthetic drainage layers are affected by two key factors: (a) overburden stress and (b) boundary conditions. The first factor pertains to the increasing loads (i.e., wastes, operating equipment, and final cover) applied to the liner that an LCRS experiences over the lifetime of the facility. The second factor pertains to the stress–strain characteristics of adjacent layers (i.e., FMLs, filters, cushions, and compacted clay). Over time and with increasing stress, adjacent layers will intrude, or extrude, into the drainage layer and result in clogging, or reduced transmissivity, of the LCRS.

New regulations applicable to LCRSs in double-lined landfills[3,9] differ in two principal ways from older standards for LCRSs in single-lined landfills and waste piles. First, LCRSs must be designed to operate through the end of the postclosure care period (30–50 years), and not simply through the active life of the unit. Secondly, in a double-lined landfill with primary and secondary LCRSs, the primary LCRS need only cover the bottom of the unit (i.e., side wall coverage is optional). The secondary LCRS, however, must cover both the bottom and the side walls.

The new regulations also require that LCRSs be chemically resistant to waste and leachate, have sufficient strength and thickness to meet design criteria, and be able to function without clogging.

26.1.2 LEAK DETECTION SYSTEMS

Described in this section are the LDS requirements that apply to the secondary LCRS between the two liners in a landfill. These requirements focus on the drainage layer component of the LCRS. Figure 26.4 illustrates the location of an LDS in a double-lined landfill that meets these requirements.

26.1.2.1 Design Criteria

The minimum design standards for granular drainage layer materials require a minimum thickness of 1 ft and a minimum hydraulic conductivity of 1 cm/s. To meet this minimum hydraulic conductivity standard for granular drainage materials, the secondary LCRS, or LDS, must be constructed of clean gravels.

For synthetic drainage materials, U.S. EPA has required a minimum hydraulic transmissivity of 5×10^{-4} m^2/s. The hydraulic transmissivity of a drainage material refers to the thickness of the drainage layer multiplied by the hydraulic conductivity. The transmissivity of granular drainage layers (1 ft × 1 cm/s) is within an order of magnitude of the 5×10^{-4} m^2/s standard for synthetic drainage layers. The hydraulic transmissivity value for synthetic drainage materials was developed to ensure that the design performance for a geonet, geocomposite, or other synthetic drainage layer is comparable with that for a 1-ft thick granular drainage layer.[5]

The standards for LDS also specify a minimum bottom slope of 2% and require the installation of a leak detection sump of appropriate size to allow the daily monitoring of liquid levels or inflow rates in the LDS. Specifically, the sump should be designed to detect a top liner leakage rate in the range of action leakage rate (ALR) specified in the leak detection rule.

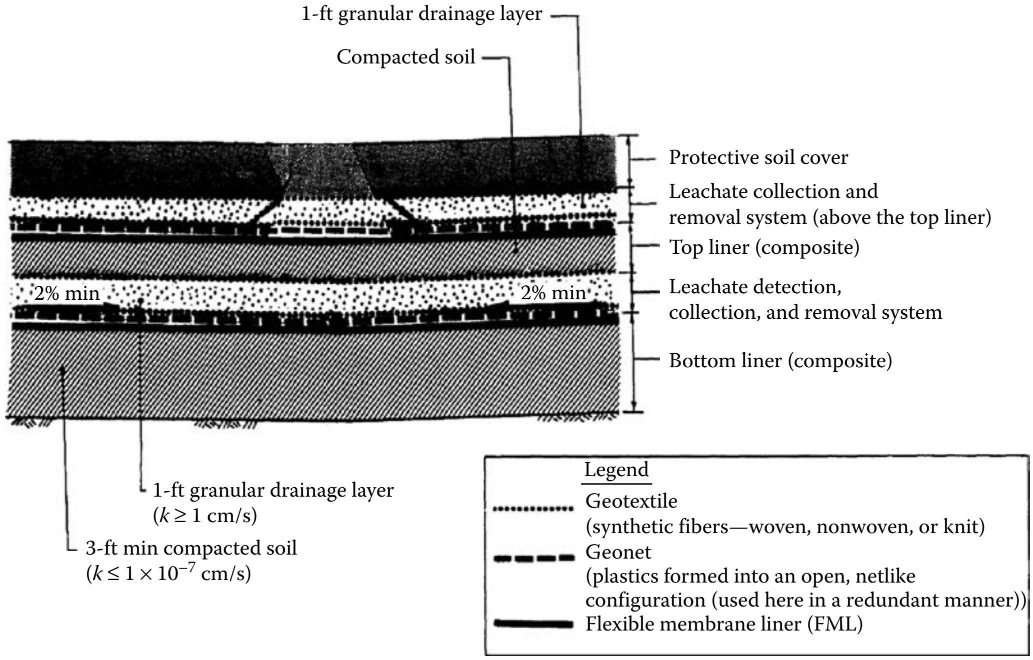


FIGURE 26.4 Location of an LDS in a double-lined landfill. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.1.2.2 Design Performance Requirements

The leak detection rule also establishes design performance standards for the LDS. Design performance standards mean that the facility design must include materials and systems that can meet the above-mentioned design criteria. If the liners and LCRS materials meet the design criteria, the design performance standards will be met. Compliance with design performance standards can be demonstrated through numerical calculations rather than through field demonstrations.

The leak detection rule outlines two design performance standards:

1. A leak detection sensitivity of 1 gallon/acre/day.
2. A leak detection time of 24 h.

The leak detection sensitivity refers to the minimum top liner leak rate that can theoretically be detected, collected, and removed by the LDS. The leak detection time is the minimum time needed for liquids passing through the top liner to be detected, collected, and removed in the nearest downgradient collection pipe. In the case of a composite top liner, the leak detection time refers to the period starting at the point when liquids have passed through the compacted soil component and ending at the point when they are collected in the collection pipe.

U.S. EPA bases its 1 gallon/acre/day leak detection sensitivity on the results of calculations that show that, theoretically, an LDS overlying a composite bottom liner with an intact FML component can detect, collect, and remove liquids from a top liner leak rate <1 gallon/acre/day. This performance standard, therefore, can be met with designs that include a composite bottom liner. Based on numerical studies, one cannot meet the leak detection sensitivity with a compacted soil bottom liner, even one with a hydraulic conductivity of 10^{-7} cm/s. Therefore, the emphasis of this standard is on selecting an appropriate bottom liner system.

Meeting the 24-h leak detection time, however, is dependent on the design of the LDS. A drainage layer meeting the design criteria, together with adequate drain spacing, can theoretically meet the 24-h detection time standard. The emphasis of the standards, therefore, is on designing and selecting appropriate materials for the secondary LCRS.

Compliance with U.S. EPA's design performance standards can be demonstrated through one-dimensional, steady-state flow calculations, instead of field tests. For detection sensitivity, the calculation of flow rates should assume uniform top liner leakage. For detection time, factors such as drain spacing, drainage media, bottom slope, and top and bottom liners should all be considered, and the worst-case leakage scenario calculated.

26.1.2.3 Applicability of LDS Requirements

Owners and operators of landfills, surface impoundments, and waste piles will be required to install double liners and LDSs.

26.1.3 CLOSURE AND FINAL COVER

Basically, U.S. EPA regulations and guidance[16] require that the final cover be no more permeable than the liner system. In addition, the cover must be designed to function with minimum maintenance, and to accommodate settlement and subsidence of the underlying waste. The regulations do not specify any design criteria for liner materials to meet the performance standard for permeability.

The guidance[16] recommends a three-layer cap design consisting of a vegetative top cover, a middle drainage layer, and a composite liner system composed of an FML over compacted low-permeability soil. The final cover is to be placed over each cell as it is completed.

Since the regulations do not specify the designs of materials for the final cover, or cap, design engineers can usually use their own judgment in designing the final cover and selecting materials. For example, if the lining system contains a high-density polyethylene (HDPE) membrane, the final cover does not necessarily need to have an HDPE membrane. The amount of flexibility in selecting FML materials for the final cover varies from region to region, based on how strictly the statutory phrase "no more permeable than" is interpreted. Nevertheless, from a design perspective, the selection of FML materials in the final cover should emphasize the physical rather than the chemical properties of the liner material, since the main objective is to minimize precipitation infiltration. Precipitation infiltration is affected mainly by the number of holes or tears in the liner, not by the water vapor transmission rates.

For the vegetative cover, U.S. EPA's guidance recommends a minimum thickness of 2 ft and final upper slopes of between 3% and 5%, after taking into account the total settlement and subsidence of the waste.[5] The middle drainage layer should have a minimum thickness of 1 ft (30 cm) and a minimum hydraulic conductivity of 10^{-3} cm/s. U.S. EPA's revised guidance upgrades that standard by an order of magnitude to 10^{-2} cm/s to reduce capillary rise and hydraulic head above the composite liner system. For the composite liner system at the bottom of the cap, it is critical that both the FML and the compacted soil components be below the average depth of frost penetration. The FML should also have a minimum thickness of 0.50 mm, but 0.0.50 mm will not be a sufficient thickness for all FML materials. The soil component under the FML must have a minimum thickness of 2 ft (60 cm) and a maximum saturated hydraulic conductivity of 10^{-7} cm/s. The final upper slope of the composite liner system must be no less than 2% after settlement. Table 26.1 summarizes specifications for each part of the final cover.

26.1.4 CONSTRUCTION QUALITY ASSURANCE

The final component of the regulatory/guidance summary discusses the construction of a hazardous waste landfill. The following section summarizes U.S. EPA's CQA program.[13,14]

TABLE 26.1
Cover Design

- Vegetative cover
  - Thickness ≥2 ft
  - Minimal erosion and maintenance (e.g., fertilization and irrigation)
  - Vegetative root growth not to extend below 2 ft
  - Final top slope between 3% and 5% after settlement or subsidence. Slopes greater than 5% not to exceed 2.0 tons/acre erosion (USDA Universal Soil Loss Equation)
  - Surface drainage system capable of conducting runoff across the cap without rills and gullies
- Drainage layer design
  - Thickness ≥1 ft
  - Saturated hydraulic conductivity $\geq 10^{-3}$ cm/s
  - Bottom slope ≥2% (after settlement/subsidence)
  - Overlain by a graded granular or synthetic filter to prevent clogging
  - Allow lateral flow and discharge of liquids
- Low-permeability liner design
  - FML component
    - Thickness ≥20 mil
    - Final upper slope ≥2% (after settlement)
    - Located wholly below the average depth of frost penetration in the area
  - Soil component
    - Thickness ≥2 ft
    - Saturated hydraulic conductivity $\leq 1 \times 10^{-7}$ cm/s
    - Installed in 6 in. lifts

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

26.1.4.1 U.S. EPA's Regulations

The regulations guidance require the owner/operator to develop a CQA plan that will be implemented by contracted, third-party engineers. The owner/operator also must submit a CQA report containing the following:

1. Summary of all observations, daily inspection/photo/video logs.
2. Problem identification/corrective measures report.
3. Design engineer's acceptance reports (for errors and inconsistencies).
4. Deviations from design and material specifications (with justifying documentation).
5. Summary of CQA activities for each landfill component.

This report must be signed by a registered professional engineer or the equivalent, the CQA officer, the design engineer, and the owner/operator to ensure that all parties are satisfied with the design and construction of the landfill. U.S. EPA will review selected CQA reports.

The CQA plan covers all components of landfill construction, including foundations, liners, dikes, LCRSs, and the final cover. According to the rule,[13] U.S. EPA may also require field permeability testing of soils on a test fill constructed prior to construction of the landfill to verify that the final soil liner will meet the permeability standards of 10^{-7} cm/s. This requirement, however, will not preclude the use of laboratory permeability tests and other tests (correlated to the field permeability tests) to verify that the soil liner will, as installed, have a permeability of 10^{-7} cm/s.

26.1.5 Summary of Minimum Technology Requirements

U.S. EPA's minimum technology guidance (MTG) and regulations for new hazardous waste land disposal facilities emphasize the importance of proper design and construction in the performance of the facility. The trend in the regulatory programs is to develop standards and recommend designs based on the current state-of-the-art technology. Innovations in technology are, therefore, welcomed by U.S. EPA and are taken into account when developing these regulations and guidance.

Regulatory requirements for hazardous waste landfill double-liner systems are given in 40 CFR 264.[3] The minimum liner system design standard generally considered to meet these requirements includes, from top to bottom[4]:

1. LCRS that limits the head of leachate on the primary liner to 0.3 m or less.
2. GM primary liner.
3. A 0.3-m-thick granular LDS drainage layer with a minimum hydraulic conductivity of 1×10^{-2} cm/s or a geosynthetic LDS drainage layer with a minimum hydraulic transmissivity of 3×10^{-5} m^2/s.
4. A GM upper component of a composite secondary liner.
5. A 0.9-m-thick CCL lower component of the composite secondary liner, with the CCL having a maximum hydraulic conductivity of 1×10^{-7} cm/s.

Final cover systems are another important component of waste containment systems used at landfills. While liner systems are installed beneath the waste, final cover (or closure) systems are installed over the completed solid waste mass. For hazardous waste landfills, 40 CFR 264 requires that the landfill be closed with a final cover system that meets certain performance criteria, most notably, that they have a permeability less than or equal to the permeability of any bottom liner system or natural subsoils present. U.S. EPA guidance documents[5,17] recommend that final cover systems for hazardous waste landfills consist of at least the following, from top to bottom:

1. A top layer containing two components: (a) either a vegetated or an armored surface layer and (b) a 0.6-m thick protection layer, comprising topsoil and/or fill soil, as appropriate.
2. A 0.3-m-thick granular drainage layer with a minimum hydraulic conductivity of 1×10^{-2} cm/s.
3. A composite hydraulic barrier, consisting of (a) a 0.5-mm-thick GM upper component and (b) a 0.6-m-thick CCL lower component, with the CCL having a minimum hydraulic conductivity of 1×10^{-7} cm/s.

26.2 LINER DESIGN: CLAY LINERS

This section discusses soil liners and their use in hazardous waste landfills. The section focuses primarily on hydraulic conductivity testing, both in the laboratory and in the field. It also covers materials used to construct soil liners, mechanisms of contaminant transport through soil liners, and the effects of chemicals and waste leachates on compacted soil liners.

26.2.1 Materials

26.2.1.1 Clay

Clay is the most important component of soil liners because the clay fraction of the soil ensures low hydraulic conductivity. In the United States, however, there is some ambiguity in defining the term "clay" because two soil classification systems are widely used. One system, published by the American Society for Testing and Materials (ASTM), is used predominantly by civil engineers.[18] The other, the U.S. Department of Agriculture's (USDA's) soil classification system, is used primarily by soil scientists, agronomists, and soil physicists.[19]

TABLE 26.2
ASTM and USDA Soil Classification by Grain Size

	Size (mm)	
	ASTM	**USDA**
Gravel	4.74 (No. 4 sieve)	2
Sand	0.075 (No. 200 sieve)	0.050
Silt	None (plasticity criterion)	0.002
Clay		

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

The distinction between various particle sizes differs between ASTM and USDA soil classification systems (see Table 26.2). In the ASTM system, for example, sand-sized particles are defined as those able to pass a No. 4 sieve but not able to pass a No. 200 sieve, fixing a grain size of between 0.075 and 4.74 mm. The USDA soil classification system specifies a grain size for sand between 0.050 and 2 mm.

The USDA classification system is based entirely on grain size and uses a three-part diagram to classify all soils (Figure 26.5). The ASTM system, however, does not have a grain size

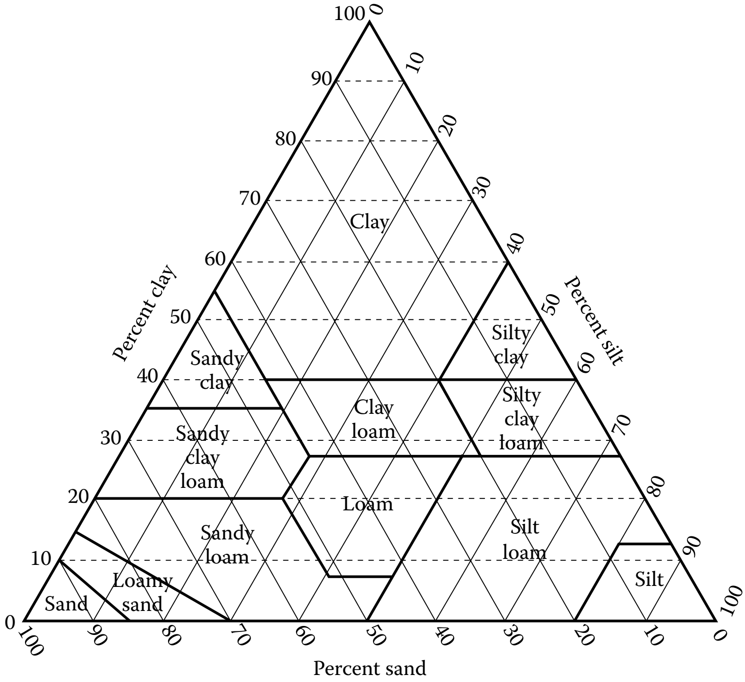


FIGURE 26.5 USDA soil classification. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

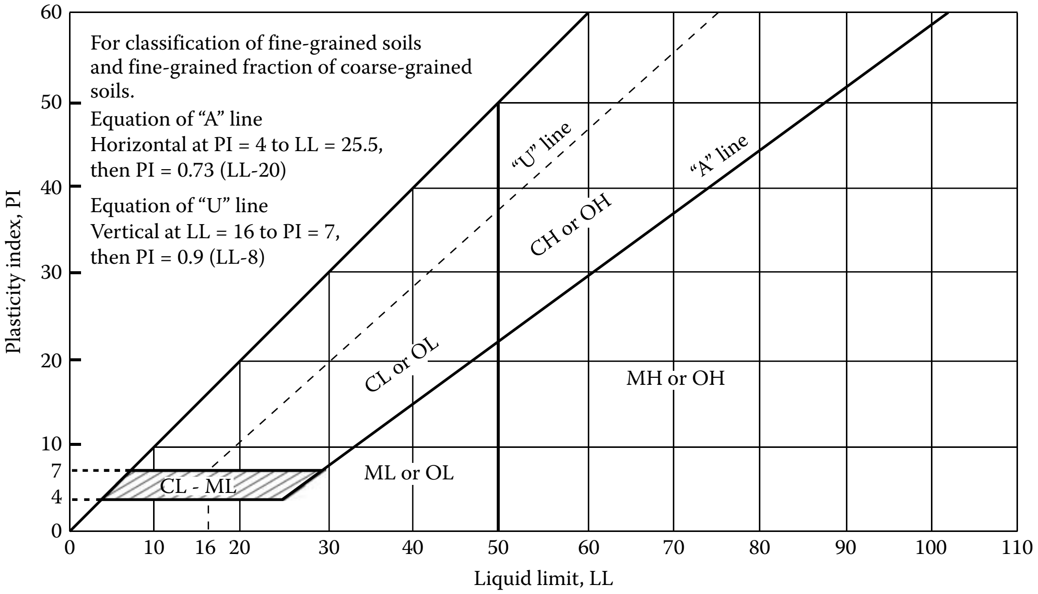


FIGURE 26.6 ASTM plasticity determination for fine-grained soils. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

criterion for classifications of clay; clay is distinguished from silt entirely upon plasticity criteria. The ASTM classification system uses a plasticity diagram and a sloping line, called the "A" line (see Figure 26.6), to distinguish between silt and clay. Soils whose data points plotted above the A line on this classification chart are, by definition, clay soils with prefixes C in Unified Soil Classification System symbol. Soils whose data points plotted below the A line are classified as silts.

U.S. EPA requires that soil liners be built so that the hydraulic conductivity is equal to or less than 1×10^{-7} cm/s. To meet this requirement, certain characteristics of soil materials should be met. First, the soil should have at least 20% fines (fine silt and clay-sized particles). Some soils with less than 20% fines will have hydraulic conductivities below 10^{-7} cm/s, but at such low fines content, the required hydraulic conductivity value is much harder to meet.[5]

Second, PI should be >10%. Soils with very high PI, >30–40%, are sticky and, therefore, difficult to work with in the field. When high PI soils are dry, they form hard clumps that are difficult to break down during compaction. On the Gulf Coast of Texas, for example, clay soils are predominantly highly plastic clays and require additional processing during construction. Figure 26.7 represents a collection of data from the University of Texas laboratory in Austin[5] showing hydraulic conductivity as a function of PI. Each data point represents a separate soil compacted in the laboratory with standard Proctor compaction procedures and at water content about 0–2% wet of optimum. Hydraulic conductivities are consistently below 10^{-7} cm/s for soils with PIs >10%.

Third, coarse fragments should be screened to no more than about 10% gravel-size particles. Soils with a greater percentage of coarse fragments can contain zones of gravel that have high hydraulic conductivities.

Finally, the material should contain no soil particles or chunks of rock larger than 1–2 in. in diameter. If rock diameter becomes a significant percentage of the thickness of a layer of soil, rocks may form a permeable "window" through a layer. As long as rock size is small compared to the thickness of the soil layer, the rock will be surrounded by the other materials in the soil.

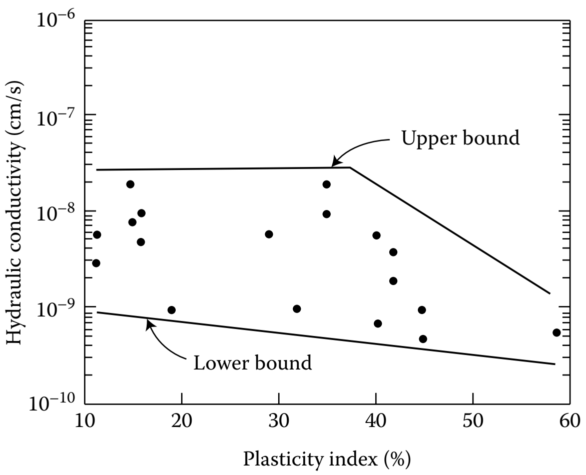


FIGURE 26.7 Hydraulic conductivity as a function of PI for soils in Austin Laboratory Tests. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.2.1.2 Blended Soils

Due to a lack of naturally occurring soils at a site, it is sometimes necessary to blend imported clay minerals with on-site soils to achieve a suitable blended material. The most common blend is a combination of on-site sandy materials and imported sodium bentonite.

Figure 26.8 shows the influence of sodium bentonite on the hydraulic conductivity of the silt/sand soil. The addition of only 4% or 5% sodium bentonite to this particular soil drops the hydraulic conductivity from 10^{-4} to 10^{-7} cm/s, a rather dramatic reduction.

Calcium bentonite, as though more permeable than sodium bentonite, has also been used for soil blends. Approximately twice as much calcium bentonite typically is needed; however, to achieve a hydraulic conductivity comparable with that of sodium bentonite. One problem with using sodium bentonite, however, is its vulnerability to attack by chemicals and waste leachates, a problem that will be discussed later.

On-site sandy soils can also be blended with other clay soils available in the area, but natural clay soil is likely to form chunks that are difficult to break down into small pieces. Bentonites, obtained in dry, powdered forms, are much easier to blend with on-site sandy soils than are wet, sticky clods of clay. Materials other than bentonite can be used, such as atapulgite, a clay mineral that is insensitive to attack by waste. Soils can also be amended with lime, cement, or other additives.

26.2.2 CLAY LINERS VERSUS COMPOSITE LINERS

Composite liner systems should outperform either FMLs or clay liners alone. Leachate lying on top of a clay liner will percolate down through the liner at a rate controlled by the hydraulic conductivity of the liner, the head of the leachate on top of the liner, and the liner's total area. With the addition of an FML placed directly on top of the clay and sealed up against its upper surface, leachate moving down through a hole or defect in the FML does not spread out between the FML and the clay liner. The composite liner system allows much less leakage than a clay liner acting alone, because the area of flow through the clay liner is much smaller.

The FML must be placed on top of the clay such that liquid does not spread along the interface between the FML and the clay and move downward through the entire area of the clay liner. An

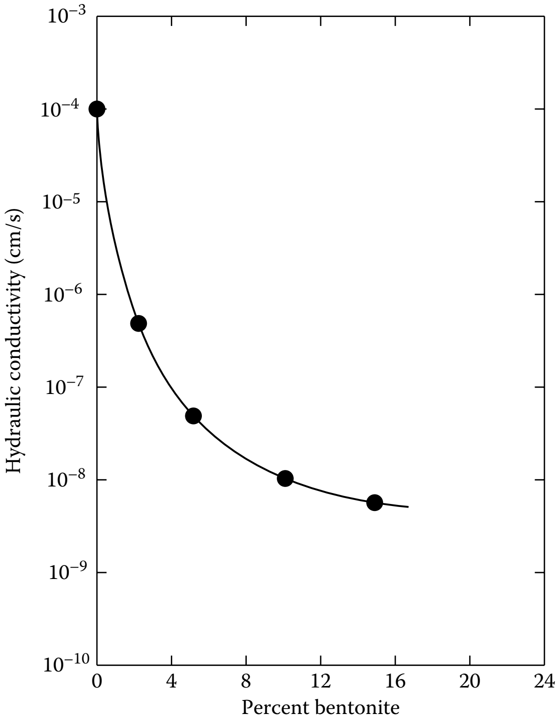


FIGURE 26.8 Influence of sodium bentonite on hydraulic conductivity. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

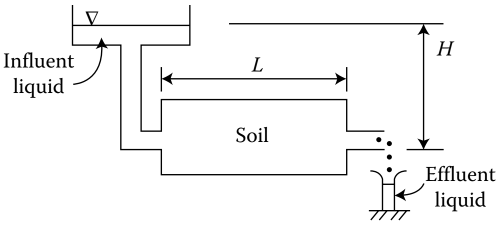
FML placed on a bed of sand, geotextiles, or other highly permeable materials would allow liquid to move through the defect in the FML, spread over the whole area of the clay liner, and percolate down as if the FML was not there. With clay liner soils that contain some rock, it is sometimes proposed that a woven geotextile be placed on top of the soil liner under the FML to prevent the puncture of rocks through the FML. A woven geotextile between the FML and the clay, however, creates a highly transmissive zone between the FML and the clay. The surface of the soil liner instead should be compacted and the stones removed so that the FML can be placed directly on top of the clay.

26.2.3 DARCY'S LAW, DISPERSION, AND DIFFUSION

Figure 26.9 illustrates Darcy's law, the basic equation used to describe the flow of fluids through porous materials. In Darcy's law, the coefficient k, hydraulic conductivity, is often called the coefficient of permeability by civil engineers.

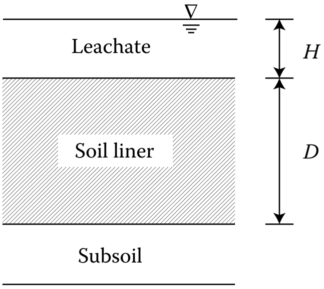
Darcy's law applied to a soil liner shows the rate of flow of liquid q directly proportional to the hydraulic conductivity of the soil and the hydraulic gradient, a measure of the driving power of the fluid forcing itself through the soil and the cross-sectional area A of the liner (see Figure 26.9).

If hydraulic conductivity is 10^{-7} cm/s, the amount of leakage for a year, per acre, is 50,000 gallons (assuming a hydraulic gradient of 1.5). If the conductivity is 10 times that value (1×10^{-6} cm/s), the leakage is 10 times greater, or 500,000 gal. Cutting the hydraulic conductivity to 10^{-8} cm/s reduces the quantity of leakage 10-fold, to 5000 gallons/acre/yr. These data demonstrate how essential low hydraulic conductivity is to minimizing the quantity of liquid passing through the soil liner.



$$Q = k\frac{H}{L}A$$

Q = Rate of flow
k = Hydraulic conductivity
H = Head loss
L = Length of flow
A = Total area



$$Q = kiA$$

i = Hydraulic gradient

$$= \frac{H + D}{D}$$

FIGURE 26.9 Application of Darcy's law. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.2.3.1 Contaminants

The transport of contaminants through the soil liner occurs by either of two mechanisms: advective transport, in which dissolved contaminants are carried by flowing water, and molecular diffusion of the waste through the soil liner. Darcy's law can be used to estimate rates of flow via advective transport by calculating the seepage velocity of the flowing water. Seepage velocity is the hydraulic conductivity times the hydraulic gradient, divided by the effective porosity of the soil. The effective porosity is defined as the volume of the pore space that is effectively conducting the flow, divided by the total volume of the soil sample (Figure 26.10).

If the liquid uniformly passes through all the pores in the soil, then the effective and total porosities are equal. However, if the flow takes place in only a small percentage of the total pore space, for example, through fractures or macropores, the effective porosity will be much lower than the total porosity. Judging the effective porosity is one of the problems in estimating seepage velocities.

If effective porosity and other parameters are known, the time of travel (TOT) for a molecule of waste transported by flowing water through the soil liner can be calculated. TOT equals the length of the particular flow path times the effective porosity, divided by the hydraulic conductivity times the hydraulic gradient (Figure 26.10).

It is possible to confirm these calculations and measure some of the parameters needed to make them by performing laboratory permeability experiments. In these experiments, clean soil is placed

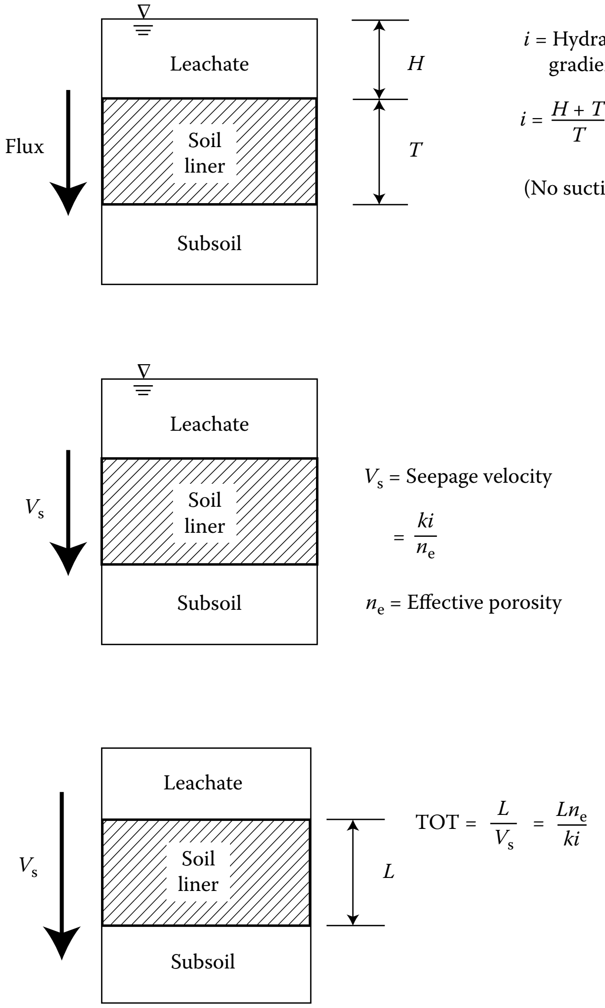


FIGURE 26.10 Advective transport. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

into columns in the laboratory, and the leachate or some other waste liquid is loaded on top of each soil column, forcing the liquid through the column over a period of time, while keeping the concentration of the influent liquid constant. The concentration of one or more chemicals in the effluent liquid is measured over time.

A plot called a breakthrough curve shows the effluent liquid concentration c divided by the influent liquid concentration c_0 as a function of pore volumes of flow (see Figure 26.11). One pore volume of flow is equal to the volume of the void space in the soil. The effective porosity of the soil is determined by measuring a breakthrough curve.

It can be expected that as the leachate invades the soil, none of the waste chemical will appear in the effluent liquid at first, only remnant soil and water. Then, at some point, the invading leachate will make its way downstream through the soil column, and come out in more or less full strength. An instantaneous breakthrough of the waste liquid never occurs, however. The breakthrough is always gradual because the invading leachate mixes with the remnant soil water through a process called mechanical dispersion.

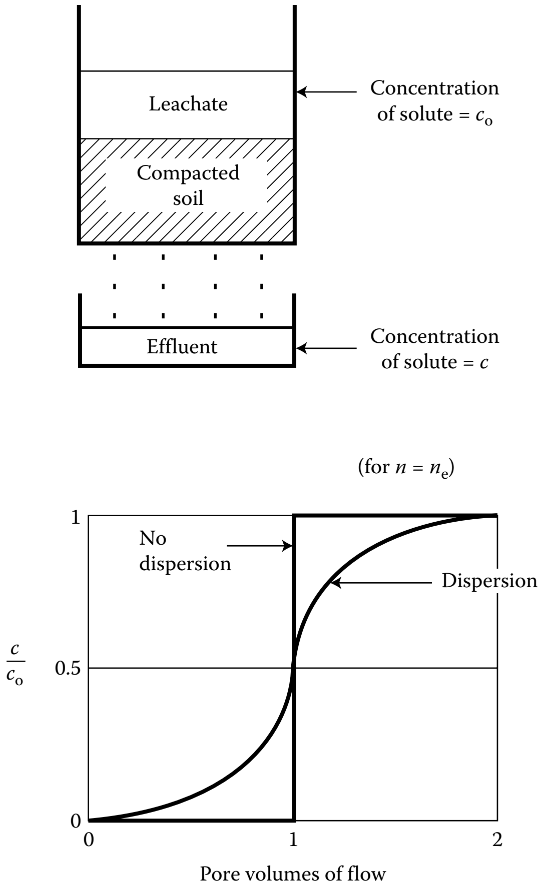


FIGURE 26.11 Effective porosities. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

Many of the waste constituents in the leachate are attenuated or retarded by the soil. For example, lead migrates very slowly through soil, whereas chloride and bromide ions migrate very quickly. With no retardation or attenuation, breakthroughs would occur at a c/c_o of 0.5–1 pore volume of flow and below. With effective and total porosities being equal, a much delayed breakthrough of chemicals that have been absorbed or attenuated by the soil could be expected.

The best way to determine effective porosity is to perform a test using a "tracer" ion that will not be absorbed significantly by the soil, such as chloride or bromide. If the breakthrough occurs in one pore volume of flow, the effective and total porosity is equal. If, instead, the breakthrough occurs at half a pore volume of flow, then the effective porosity is half the total porosity.

26.2.3.2 Molecular Diffusion

Chemicals can pass through soil liners by molecular diffusion as well as by advective transport. One can study the molecular diffusion of chemicals in the soil by compacting soil at the bottom of an impermeable beaker and ponding waste liquid or leachate on top of the soil. At the start of the experiment, the concentration c is equal to c_o in the waste liquid. The soil is clean. Even though no water flows into the soil by advection, chemicals move into the soil by the process of molecular diffusion. Eventually, the concentration of the waste liquid and the soil will be one and the same (see Figure 26.12).

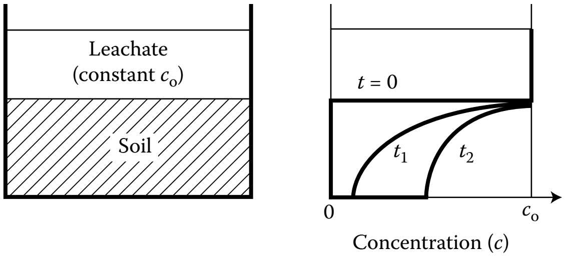


FIGURE 26.12 Molecular diffusion. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

Calculations show that after 10–30 years, molecular diffusion begins to transport the first molecules of waste 3 ft downward through a compacted soil liner. Accordingly, even with a perfectly impermeable liner with 0 hydraulic conductivity, in 1–3 decades contaminants will begin to pass through the soil liner due to molecular diffusion.

The rate of diffusion is sensitive to a number of parameters. For conservative ions that are not attenuated, the transfer time is 1–3 decades. For ions that are attenuated, transfer time is much longer. The mass rate of transport by molecular diffusion, however, is so slow that even though chemicals begin to show up in 1–3 decades, the total amount released per unit of area is small.

FMLs permit the release of organics and vapors via molecular diffusion by almost the same process. Transport times for organic chemicals through FMLs typically range from a few hours to a few days.

26.2.4 LABORATORY TESTS FOR HYDRAULIC CONDUCTIVITY

The hydraulic conductivity[20] of a soil liner is the key design parameter. The important variables in hydraulic conductivity testing in the laboratory are[5]

1. Representativeness of the sample
2. Degree of water saturation
3. Stress conditions
4. Confinement conditions
5. Testing details.

26.2.4.1 Representativeness of Samples: Case Histories

Representativeness of the soil sample being tested is the most crucial factor. Two case histories illustrate the importance and the difficulty of obtaining representative samples.

26.2.4.1.1 Klingerstown, PA

A test pad constructed under U.S. EPA sponsorship in Klingerstown, PA, consisted of a pad of clay soil 30 ft wide, 75 ft long, and 1 ft thick. The clay liner was built in three lifts, or layers, each lift being 4 in. thick. The liner was built up on a concrete pad so that researchers could crawl under and collect and then measure the liquid coming out of the bottom. A shelter was built over the test pad and about 1 ft of water ponded over the surface.

The investigators divided the collection units into a number of subunits, each subunit measuring 3 ft by 3 ft. A total of 250 different collection units underneath the soil liner were monitored independently to determine the rate of flow. The objective was to correlate the variability of the hydraulic conductivity of the liner with the molding water content of the soil and with the dry density of the compacted soil.

The investigators also installed 60 1-ft diameter rings in the surface of the liner, so that they could measure independently 60 different infiltration rates on the surface of the liner. Each of the 3-ft^2 blocks was assigned an average hydraulic conductivity based on many months of testing and observation. The conductivity for the rest of the liner varies between 10^{-6} and 10^{-8} cm/s, a 100-fold variation of hydraulic conductivity.

For a laboratory test on this soil, the test specimen would need to measure about 3 in. in diameter and 3 in. in height. Finding a 3-in. diameter sample representative of this large mass of soil presents a challenge, since small samples from larger quantities of material inevitably vary in hydraulic conductivity.

The experiments resulted in two interesting sidelights. First, the average of all the hydraulic conductivities was $2\text{–}3 \times 10^{-7}$ cm/s. Dye was poured into the water inside some of the 1-ft diameter rings installed on the surface of the liner to determine if the dye came out directly beneath the rings or off to the side. In some cases it came out directly beneath the ring and in some it wandered off to the side. It took only a few hours, however, for the dye to pass through the soil liner, even with an average conductivity only slightly greater than 1×10^{-7} cm/s. A few preferential flow paths connected to some of the rings allowed very rapid transit of the dye through the soil liner.

The second interesting sidelight was the conclusion that no relationship existed between *in situ* hydraulic conductivity and either molding water content of the soil or the dry density of the compacted soil.

The soil used in the experiment was a low plasticity sandy material with a PI of about 11%. The variations in hydraulic conductivity probably reflected zones of material that contained more sand in some places and more clay in others. Tests have been performed on a couple of liners in the field where liquid flowing into the soil liners has been dyed and traced by cutting a cross section or trench through the liner. The result seems to indicate that dyed liquid finds a defect in the top lift, moves down and spreads along a more permeable zone between lifts; finds another defect, moves downward, spreads; finds another defect and so forth.

The problem arises in determining from where a representative sample should be taken. Even if 25 samples were picked randomly in a grid pattern from that zone for 25 independent measures of hydraulic conductivity, it would be unclear how to arrive at a single representative measure. The flow through a 3-in. diameter specimen is much too small to mimic the patterns of fluid flow that occur in the field under similar conditions.

26.2.4.1.2 Houston, TX

A second case history that demonstrates the difficulty of obtaining representative samples involves a trial pad constructed in Houston. A 1-ft thick clay liner was compacted over a gravel underdrain with an area roughly 50 ft by 50 ft. The entire area of the liner was drained and the flow from an area roughly 16 ft by 16 ft was carefully collected and measured.

The liner was first built on top of the underdrain, the soil compacted with a padfoot roller, and water ponded on top of the liner. Infiltrometers measured the rate of inflow, and a lysimeter measured the rate of outflow. The soil used in the experiment was highly plastic with a PI of 41%.

The liner was compacted with two lifts, each 6-in. thick. A 1-ft^3 block of soil was carved from the liner, and cylindrical test specimens were trimmed from upper and lower lifts and measured for hydraulic conductivity. A 3-in. diameter specimen also was cut, and hydraulic conductivity parallel to the lift interface was measured. The actual *in situ* hydraulic conductivity, a high 1×10^{-4} cm/s, was verified both by the infiltration measurements and the underdrain measurements.

The tests were replicated under controlled conditions using soil collected from the liner in thin-walled 3-in. diameter sample tubes. The laboratory measures of hydraulic conductivity were consistently 1×10^{-9} cm/s, five orders of magnitude lower than the field value of 1×10^{-4} cm/s. The laboratory tests yielded a hydraulic conductivity 100,000 times different from that from the field test. Apparently, the flow through the 3-in. specimens did not mimic the flow on a larger scale through the entire soil liner. The sample trimmed horizontally at the lift interface was actually obtained by taking a 3-in. diameter sample from a sample collected with a 5-in. diameter tube. The hydraulic conductivity with flow parallel to the lift interface was two orders of magnitude higher. Of all the values recorded from the lab tests, only the one obtained from the upper lift of the block sample was close to the field value of 1×10^{-4} cm/s. Apparently, that one block sample happened to hit one of the more permeable zones and, more or less by accident, yielded a lab measurement that agreed with the field measurement.

26.2.4.2 Degree of Water Saturation

The hydraulic conductivity obtained in a laboratory test can also be affected by the amount of gas present in the soil. Dry soils are less permeable than wet soils. A dry soil is primarily filled with air. Because invading water does not flow through air-filled voids, but flows only through water-filled voids, the dryness of a soil tends to lower the permeability.

Some engineers believe that hydraulic conductivity tests on compacted clay soil should be performed on fully saturated soils in an attempt to measure the highest possible hydraulic conductivity. Most, if not all, of the gas can be eliminated from laboratory hydraulic conductivity tests by backpressure saturation of the soil. This technique pressurizes the water inside the soil, compressing the gas and dissolving it in the water. Increasing the backpressure will increase the degree of water saturation and reduce the amount of air, thereby increasing hydraulic conductivity.[5, 21]

26.2.4.3 Stress Conditions

Another factor substantially influencing the hydraulic conductivity of compacted clay soil is the overburden, or confining pressure, acting on the soil. The weight of 1 ft of soil overburden is roughly equivalent to 1 psi. If two identical samples of soil are buried, one near the ground surface and one at depth, the soil near the ground surface is likely to be more permeable than the soil buried at depth, simply because the soil buried at depth is squeezed into a more compact configuration by the overburden pressure. Thus, soil has a lower porosity with increasing depth.

In a series of experiments, slabs of clay were compacted in the lab and then trimmed to produce cylindrical test specimens. One sample of the clay was compacted and then trimmed for a test specimen immediately, while the other was allowed to desiccate for a period of time before being trimmed. The one that desiccated had tiny cracks as a result of the desiccation process, and was much more permeable than the soil that had not been desiccated. As confining stress increased, the hydraulic conductivity decreased because the soil was compacted into a less porous condition.

Although the sample that was cracked from desiccation was obviously more permeable, at a very high stress the hydraulic conductivities were essentially identical. With enough confining pressure acting on the soil, the cracks that had existed earlier closed up completely so that the soil was no longer highly permeable.

One implication of these experiments for laboratory hydraulic conductivity testing is that conductivity values can vary remarkably depending on the confining stress. It is essential that the confining stress used in a laboratory test be of the same magnitude as the stress in the field.

Another important implication is that highly permeable soil liners generally have defects, such as cracks, macropores, voids, and zones, that have not been compacted properly. One opportunity to eliminate those defects is at the time of construction. Another opportunity arises after the landfill is in operation, and the weight of overlying solid waste or of a cover over the whole system further compresses the soil. This compression, however, occurs only on the bottom liners, as there is not much overburden stress on a final cover placed over a solid waste disposal unit. This is one reason why it is more difficult to design and implement a final cover with low hydraulic conductivity than it is for a bottom liner. Not only is there lower stress acting on a cover than on a liner, but also the cover is subjected to many environmental forces, whereas the liner is not.

26.2.4.4 Double-Ring and Flexible-Wall Permeameters

A double-ring permeameter separates flow that occurs through the central part of the soil sample from flow that occurs near the side wall. The permeameter is designed such that a ring sticks into the bottom of the soil sample, thereby detecting side wall leakage that might invalidate the results of laboratory conductivity tests. Another kind of permeameter cell is a flexible-wall permeameter in which the soil specimen is confined by a thin, flexible membrane, usually made of latex. The latex membrane conforms to any irregularities in the sample, an advantage when collecting irregularly shaped specimens from the field.

26.2.4.5 Termination Criteria

When conducting laboratory hydraulic conductivity tests, two criteria should be met before testing is terminated. First, the rate of inflow should be within 10% of the rate of outflow. Measuring both the rate of inflow and the rate of outflow is necessary to detect problems such as a leak in the system or evaporation from one of the reservoirs. Second, a plot of hydraulic conductivity versus time or pore volume of flow should essentially level off, indicating that hydraulic conductivity is steady.

26.2.5 FIELD HYDRAULIC CONDUCTIVITY TESTING

In situ, or field, hydraulic conductivity testing operates on the assumption that by testing larger masses of soil in the field one can obtain more realistic results. There are actually four kinds of *in situ* hydraulic conductivity tests[5]:

1. Borehole tests
2. Porous probes
3. Infiltrometer tests
4. Underdrain tests.

To conduct a borehole test, one simply drills a hole in the soil, fills the hole with water, and measures the rate at which water percolates into the borehole.

The second type of test involves driving or pushing a porous probe into the soil and pouring water through the probe into the soil. With this method, however, the advantage of testing directly in the field is somewhat offset by the limitations of testing such a small volume of soil.

A third method of testing involves a device called an infiltrometer. This device is embedded into the surface of the soil liner such that the rate of flow of a liquid into the liner can be measured. Infiltrometers have the advantage of being able to permeate large volumes of soil, whereas the first two devices cannot.

A fourth type of test utilizes an underdrain, such as the one at the Houston test site discussed earlier.

Underdrains are the most accurate *in situ* permeability testing devices because they measure exactly what comes out from the bottom of the liner. They are, however, slow to generate good data for low-permeability liners because they take a while to accumulate measurable flow. Also, underdrains must be put in during construction, so there are fewer underdrains in operation than there are other kinds of testing devices. They are highly recommended for new sites, however.

The two forms of infiltrometers popularly used are open and sealed. Four variations are available. Open rings are less desirable because with a conductivity of 10^{-7} cm/s, it is difficult to separate a 0.002 in./day drop in water level of the pond from evaporation and other losses. With sealed rings, however, very low rates of flow can be measured. Single-ring infiltrometers allow lateral flow beneath the ring, complicating the interpretation of test results. Single rings are also susceptible to the effects of temperature variation; as the water heats up, the whole system expands and as it cools down, the

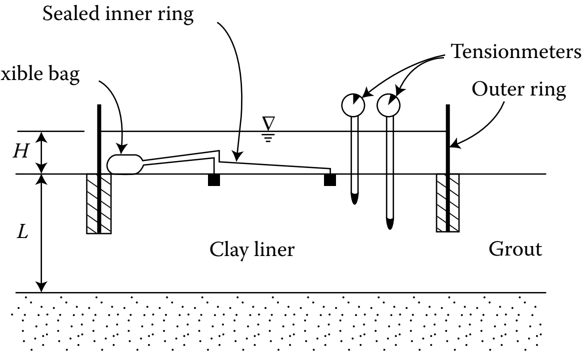


FIGURE 26.13 Details of a sealed double-ring infiltrometer. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

whole system contracts. This situation could lead to erroneous measurements when the rate of flow is small. The sealed double-ring infiltrometer has proven the most successful and is the one used currently. The outer ring forces the infiltration from the inner ring to be more or less one dimensional. Covering the inner ring with water insulates it substantially from temperature variation.

Figure 26.13 shows the double-ring device currently being used. It consists of a 12 ft by 12 ft outer ring and a 5-ft diameter inner ring.[22] Tensiometers are embedded at various depths to establish the depth of water penetration into the soil so that hydraulic conductivity can be calculated.

Rate of infiltration is measured by a small flexible bag. As water infiltrates from the inner ring into the soil, the flexible bag is gradually compressed as water leaves it to enter the ring. To determine how much flow has taken place, the flexible bag is disconnected, dried off, and weighed. Then it can either be refilled or replaced with a fresh bag.

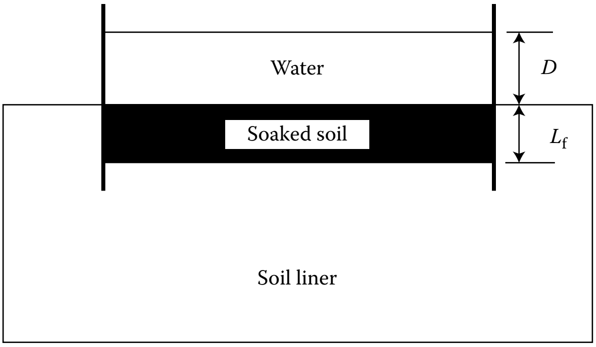
The flexible bag also serves to stabilize the pressure between the inner and outer rings. If the water level in the outer ring changes, the hydrostatic pressure on the flexible bag changes by precisely the same amount. Thus, even though the water level in the outer ring fluctuates, the differential pressure between the inner and outer rings is always zero. Overall, this simple device compensates for water level changes and allows a range of measurements.

The sealed double-ring infiltrometer is best used on a test pad. The width of the test pad is usually about 40 ft by 50 ft; the thickness of the test pad is usually 2 or 3 ft. The test pad is always covered to prevent desiccation after construction has been completed.

The tests do not directly measure the hydraulic conductivity k of the soil. Instead they measure the infiltration rate I for the soil. Since hydraulic conductivity is the infiltration rate divided by the hydraulic gradient i (see equations in Figure 26.14), it is necessary to determine the hydraulic gradient before k can be calculated. The following equation (with terms defined in Figure 26.14) can be used to estimate the hydraulic gradient:

$$i = \frac{(D + L_\mathrm{f})}{L_\mathrm{f}}. \tag{26.1}$$

This equation assumes the pressure head at the wetting front to be equal to zero. The value of the pressure head is, however, a source of disagreement and one of the sources of uncertainty in this test. The assumption that the pressure head is zero is a conservative assumption, tending to give a high hydraulic conductivity.



l = Infiltration rate
= (quantity of flow/area)/time
= $(Q/A)/t$

k = Hydraulic conductivity
= $Q/(iAt) = l/i$

FIGURE 26.14 Hydraulic gradient. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

A hydraulic conductivity test is terminated when the hydraulic conductivity drops below 10^{-7} cm/s (see Figure 26.15). It usually takes 2–8 weeks to reach that point, and is usually clear after about 2 months whether or not that objective will be achieved.

The cost of the equipment to build a sealed double-ring infiltrometer in terms of 2007 USD[23] is about USD4200. The tensiometers, grout, and equipment rental typically add another USD2100. The total cost for equipment and installation plus the periodic monitoring of the flow rate and analysis of test data is ~USD14,000, not including the cost of a trial pad. The sealed double-ring infiltrometer itself is reusable; therefore the USD4200 cost of the rings is recoverable. In comparison with the cost of infiltrometer installation and operation, a single laboratory hydraulic conductivity test costs only USD280–560.

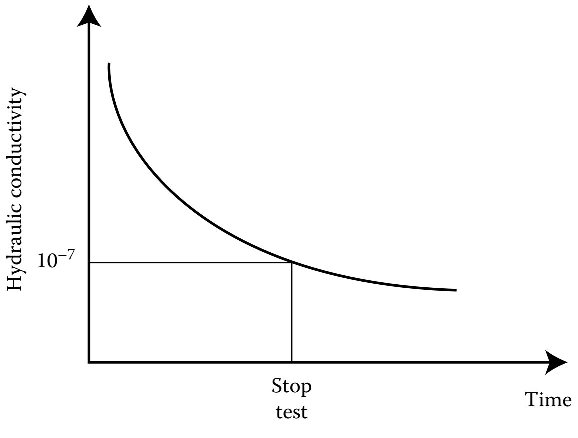


FIGURE 26.15 Termination of testing. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.2.6 FIELD TESTS VERSUS LABORATORY TESTS

A comprehensive program of testing soil liner materials will involve both laboratory and field tests. Field tests provide an opportunity to permeate a larger, more representative volume of soil than do laboratory tests. A field test is also more comprehensive and more reliable.

A primary advantage of laboratory tests is that they are less expensive and so more of them can be performed. Also, certain conditions can be simulated in a lab that cannot be duplicated in the field. One can saturate the soil fully in the laboratory, getting rid of all the gas. One can also vary the overburden stress in the lab, which cannot be done conveniently in the field. Finally, in the lab, actual waste liquids can be passed through a column of material for testing, a condition that could not be duplicated in the field.

There is a radical variation in the reliability of field tests versus laboratory tests. In the Houston test pad discussed earlier, the real value for hydraulic conductivity in the field was 1×10^{-4} cm/s, while the lab value was 1×10^{-9} cm/s, a 100,000-fold difference in the values.

At the Keele Valley landfill, just outside Toronto, however, some excellent field data have been obtained. At this particular site, a 3-ft clay liner spanning 10 acres is monitored by a series of underdrains. Each underdrain measures $15\,m^2$ and is made of HDPE. The underdrains track the liquid as it moves down through the soil liner. The underdrains have been monitored for more than 2 years and have consistently measured hydraulic conductivities of about 1×10^{-8} cm/s. Those field values are essentially identical to the laboratory values.

The clay liner at Keele Valley was built very carefully with strict adherence to CQA. The laboratory and field values are the same because the liner is essentially free of defects. Lab and field values differ when the soil liner in the field contains defects that cannot be simulated accurately on small specimens. If the soil is homogeneous, lab and field tests should compare very well.

26.2.7 ATTACK BY WASTE LEACHATE

26.2.7.1 Acids and Bases

Acids can attack soil by dissolving the soil minerals into other constituents. Typically, when acids are passed through soil, hydraulic conductivity drops because the acids dissolve the materials that help neutralize them. After large amounts of acid wash into the soil, hydraulic conductivity decreases.

There is real concern over waste impoundments used to store acidic liquid. Small amounts of acid such as that contained in a barrel in a solid waste landfill underlain by a 3-ft thick liner will not inflict a major damage on the soil liner. A large volume of liquid in the impoundment, however, can damage the soil seriously.

26.2.7.2 Neutral Inorganic Compounds

Nonacidic liquids can change the hydraulic conductivity in other ways. Soil is made up of colloidal particles that have negative charges along the surface. Water is a polar molecule, with atoms arranged or aligned asymmetrically. This alignment allows the water molecule to be attracted electrochemically to the surfaces of the negatively charged soil particles.

It is also possible for ions in the water, especially positively charged ions, or cations, to be attracted to the negatively charged surfaces. This leads to a zone of water and ions surrounding the clay particles, known as the diffuse double layer.

The water and ions in the double layer are attracted so strongly electrochemically to the clay particles that they do not conduct fluids. Fluids moving through the soil go around the soil particles and also around the double layer. The hydraulic conductivity of the soil, then, is controlled very strongly by the thickness of these double layers. When the double layers shrink, they open up flow paths resulting in high hydraulic conductivity. When the layers swell, they constrict flow paths, resulting in low hydraulic conductivity.[20,24]

The Gouy–Chapman theory relates electrolyte concentration, cation valence, and dielectric constant to the thickness of this double layer (see Equation 26.2). This theory was originally developed for dilute suspensions of solids in a liquid. However, experience confirms that the principles can be applied qualitatively to soil, even compacted soil that is not in suspension.[5]

$$T\alpha\frac{D}{\sqrt{n_o v^2}}, \tag{26.2}$$

where T is the thickness of the double layer, D is the dielectric constant, n_o is the electrolyte concentration, and v is the cation valence.

The following application of the Gouy–Chapman theory uses sodium bentonite. The ion in the soil is sodium, which has a charge of +1. The electrolyte valence in the Gouy–Chapman theory is $v = 1$. The permeating liquid is rich in calcium, and calcium has a charge of +2. As calcium replaces sodium, the valence (v) in the Gouy–Chapman equation goes from 1 to 2. A rise in v increases the denominator, thus decreasing the thickness (T). As T decreases and the double layer shrinks, flow paths open up making the soil more permeable.

Since calcium bentonite, typically, is 100–1000 times more permeable than sodium bentonite, the introduction of this permeating liquid could change hydraulic conductivity substantially.

Soils containing polyvalent cations having high valence and high electrolyte concentration have a high conductivity, whereas the soils containing monovalent cations, such as sodium, have a low k. Distilled water at the extreme end of the spectrum is free of electrolytes. In the Gouy–Chapman equation, the electrolyte concentration n_o would be 0. The denominator, therefore, would go to 0 and the T value to infinity.

Consequently, if the free ions in the soil water are leached out, the double layers swell tremendously, pinching off flow paths and resulting in very low hydraulic conductivity. Data have shown hydraulic conductivity to be as much as two to three orders of magnitude lower when measured with distilled water than with other kinds of water. For this reason, distilled water should not be used in testing the hydraulic conductivity of a clay liner.

An ASTM standard recommends the use of 0.005 normal calcium sulfate as the standard permeating water, because of its medium range electrolyte concentration. Calcium sulfate, with divalent calcium, will usually not reduce hydraulic conductivity.

26.2.7.3 Neutral Organic Compounds

Organic chemicals can cause major changes in hydraulic conductivity. The dielectric constant (D) of many of the organic solvents used in industry is very low. For example, the dielectric constant of water is about 80, whereas that of trichloroethylene is about 3. Using the Gouy–Chapman equation, if D decreases, which means the numerator decreases, the value of T will also decrease, causing the double layer to shrink. The effect of replacing water with an organic solvent then is to shrink the double layer and open up flow paths.

In addition to opening up flow paths, as the double layers shrink, the solvent flocculates the soil particles, pulling them together and leading to cracking in the soil. Permeation of the soil with an organic chemical, such as gasoline, may produce cracking similar to that associated with desiccation. The organic solvent, however, produces a chemical desiccation rather than a desiccation of the soil by drying out.

Laboratory test data indicate that if the organic chemical is present in a dilute aqueous solution, the dielectric constant will not be dangerously low. Dielectric constants above 30 will generally not lower the conductivity substantially enough to damage the soil. Two criteria need to be met for a liquid to not attack clay liners: (a) the solution must contain at least 50% water and (b) no separate phase or organic chemicals should be present.

26.2.7.4 Termination Criteria

Chemical compatibility studies with hydraulic conductivity tests must be performed over a long enough period of time to determine the full effects of the waste liquid. Termination criteria include equal inflow and outflow of liquid, steady hydraulic conductivity, and influent/effluent equilibrium. At least two pore volumes of liquid must be passed through the soil to flush out the soil water and bring the waste leachate into the soil in significant quantities. Reasonable equilibrations of the influent and effluent liquids occur when the pH values of the waste influent and effluent liquids are similar and the key organic and inorganic ions are at full concentrations in the effluent liquid.

26.2.7.5 Resistance to Leachate Attack

It is possible to make soils more resistant to chemical attack. Many of the same methods used to lower hydraulic conductivity can stabilize materials against leachate attack, including greater compaction, an increase in overburden stress, and the mixing of additives such as lime cement or sodium silicate with the natural soil materials.[25]

An experiment was conducted using a soil called S1, an illitic clay containing chlorite from Michigan. Two sets of data showd the results of permeation of the regular soil, first with water and then with pure reagent grade heptane. The heptane caused the hydraulic conductivity of the regular compacted soil to skyrocket. About 8% cement was then added to the soil.

After treatment of the soil with cement, however, the heptane did not affect the soil even after a pore volume of flow. The cement glued the soil particles together so that the soil became invulnerable to attack, rather than causing it to undergo chemical desiccation.

26.3 FLEXIBLE MEMBRANE LINERS

This section discusses several material and design considerations for FMLs. It highlights some of the problems encountered in designing "bathtub" systems for hazardous waste landfills and describes the impact of regulations on material and design considerations.

26.3.1 Composite Liners: Clay versus Synthetic Components

After a landfill site has been chosen and a basin has been excavated, the basin is lined with one or more layers of water-retaining material (liners) that form a "leachate bathtub." The contained leachate is pumped out through a network of pipes and collector layers. Liners may be constructed of synthetic polymer sheets or of clay. U.S. EPA's MTG[3,6,7] relies on a composite liner that utilizes the advantages obtained from combining both liner systems.

Understanding the basic hydraulic mechanisms for synthetic liners and clay liners is very important in appreciating the advantages of a composite liner. Clay liners are controlled by Darcy's law ($Q = kiA$). In clay liners, the factors that most influence liner performance are hydraulic head and soil permeability. Clay liners have a higher hydraulic conductivity and thickness than do synthetic liners. Additionally, leachate leaking through a clay liner will undergo chemical reactions that reduce the concentration of contaminants in the leachate.

Leakage through a synthetic liner is controlled by Fick's first law, which applies to the process of liquid diffusion through the liner membrane. The diffusion process is similar to flow governed by Darcy's law except that it is driven by concentration gradients and not by hydraulic head. Diffusion rates in membranes are very low in comparison with hydraulic flow rates even in clays. In synthetic liners, therefore, the factor that most influences liner performance is penetrations. Synthetic liners may have imperfect seams or pinholes, which can greatly increase the amount of leachate that leaks out of the landfill.

Clay liners, synthetic liners, or combinations of both are required in landfills. Figure 26.1 depicted the synthetic/composite double-liner system that appears in U.S. EPA's MTG. As explained

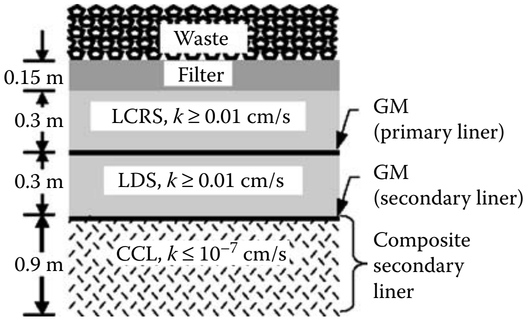


FIGURE 26.16 Profile of the MTG double-liner system. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

earlier, the system has two synthetic FMLs: the primary FML, which lies between two LCRS, and the secondary FML, which overlies a CCL to form a composite secondary liner. The advantage of the composite liner design is that by putting a fine-grain material beneath the membrane, the impact of given penetrations can be reduced by many orders of magnitude (10^5 times).[5]

Figure 26.16 is a profile of a liner according to U.S. EPA's MTG. The minimum hydraulic conductivity in the secondary leachate collection system is 1×10^{-2} cm/s. To meet this requirement, either a granular material or a net made of synthetic material must be used to build the secondary leachate collection system.

26.3.2 MATERIAL CONSIDERATIONS

Synthetics are made up of polymers—natural or synthetic compounds of high molecular weight. Different polymeric materials may be used in the construction of FMLs[26,27]:

1. Thermoplastics—polyvinyl chloride (PVC)
2. Crystalline thermoplastics—HDPE, linear low-density polyethylene (LLDPE)
3. Thermoplastic elastomers—chlorinated polyethylene (CPE), chlorylsulfonated polyethylene (CSPE)
4. Elastomers—neoprene, ethylene propylene diene monomer (EPDM)

Typical compositions of polymeric GMs are depicted in Table 26.3. As the table shows, the membranes contain various admixtures such as oils and fillers that are added to aid the manufacturing of the FML but may affect future performance. In addition, many polymer FMLs will cure once installed, and the strength and elongation characteristics of certain FMLs will change with time. It is important therefore to select polymers for FML construction with care. Chemical compatibility, manufacturing considerations, stress–strain characteristics, survivability, and permeability are some of the key issues that must be considered.

26.3.2.1 Chemical Compatibility

The chemical compatibility of an FML with waste leachate is an important material consideration.

Chemical compatibility and U.S. EPA Method 9090 tests must be performed on the synthetics that will be used to construct FMLs. Unfortunately, there is usually a lag period between the time these tests are performed and the actual construction of a facility. It is very rare that at the time of the 9090 test, enough material is purchased to construct the liner. This means that the material used for testing is not typically from the same production lot as the synthetics installed in the field. The molecular structure of different polymers can be analyzed through differential scanning calorimeter

TABLE 26.3
Basic Composition of Polymeric GM

	Composition of Compound Type (Parts by Weight)		
Component	**Crosslinked**	**Thermoplastic**	**Semicrystalline**
Polymer or alloy	100	100	100
Oil or plasticizer	5–40	5–55	0–10
Fillers			
Carbon black	5–40	5–40	2–5
Inorganics	5–40	5–40	—
Antidegradants	1–2	1–2	1
Crosslinking system			
Inorganic system	5–9	—	—
Sulfur system	5–9	—	—

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

or thermogravimetric testing. This testing or "fingerprinting" can ensure that the same material as used for the 9090 test was used in the field.

26.3.2.2 Manufacturing Considerations

PE sheets are produced in various ways[5]:

1. Extrusion—HDPE
2. Calendaring—PVC
3. Spraying—urethane.

In general, manufacturers are producing high-quality PE sheets. However, the compatibility of extrusion welding rods and HDPE sheets can be a problem. Some manufacturing processes can cause HDPE to crease. When this material creases, stress fractures will result. If the material is taken into the field to be placed, abrasion damage will occur on the creases. Manufacturers have been working to resolve this problem and, for the most part, sheets of acceptable quality are now being produced.

26.3.2.3 Stress–Strain Characteristics

Table 26.4 depicts the typical mechanical properties of HDPE, CPE, and PVC. Tensile strength is a fundamental design consideration. Another stress–strain consideration is that HDPE, a material used frequently at hazardous waste facilities, has a high thermal coefficient of expansion, 3–4 times that of other flexible membranes. This means that during the course of a day (particularly in the summer), 100°F variations in the temperature of the sheeting are routinely measured. A 600-ft long panel, for example, may grow 6 ft during a day.

26.3.2.4 Survivability

Various tests may be used to determine the survivability of unexposed polymeric GMs. Puncture tests are frequently used to estimate the survivability of FMLs in the field. During a puncture test, a 5/16 steel rod with rounded edges is pushed down through the membrane. A very flexible membrane that has a high strain capacity under biaxial tension may allow that rod to penetrate almost to

TABLE 26.4
Typical Mechanical Properties of Membrane Liners

	HDPE	CPE	PVC
Density (g/cm^3)	>0.935	1.3–1.37	1.24–1.3
Thermal coefficient of expansion	12.5×10^{-5}	4×10^{-5}	3×10^{-5}
Tensile strength (psi)	4800	1800	2200
Puncture (lb/mil)	2.8	1.2	2.2

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

the bottom of the chamber. Such a membrane has a very low penetration force but a very high penetration elongation, and may have great survivability in the field. HDPEs will give a very high penetration force, but have very high brittle failure. Thus, puncture data may not properly predict field survivability.

26.3.2.5 Permeability

Permeability of an FML is evaluated using the Water Vapor Transmission test.[28] A sample of the membrane is placed on top of a small aluminum cup containing a small amount of water. The cup is then placed in a controlled humidity and temperature chamber. The humidity in the chamber is typically 20% relative humidity, while the humidity in the cup is 100%. Thus, a concentration gradient is set up across the membrane. Moisture diffuses through the membrane, and with time the liquid level in the cup is reduced. The rate at which moisture is moving through the membrane is measured. From that rate, the permeability of the membrane is calculated with the simple diffusion equation (Fick's first law). It is important to remember that even if a liner is installed correctly with no holes, penetrations, punctures, or defects, liquid will still diffuse through the membrane.

26.3.3 Design Elements

A number of design elements must be considered in the construction of FMLs[5,29]:

1. MTG
2. Stress considerations
3. Structural details
4. Panel fabrication.

26.3.3.1 Minimum Technology Guidance

U.S. EPA has set MTG for the design of landfill and surface impoundment liners to achieve *de minimis* leakage. *De minimis* leakage is 1gal/acre/day. FMLs must be a minimum of 0.75mm thick, or 1.13mm thick if exposed for more than 30 days. There may, however, be local variations in the requirement of minimum thickness, and these variations can have an impact on costs. For example, membranes cost ~USD0.56/mm/ft^2, so that increasing the required thickness of the FML from 0.75 to 1.5mm mils will increase the price to USD0.42/ft^2 or USD17,000 per acre (in terms of 2007 USD).

26.3.3.2 Stress

Stress considerations must be considered for side slopes and the bottom of a landfill. For side slopes, self-weight (the weight of the membrane itself) and waste settlement must be considered; for the bottom of the facility, localized settlement and normal compression must be considered.

The primary FML must be able to support its own weight on the side slopes. In order to calculate self-weight, the FML-specific gravity, friction angle, FML thickness, and FML yield stress must be known.

Waste settlement is another consideration. As waste settles in the landfill, a downward force will act on the primary FML. A low friction component between the FML and underlying material prevents that force from being transferred to the underlying material, putting tension on the primary FML. A 12-in. direct shear test is used to measure the friction angle between the FML and underlying material.

An example of the effects of waste settlement can be illustrated by a recent incident at a hazardous waste landfill facility in California.[5] At this facility, waste settlement led to sliding of the waste, causing the standpipes (used to monitor secondary leachate collection sumps) to move 60–90 ft downslope in 1 day. Because there was a very low coefficient of friction between the primary liner and the geonet, the waste (which was deposited in a canyon) slid down the canyon. There was also a failure zone between the secondary liner and the clay. A two-dimensional slope stability analysis at the site indicated a factor of safety (FS) greater than 1. A three-dimensional slope stability analysis, however, showed that the safety factor had dropped below one. Three-dimensional slope stability analyses should therefore be considered with canyon and trench landfills.

Since more trenches are being used in double FML landfills, the impact of waste settlement along such trenches should be considered. Figure 26.17 is a simple evaluation of the impact of waste settlement along trenches on the FML. Settlements along trenches will cause strain in the membrane, even if the trench is a very minor ditch. Knowing that when biaxial tension is applied to HDPE, the material fails at a 16–17% strain, it is possible that the membrane will fail at a moderate settlement ratio.

Another consideration is the normal load placed on the membranes as waste gets piled up. Many of the new materials on the market, particularly some of the LLDPE liners, will take a tremendous

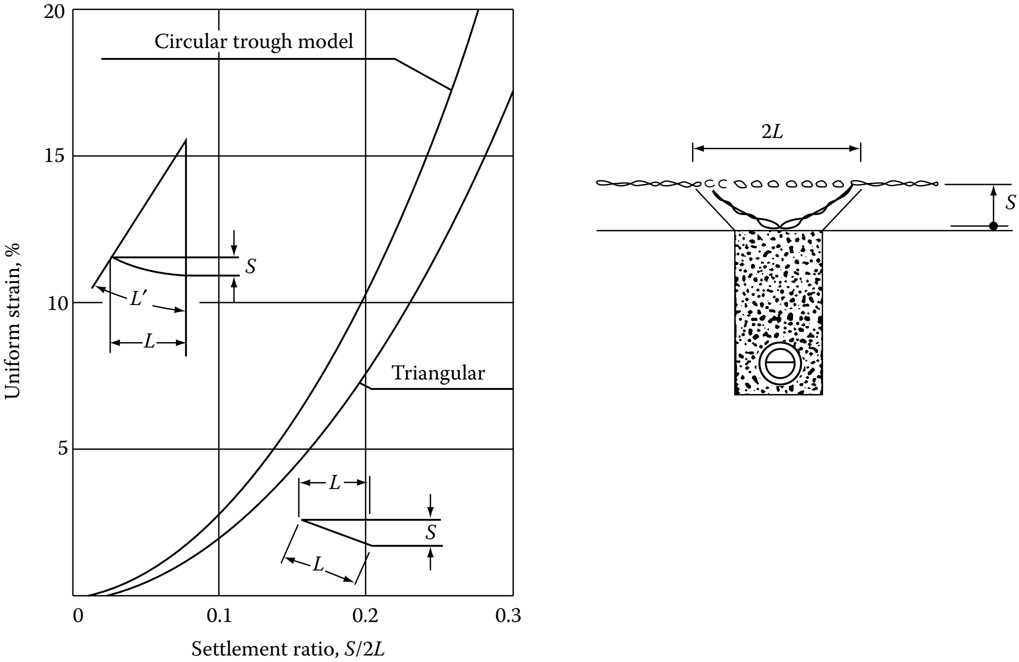


FIGURE 26.17 Settlement trough models. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

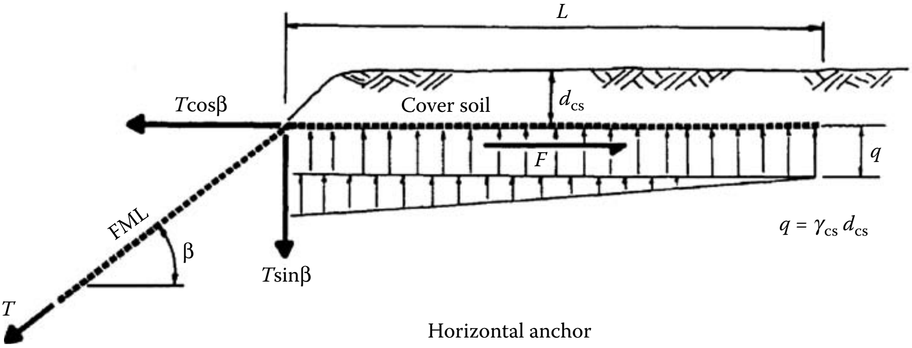
amount of normal load without failure. The HDPEs, on the other hand, have a tendency for high brittle failure.

26.3.3.3 Structural Details

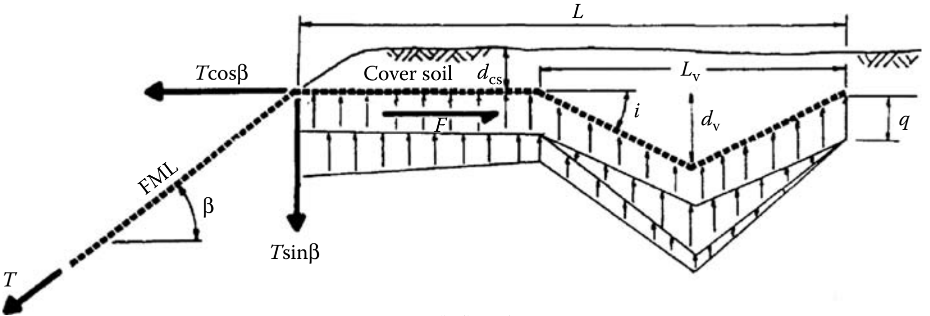
Double-liner systems are more prone to defects in the structural details (anchorage, access ramps, collection standpipes, and penetrations) than single-liner systems.

26.3.3.3.1 Anchorage

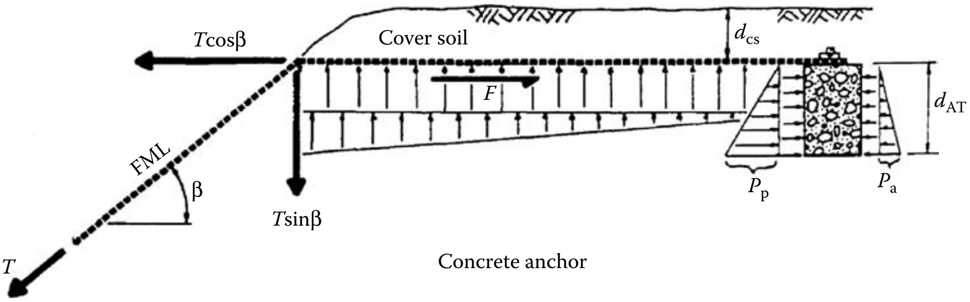
Anchor trenches can cause FMLs to fail in one of the two ways: by ripping or by pulling out. The pullout mode is easier to correct. It is possible to calculate pullout capacity for FMLs placed in various anchorage configurations (Figure 26.18). In the "V" anchor configuration, resistance can be



Horizontal anchor



"V" anchor



Concrete anchor

FIGURE 26.18 Forces and variables—anchor analysis. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

increased by increasing the "V" angle. A drawback to using the "V" design for getting an accurate estimate of pullout capacity is that it uses more space.

26.3.3.3.2 Ramps

Most facilities have access ramps (Figure 26.19), which are used by trucks during construction and by trucks bringing waste into the facility. The figure also depicts a cross section of a typical access ramp. The double FML integrity must be maintained over the entire surface of the ramp. Because ramps can fail due to traffic-induced sliding, roadway considerations, and drainage, these three factors must be considered during the design and construction of access ramps.

The weight of the roadway, the weight of a vehicle on the roadway, and the vehicle braking force—all these must be considered when evaluating the potential for slippage due to traffic. The vehicle braking force should be much larger than the dead weight of the vehicles that will use it. Wheelloads also have an impact on the double FML system and the two leachate collection systems below the roadway. Trucks with maximum axle loads (some much higher than the legal highway loads) and 90psi tires should be able to use the ramps. Swells or small drains may be constructed along the inboard side of a roadway to ensure that the ramp will adequately drain water from the roadway. The liner system, which must be protected from tires, should be armored in the area of the drainage swells. A sand subgrade contained by a geotextile beneath the roadway can prevent local sloughing and local slope failures along the side of the roadway where the drains are located. The sand subgrade tied together with geotextile layers forms, basically, 800-ft long sandbags stacked on top of one another.

26.3.3.3.3 Vertical Standpipes

Landfills have two LCRSs: a primary LCRS and a secondary LCRS. Any leachate that penetrates the primary system and enters the secondary system must be removed. Vertical standpipes are used

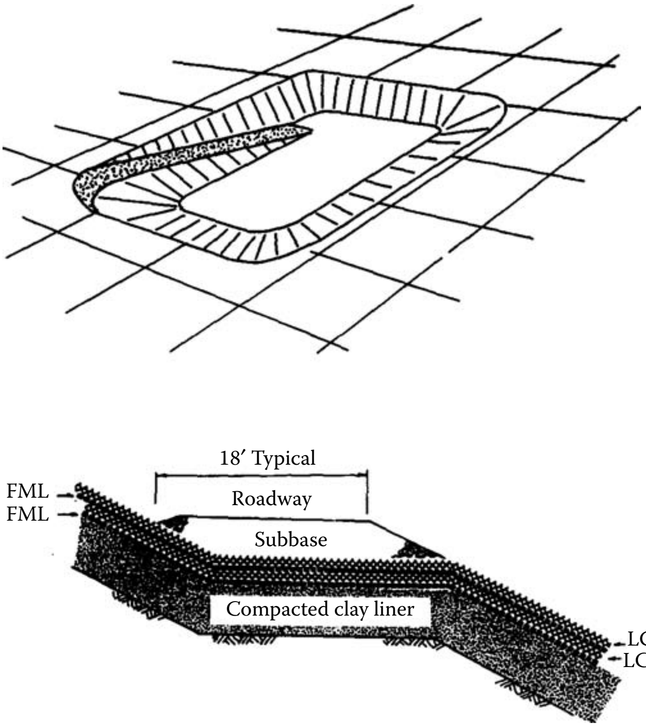


FIGURE 26.19 Geometry and cross section of a typical access ramp. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

to access the primary leachate collection sumps. As waste settles over time, downdrag forces can have an impact on standpipes. Those downdrag forces can lead to puncture of the primary FML beneath the standpipe.

To reduce the amount of downdrag force on the waste pile, standpipes can be coated with viscous or low friction coating. Standpipes can be encapsulated with multiple layers of HDPE. This material has a very low coefficient of friction that helps reduce the amount of downdrag force on the waste piles.

Downdrag forces also affect the foundation or subgrade beneath the standpipe. If the foundation is rigid, poured concrete, there is a potential for significant strain gradients. A flexible foundation will provide a more gradual transition and spread the distribution of contact pressures over a larger portion of the FML than will a rigid foundation. To soften rigid foundations, encapsulated steel plates may be installed beneath the foundation.

26.3.3.3.4 Standpipe Penetrations

The secondary leachate collection system is accessed by collection standpipes that must penetrate the primary liner. There are two methods of making these penetrations: rigid or flexible. In the rigid penetrations, concrete anchor blocks are set behind the pipe with the membranes anchored to the concrete. Flexible penetrations are preferred since these allow the pipe to move without damaging the liner. In either case, standpipes should not be welded to the liners. If a vehicle hits a pipe, there is a high potential for creating major tears in the liner at depth.

26.3.3.3.5 Wind Damage

During the installation of FMLs, care must be taken to avoid damage from wind. Designers should determine whether wind will affect an installation and, if so, how many sandbags will be needed to anchor the FML panels as they are being placed in the field.

26.3.3.3.6 Surface Impoundments versus Landfills

There are significant differences in structural considerations between landfills and surface impoundments. First, liners used in surface impoundments have a long-term exposure to the waste and to sunlight. In addition, surface impoundments have a potential for gas in the LCRS because there will always be the potential for organic material beneath the system.

Long-term exposure can be stopped using either soil or a nonwoven fabric to cover the membrane in a surface impoundment. Another option is to drape a heavy, nonwoven fabric with base anchors in it over the membrane. This nonwoven material is cheaper, safer, and more readily repaired than a soil cover.

Gas- or liquid-generated “whales” can be a serious problem in surface impoundments. Water-induced “whaling” can be a problem in facilities that are located where there is a high water table. Stormwater can also enter a collection system through gas vents. In gas vent designs, care should be taken to ensure that the vent is placed higher than the maximum overflow level. If excess water in the leachate collectors is causing whaling, the perimeter should be checked to determine where water is entering. To repair a water-generated whale, the excess water should be pumped out of the sump and its source stopped. If there is gas in the whale (the liner is inflated and visible above the water surface), the facility must be rebuilt from scratch.

26.3.3.4 Panel Fabrication

The final design aspect to consider is the FML panel layout of the facility. Three factors should be considered when designing an FML panel layout[5,30]:

1. Seams should run up and down on the slope, not horizontally.
2. The field seam length should be minimized whenever possible.
3. There should be no penetration of an FML below the top of the waste.

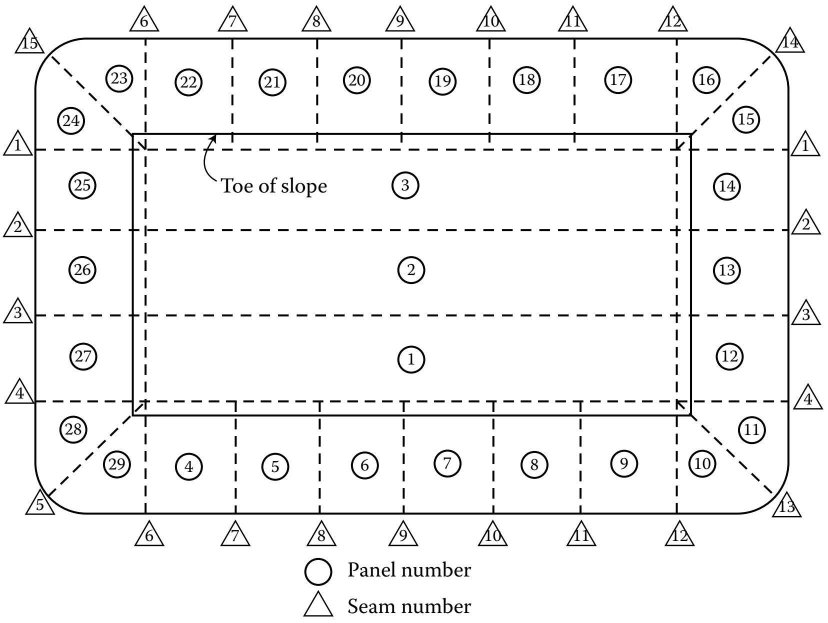


FIGURE 26.20 Panel-seam identification scheme. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

Panels must be properly identified to know where they fit in the facility. Figure 26.20 depicts the panel-seam identification scheme used for this purpose. This numbering scheme also assures a high-quality installation, since seam numbers are used to inventory all samples cut from the FML panel during installation. The samples cut from the panels are tested to ensure that the installation is of high quality. Quality assurance and the panel-seam identification scheme are discussed in more detail in Chapter 7.

26.4 ELEMENTS OF LIQUID MANAGEMENT AT WASTE CONTAINMENT SITES

The drainage system for removing leachate or other aggressive liquids from landfills, surface impoundments, and waste piles is critically important. Even if a liner has no leaks, the phenomenon of molecular diffusion will allow some of the organics from the liquids ponded on top of the liner system to leach through the FML and the clay. The timely collection and removal of that leachate is at the heart of this section.

This section presents an overview of collector design and materials, followed by a discussion of the three parts of a liquid management system: the LCRS above the primary liner, the secondary leak detection, collection, and removal (LDCR) system between the primary and secondary liners, and the surface water collection system above the closure of the completed facility. The section concludes with a discussion of gas-collector and removal systems.

26.4.1 Overview

Leachate refers to rainfall and snowmelt that combine with liquid in the waste and gravitationally moves to the bottom of a landfill facility. During the course of its migration, the liquid takes on the pollutant characteristics of the waste itself. As such, leachate is both site-specific and waste-specific with regard to both its quantity and quality. The first part of the collector system to intercept the leachate is the primary leachate collection and removal (PLCR) system located directly below the waste and above the primary liner. This system must be designed and constructed on a site-specific basis to remove the leachate for proper treatment and disposal.

The second part of a leachate collection system is between the primary and secondary liners. Varying with State or region, it is called by a number of names including the secondary leachate collection and removal (SLCR) system, the leak detection network, or the leak questioning system. It will be referred to here as the LDCR system. The main purpose of this system is to determine the degree of leakage, if any, of leachate through the primary liner. Ideally, this system would collect only negligible quantities of leachate; however, it must be designed on the basis of a worst-case scenario.

The third part, called the surface water collection and removal (SWCR) system, lies above the waste system in a cap or closure above the closed facility. Its purpose is to redirect surface water coming through the cover soil from the flexible membrane in the cap to the outside perimeter of the system. The location of all three parts of the liquid management system is illustrated in Figure 26.21.

26.4.1.1 Drainage Materials

The drainage materials for the liquid management system must allow for unimpeded flow of liquids for the intended lifetime of the facility. In a leachate collection system, the drains may consist of pipes, soil (gravel), geonets, or geocomposites.

Perforated drainage pipes have the advantage of common usage and design, and they transmit fluids rapidly. They do, however, require considerable vertical space and are susceptible to particulate

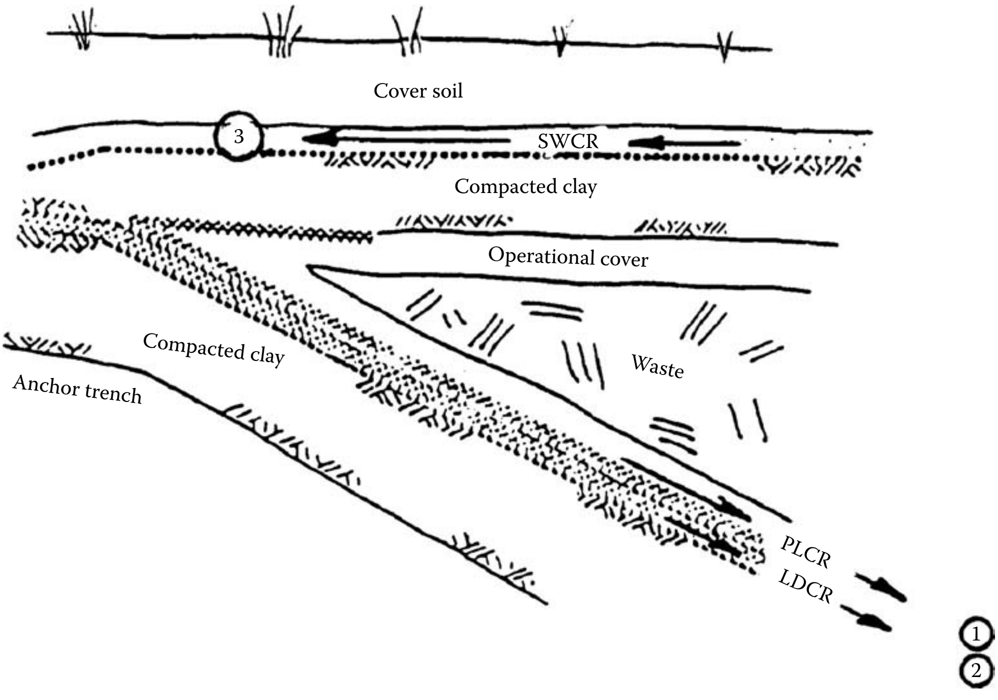


FIGURE 26.21 Three elements of a liquid management drainage system in a double-lined solid waste facility. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

clogging, biological clogging, and creep (deflection). Creep is of concern for both PVC and HDPE pipe materials.

The synthetic materials that best meet in-plane flow rate regulations are called geonets. Geonets require less space than perforated pipe or granular material, promote rapid transmission of liquids, and, because of their relatively open apertures, are less likely to clog. They do, however, require geotextile filters above them and can experience problems with creep and intrusion.

Another synthetic material is called a drainage geocomposite, many types of which are available. Geocomposites have most of the same advantages and disadvantages of geonets. They are generally not used for primary or secondary leachate collection systems, however, because of their relatively low crush strength. The crush strength, or normal strength perpendicular to the plane, of currently available products is not sufficient to carry the weight of a large landfill. Geocomposites are useful, however, for surface water-collector systems, where the applied normal stresses are quite low.

26.4.1.2 Filtration Materials

The openings in drainage materials, whether holes in pipes, voids in gravel, or apertures in geonets, must be protected against invading fine particle-sized materials. An intermediate material, having smaller openings than those of the drainage material, must be used as a filter. Commonly in a pipe or gravel drain, a medium-coarse to fine sandy soil is used as a filter. Sand, however, has the disadvantages of taking up vertical space and moving under various loading conditions.

Geotextiles used as filters avoid these problems. The open spaces in the fabric allow liquid flow while simultaneously preventing upstream fine particles from fouling the drain. Geotextiles save vertical space, are easy to install, and have the added advantage of remaining stationary under load. As with sand filters, clogging can occur, and because geotextiles are a new technology, much not is known about them. Geotextiles are being used more and more not only for filters, but also as cushioning materials above and/or below FMLs.

26.4.1.3 Geosynthetics

Geosynthetic materials play a key role in liquid management systems. The five major categories of geosynthetics are[5]

1. Geotextiles
2. Geogrids
3. Geonets
4. GMs
5. Geocomposites.

Geotextiles are either woven or nonwoven fabrics made from polymeric fibers. Woven geotextiles are fabrics made up of webbed fibers that run in perpendicular directions. For filtration, the spaces between the fibers are the most important element. These spaces or voids must be large enough to allow unimpeded liquid flow but small enough to keep out invading particulates. The geotextiles must also be sufficiently strong to cover and reinforce the apertures, or openings, of the drainage materials they are meant to protect.

In nonwoven geotextiles, the fibers are much thinner but far more numerous. The various types are needle-punched, resin-bond, and melt-bond. All contain a labyrinth of randomly oriented fibers that cross one another so that there is no direct line of flow. The fabric must have enough open space to allow liquid to pass through, while simultaneously retaining any upstream movement of particles. The needle-punched nonwoven type is very commonly used as a filter material.

Geogrids are very strong in transverse and longitudinal directions, making them useful as reinforcing materials for either soil or solid waste. Generally, they are used to steepen the side slopes of interior cells or exterior containment slopes of a facility. Recently, they have also been used in the construction of "piggyback" landfills, that is, landfills built on top of existing landfills, to reinforce the upper landfill against differential settlements within the lower landfill.

Geonets are formed with intersecting ribs made from a counterrotating extruder. A typical geonet is about 1/4-in. thick from the top of the upper rib to the bottom of the lower rib. The rapid transmission rate (1 cm/s permeability) is due to clear flow paths in the geonets, as opposed to particle obstructions in a granular soil material. There are two main concerns with geonets. First, the crush strength at the rib's intersection must be capable of maintaining its structural stability without excessive deformation or creep. Second, adjacent materials must be prevented from intruding into the rib apertures, cutting off or reducing flow rates.

Foamed geonets are relatively new products made with a foaming agent that produces a thick geonet structure (up to 1/2 in.) with very high flow rates. These improved flow rates result from the thicker product, but eventually the nitrogen gas in the rib voids diffuses through the polymer structure, leaving behind a structure with reduced thickness. The result over the long term is a solid rib geonet thickness equivalent to other nonfoamed geonets.

The fourth type of geosynthetic is a GM or an FML. It is the primary defense against escaping leachate and is of crucial importance.

The final category of geosynthetics is drainage geocomposites. These are polymeric materials with built-up columns, nubs, or other deformations that allow planar flow within their structure. A drainage geocomposite having 1-in. high columns can carry the flow of a 4–5-in. diameter pipe. Many products, however, have low crush strengths that are inadequate for deep landfills or surface impoundments. They are useful, however, for surface water-collector systems above the closed facility where they only need to support ~4 ft of soil and construction placement equipment.

26.4.1.4 Design-by-Function Concepts

Whatever parameter of a specific material one is evaluating, a required value for the material must be found using a design model, and an allowable value for the material must be determined by a test method. The allowable value divided by the required value yields the design ratio (DR), or the resulting FS. This design-by-function concept is necessary to design and evaluate new materials that are both feasible and safe for a variety of situations.

In evaluating drainage and filtration materials, an allowable flow rate is divided by a required flow rate to obtain the DR or FS according to the equations below[5]:

1. For drainage

$$\mathrm{DR} = \frac{q_{\text{allow}}}{q_{\text{reqd}}} \tag{26.3}$$

or

$$\mathrm{DR} = \frac{\Psi_{\text{allow}}}{\Psi_{\text{reqd}}} \tag{26.4}$$

where DR is the design ratio, q is the flow rate per unit width, and Ψ is the transmissivity.

2. For filtration

$$\mathrm{DR} = \frac{q'_{\text{allow}}}{q'_{\text{reqd}}} \tag{26.5}$$

or

$$\mathrm{DR} = \frac{\Psi'_{\text{allow}}}{\Psi'_{\text{reqd}}} \tag{26.6}$$

where DR is the design ratio, q' is the flow rate per unit area, and Ψ' is the permittivity.

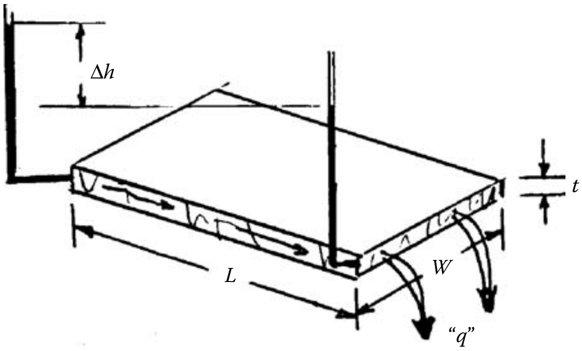


FIGURE 26.22 Variables for calculating in-plane flow rates (transmissivity). (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

Transmissivity is simply the coefficient of permeability, or the hydraulic conductivity (k), within the plane of the material multiplied by the thickness (T) of the material. Because the compressibility of some polymeric materials is very high, the thickness of the material needs to be taken into account. Darcy's law, expressed by the equation $Q = kiA$, is used to calculate the rate of flow, with transmissivity equal to kT and i equal to the hydraulic gradient (see Figure 26.22):

$$\begin{aligned} Q &= kiA \\ Q &= k\left(\frac{\Delta h}{L}\right)(wT) \\ \frac{Q}{w} &= (kT)\left(\frac{\Delta h}{L}\right) \end{aligned} \tag{26.7}$$

If $\theta = kT$,

$$\frac{Q}{w} = \theta(i) \tag{26.8}$$

where Q/w is the flow rate per unit width and θ is the transmissivity.

With a liquid flowing across the plane of the material, as in a geotextile filter, the permeability perpendicular to the plane can be divided by the thickness, T, to obtain a new value, permittivity (see Figure 26.23). In crossplane flow, T is in the denominator; for planar flow, it is in the numerator. Crossplane flow is expressed as

$$Q = kiA \tag{26.9}$$

$$\begin{aligned} Q &= k\left(\frac{\Delta h}{T}\right)A \\ Q &= \left(\frac{k}{T}\right)\Delta hA \\ \psi &= \left(\frac{k}{T}\right) = \frac{Q}{\Delta hA} \end{aligned} \tag{26.10}$$

where ψ is the permittivity and Q/A is the flow rate per unit area (flux).

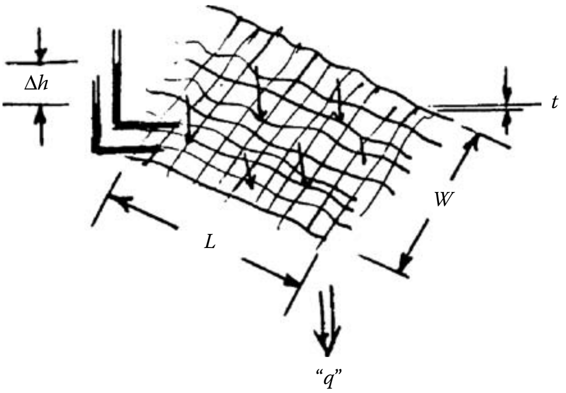


FIGURE 26.23 Variables for calculating crossplane flow rates (permittivity). (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

Thus, both transmissivity and permittivity values allow for the thickness to be avoided in subsequent analyses.

Table 26.5 shows some of the ASTM test methods and standards for drainage and filter materials used in primary leachate collection and leachate detection and collection systems.

26.4.2 PLCR Systems

The various design options for primary leachate collection systems are granular soil drains, perforated pipe collectors, geonet drains, sand filters, and geotextile filters. Figure 26.24 shows a cross section of a primary leachate collection system with a geonet drain on the side slope leading into a gravel drain at the bottom. This gravel drain then leads into a perforated pipe collector. A geotextile acts as a filter protecting the geonet, and sand acts as a filter for the drainage gravel. Quite often, the sideslope geotextile extends over the bottom sand filter as shown in Figure 26.24.

TABLE 26.5
Test Methods and Standards for Drainage and Filter Material

ASTM Test Designation (or Other)	Used to Determine	Material	Value Used for
D2434	Permeability	Soil	PLCR, LDCR
D2416	Strength	Underdrain pipe	PLCR, LDCR
F405, F667	General specification	HDPE pipe	PLCR, LDCR
D4716	Transmissivity	Geonet, geocomposite	PLCR, LDCR
D4491	Permittivity	Geotextile	PLCR filter
D4751	Apparent opening size	Geotextile	PLCR filter
CW-02215[a]	Gradient ratio	Geotextile	PLCR filter
GRI-GT1[b]	Long-term flow	Geotextile	PLCR filter

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

[a] U.S. Army Corps of Engineers Test Method.

[b] Geosynthetic Research Institute Test Method.

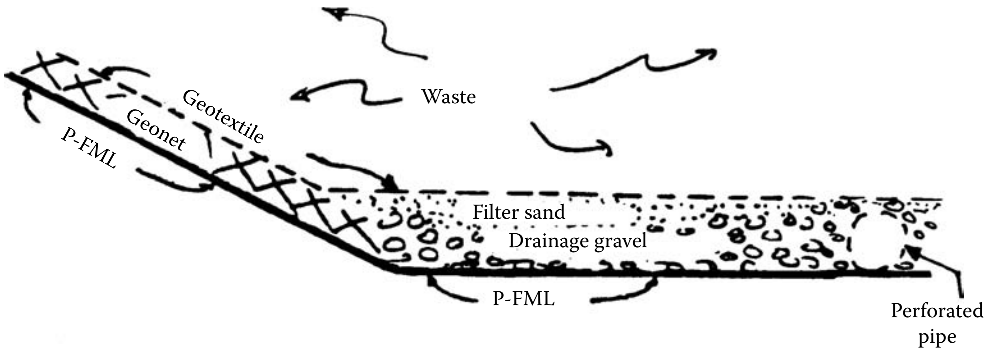


FIGURE 26.24 Cross section of primary leachate collection systems. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.4.2.1 Granular Soil (Gravel) Drainage Design

The MTG regulations require that granular soil drainage materials must[5]

- Be 30 cm (12 in.) thick
- Have 1 cm/s (2 ft/min) permeability (hydraulic conductivity)
- Have a slope greater than 2%
- Include perforated pipe
- Include a layer of filter soil
- Cover the bottom and side walls of the landfill.

To calculate the required flow rate, Q, in granular soil drainage designs based on MTG values:

$$\begin{aligned} Q &= kiA \\ &= (2)(0.02)(1\times 1) \\ &= 0.04\,\text{ft}^3/\text{min}. \end{aligned} \tag{26.11}$$

26.4.2.2 Perforated Collector Pipe Design

The original perforated collector pipes in landfills were made of concrete like those used in highway underdrain systems. As landfills became higher, the strength of such pipes became inadequate. Today, perforated PVC pipes are commonly used, as are HDPE pipes. New regulations require that all materials be tested for chemical resistance as part of the permit-approval process.

The three steps in designing perforated collector pipes are as follows:

1. Obtain the required flow.[14]
2. Obtain the required pipe size using the required flow and the maximum slope.[31]
3. Check the pipe strength and obtain its ring deflection to determine tolerance against crushing.[32]

26.4.2.3 Geonet Drainage Design

Table 26.6 presents a compilation of various geonets. The structure and properties of each are also identified. Geonets used in drainage design must be chemically resistant to the leachate, support the

TABLE 26.6
Types and Physical Properties of Geonets (All are PE)

Manufacturer/ Agent	Product Name	Structure	Roll Size (ft)	Width/ Length (m)	Thickness		Approximately (in.)	Aperture Size (mm)
					(mil)	(mm)		
Carthage Mills	FX-2000 Geo-Net	Extruded ribs	7.5/300	2.3/91	200	5.1		
	FX-2500 Geo-Net	Extruded ribs	7.5/300	2.3/91	250	6.3		
	FX-3000 Geo-Net	Extruded ribs	7.5/220	2.3/67	300	7.6		
Conwed Plastics	XB8110	Extruded ribs	6.9/300	2.1/91	250	6.3	0.3 × 0.3	8 × 8
	XB8210	Extruded ribs	6.9/300	2.1/91	160	4.1	0.35 × 0.35	9 × 9
	XB8310	Extruded ribs	6.9/300	2.1/91	200	5.1	0.3 × 0.4	8 × 10
	XB8410	Extruded ribs	6.9/220	2.1/67	300	7.6	0.25 × 0.25	6 × 6
	XB8315CN	Extruded ribs	6.9/300	2.1/91	200	5.1	0.3 × 0.3	8 × 8
Fluid Systems Inc.	TN-1001	Extruded ribs	7.5/300	2.3/91	250	6.3		
Tex-Net (TN)	TN-3001	Extruded ribs	7.5/300	2.3/91	200	5.1		
	TN-4001	Extruded ribs	7.5/300	2.3/91	300	7.6		
	TN-3001 CN	Extruded ribs	7.5/300	2.3/91	200	5.1		
Poly-Net (PN)	PN-1000	Foamed and extruded ribs	6.75/300	2.0/91	250	6.3	0.3 × 0.3	8 × 8
	PN-2000	Extruded ribs	6.75/300	2.0/91	160	4.1	0.3 × 0.4	9 × 9
	PN-3000	Extruded ribs	6.75/300	2.0/91	200	5.1	0.35 × 0.35	8 × 10
	PN-4000	Foamed and extruded ribs	6.75/300	2.0/91	300	7.6	0.25 × 0.25	6 × 6
Geosynthetics	GSI Net 100	Foamed and extruded ribs	—	—	250	6.3		
	GSI Net 200	Extruded ribs	—	—	160	4.1		
	GSI Net 300	Extruded ribs	—	—	200	5.1		
Gundle	Gundnet XL-1	Extruded ribs	6.2/100	1.9/30	250	6.3	0.3 × 0.3	8 × 8
	Gundnet XL-3	Extruded ribs	6.2/100	1.9/30	200	5.1	0.3 × 0.3	8 × 8
Low Brothers	Lotrak 8	Extruded mesh	6.6/164	2.0/50	120	3.0	0.3 × 0.3	8 × 9
	Lotrak 30	Extruded mesh	6.6/164	2.0/50	200	5.2	1.2 × 1.2	30 × 27
	Lotrak 70	Extruded mesh	6.6/164	2.0/50	290	7.3	2.8 × 2.8	70 × 70
Tenax	CE 1	Extruded ribs	4.8/66	1.5/20	250	6.3	0.3 × 0.25	8 × 6
	CE 2	Extruded ribs	7.4/82	3.8/25	200	5.1	0.3 × 0.35	9 × 9
	CE 3	Extruded ribs	7.4/82	2.2/25	160	4.1	0.3 × 0.25	8 × 6
	CE 600	Extruded ribs	5.5/100	1.67/30.5	160	4.1	0.3 × 0.25	8 × 6
Tensar	DN1-NS1100	Extruded ribs	5.2/98	1.6/30	220	5.6	0.3 × 0.3	8 × 8
	DN3-NS1300	Extruded ribs	6.2/98	1.9/30	150	3.8	0.3 × 0 3	8 × 8
	-NS1400	Extruded ribs	6.2/98	1.9/30	200	5.1	0.3 × 0.3	8 × 8

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

entire weight of the landfill, and be evaluated by the ASTM test D4716[33] with regard to allowable flow rate or transmissivity. This allowable value must then be compared with the required value in the design-by-function equation presented earlier.

In the D4716 flow test,[33] the proposed collector cross section should be modeled as closely as possible. The candidate geonet will usually be sandwiched between an FML beneath and a geotextile above. Soil, perhaps simulating the waste, is placed above the geotextile, and the load platen from the test device are placed above the soil. Applied normal stress is transmitted through the entire system. Then planar flow, at a constant hydraulic head, is initiated and the flow rate through the geonet is measured.

The required flow rate can be calculated (1) directly from MTG or (2) on the basis of surface water inflow rate. To be conservative, all three calculations should be performed and the worst-case situation (e.g., that with the highest flow rate) used for the required flow rate. The various equations for determining the required flow rate or transmissivity appear below:

1. Geonet must be equivalent to MTG regulations for natural materials:

$$\theta > 2\ \mathrm{ft^3/min\text{-}ft}.$$

2. Based on surface water inflow[14]

$$Q = CIA \tag{26.12}$$

where Q is the surface water inflow, C is the runoff coefficient, I is the average runoff intensity, and A is the surface area.

Generally, geonets result in high factors of safety or DRs, unless creep becomes a problem or if adjacent materials intrude into the apertures.

26.4.2.4 Granular Soil (Sand) Filter Design

There are three parts for an analysis of a sand filter to be placed above drainage gravel. The first determines whether or not the filter allows adequate flow of liquids through it. The second evaluates whether the void spaces are small enough to prevent solids being lost from the upstream materials. The third part estimates the long-term clogging behavior of the filter.

In the design of granular soil (sand) filter materials, the particle-size distribution of the drainage system and that of the invading (or upstream) soils is required. The filter material should have its

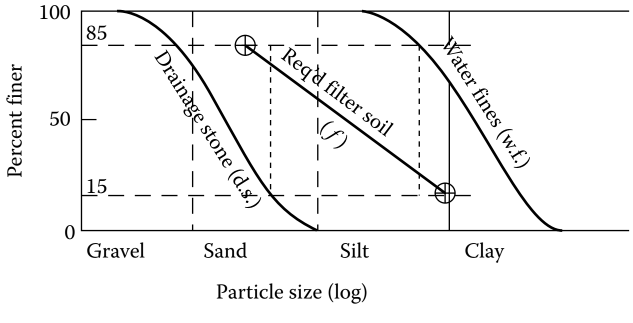


FIGURE 26.25 Design based on particle-size curves. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

large and small size particles intermediate between the two extremes (see Figure 26.25). Adequate flow and adequate retention are the two focused design factors, but perhaps the most important is clogging. There is no quantitative method to assess soil filter clogging, although empirical guidelines are found in geotechnical engineering references.

26.4.2.5 Geotextile Filter Design

Geotextile filter design parallels sand filter design with some modifications. The three elements of adequate flow, soil retention, and clogging prevention remain the same.

Adequate flow is assessed by comparing the allowable permittivity with the required permittivity. Allowable permittivity uses the ASTM D4491 test method,[34] which is well established. The required permittivity utilizes an adapted form of Darcy's law. The resulting comparison yields a DR, or FS, that is the focus of the design.[5]

$$\mathrm{DR} = \frac{\Psi_{\mathrm{allow}}}{\Psi_{\mathrm{reqd}}} \tag{26.13}$$

where Ψ_{allow} is the permittivity from ASTM Test D4491, $\Psi_{\mathrm{reqd}} = (Q/A)(1/h_{\mathrm{max}})$, Q/A is the inflow rate per unit area, and $h_{\mathrm{max}} = 12$ in.

The second part of the geotextile filter design is determining the opening size necessary for retaining the upstream soil or particulates in the leachate. It is well established that the 95% opening size is related to the particles to be retained in the following type of relationship.

$$\mathrm{O}_{95} < \mathrm{fct.}(\mathrm{d}_{50}, \mathrm{CU}, \mathrm{D}_{\mathrm{R}}) \tag{26.14}$$

where $\mathrm{O}_{95} = 95\%$ opening size of geotextile (U.S. Army Corps of Engineers CW 02215 test method),[35] $\mathrm{d}_{50} = 50\%$ size of upstream particles, CU is the uniformity of the upstream particle sizes, and D_{R} is the relative density of the upstream particles.

The O_{95} size of a geotextile in the equation is the opening size at which 5% of a given size glass bead passes through the fabric. This value must be less than the particle-size characteristics of the invading materials. In the test for the O_{95} size of the geotextile, a sieve with a very coarse mesh in the bottom is used as a support. The geotextile is placed on top of the mesh and is bonded to the inside so that the glass beads used in the test cannot escape around the edges of the geotextile. This particular test determines the O_{95} value. To verify the FS for particle retention in the geotextile filter, the particle-size distribution of retained soil is compared with the allowable value using any of a number of existing formulae.

The third consideration in geotextile design is long-term clogging. The test method adopted by ASTM is called the Gradient Ratio Test. It was originally formulated by the U.S. Army Corps of Engineers and is listed in CW 02215. In the test, the hydraulic gradient of 1 in. of soil plus the underlying geotextile is compared with the hydraulic gradient of 2 in. of soil. If the gradient ratio is <3, the geotextile will probably not clog. If the gradient ratio is >3, the geotextile will probably clog. An alternate to this procedure is a long-term column flow test that is also performed in a laboratory. The test models a given soil-to-fabric system at the anticipated hydraulic gradient. The flow rate through the system is monitored. A long-term flow rate at a constant value indicates an equilibrium between the soil and the geotextile system. If clogging occurs, the flow rate will gradually decrease until it stops altogether.

26.4.2.6 Leachate Removal Systems

Figure 26.26 shows a low-volume sump in which the distance from the upper portion of the concrete footing to the lower portion is ~1 ft. One foot is an important design number because U.S. EPA regulations specify a maximum leachate head of 1 ft. Low-volume submersible sumps present

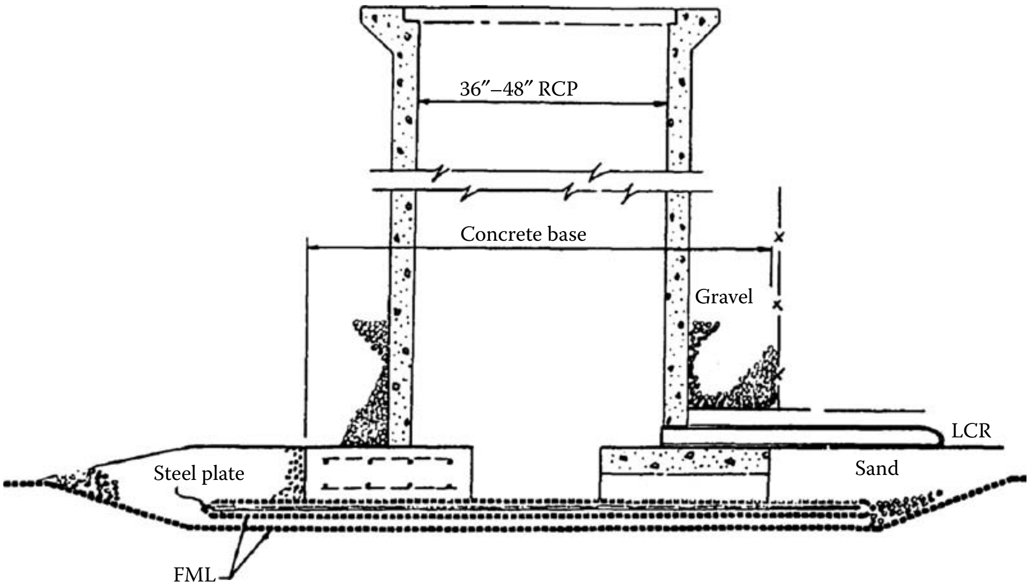


FIGURE 26.26 Leachate removal system with a low-volume sump. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

operational problems, however. Since they run dry most of the time, there is a likelihood of their burning out. For this reason, landfill operators prefer to have sumps with depths between 3 and 5 ft instead of 1 ft (Figure 26.27), even though the leachate level in a high-volume sump will be greater than the 1-ft maximum.

The leachate removal standpipe must be extended through the entire landfill from liner to cover and then through the cover itself. It must also be maintained for the entire postclosure care period of 30 years or longer.

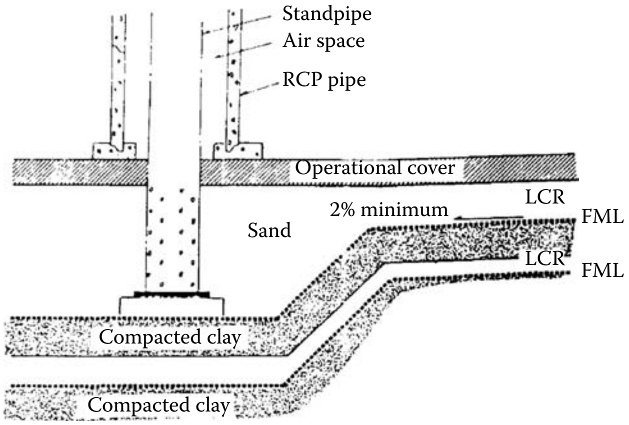


FIGURE 26.27 Leachate removal system with a high-volume sump. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.4.3 LDCR Systems

The LDCR system is located between the primary and secondary liners in landfills, surface impoundments, and waste piles. It can consist of either granular soils (i.e., gravels) or geonets.

26.4.3.1 Granular Soil (Gravel) Drainage Design

As with the primary leachate collection system above the liner, LDSs between liners are designed by comparing allowable flow rates with required flow rates. The allowable flow is evaluated as discussed in the section on granular soil (gravel) drainage design for PLCR systems. The required flow is more difficult to estimate. This value might be as low as 1 gallon/acre/day or many times that amount. It is site specific and usually is a rough estimate. Past designs have used 100 gal/acre/day for the required flow rate. Data from the field monitoring of response action plans (RAPs) will eventually furnish more realistic values. A pipe network for leachate removal is required when using granular soils.

26.4.3.2 Geonet Drainage Design

For a geonet LDCR system, the flow rate for the geonet is determined in the laboratory by using the ASTM D4716 test method, and the value is modified to meet site-specific situations. The geonet flow rate DR is then determined in the same way as for the granular system. No pipe network is needed.

A concern when using geonets with a composite primary liner design is the effect of geotextile intrusion and creep on the allowable flow rate. In composite primary liner systems, the geonet is placed immediately below a clay liner with a geotextile as an intermediate barrier. The design of this geotextile is important because clay particles can go through large voids in an open woven geotextile, necessitating the use of a needle-punched nonwoven geotextile of at least 8–10 oz/yd^2. Even with this precaution, the laboratory test to evaluate the allowable flow rate should simulate the anticipated cross section in every detail.

26.4.3.3 Response Time

U.S. EPA specifies that the minimum detection time for the leachate entering the LDS of an LDCR system is <24 h. Response time calculations are based on velocity in the geonet and/or granular soil drainage layer. Darcy's law is used to calculate flow velocity in the geonet, and a "true" velocity must be used for granular soil.

26.4.3.4 Leak Detection Removal Systems

LDRS require monitoring, sampling, and leachate removal. Any leachate that penetrates the primary liner system and enters the secondary system must be removed. During construction, the LDCR system may accept runoff water, but once the landfill is in operation it only removes any leakage coming through the primary liner. The most common removal system consists of a relatively large diameter pipe running down the side wall between the primary and secondary liners to the low point (sump) in the LDCR. The pipe must penetrate the primary liner at the top. A submersible pump is lowered through the pipe periodically for "questioning" of the quantity of fluid coming into the system. The choice of monitoring and retrieval pump depends on the quantity of leachate being removed.

An alternate system, one based on gravity, requires penetration of both the FML and clay components of the secondary composite liner system. It also requires a monitoring and collection manhole on the opposite side of the landfill cell. The manhole and connecting pipe, however, become an underground storage tank that needs its own secondary containment and LDSs.

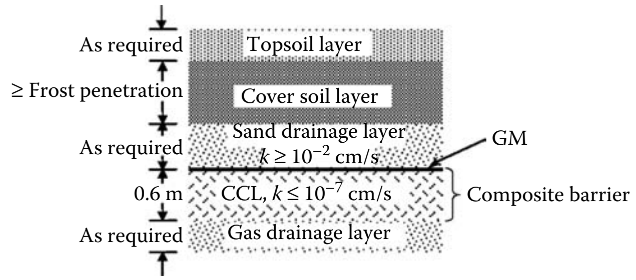


FIGURE 26.28 Final cover system. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.4.4 SWCR Systems

The third part of liquids management is the SWCR system. It is placed on top of the completed facility and above the cover FML. The rainwater and snowmelt that percolate through the top soil and vegetative cover must be removed to a proper upper drainage system. Figure 26.28 illustrates the major components of a surface water-collector system. The design quantity for the amount of fluid draining into the surface water-collector system can be determined by either a water balance method or the computer program HELP (Hydrologic Evaluation Landfill Performance Model)[36,37] (see Figure 26.29).

Surface water drainage systems can be composed of granular soils, geonets, or geocomposites, but the majority of drainage systems use granular soil. This is particularly true in frost regions where it is necessary to have 3–6 ft of soil above the FML to satisfy the requirements for frost

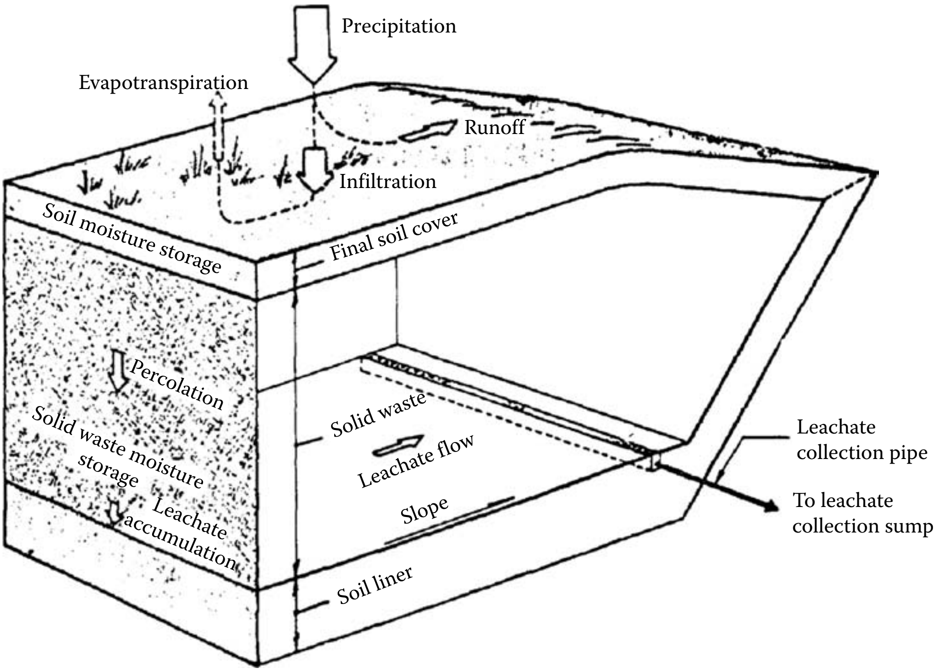


FIGURE 26.29 Design methodology to estimate cover soil infiltration into the SWCR system. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

penetration. In such cases, 1 ft of granular soil thickness can serve as the surface water collector. If good drainage materials are not available, if the site is too extensive, or if natural materials would add undesired thickness, a geonet or geocomposite can be used. The advantage of drainage geocomposites is their higher flow rate capabilities over geonets or granular soils. All geocomposites systems have polymer cores protected by a geotextile filter. Although many of the polymers cannot withstand aggressive leachates, this is not an issue in a surface drainage collector where the only contact is with water. The crush strengths of the geocomposites are generally lower than that of geonets, but that too is not a problem in a surface water collector. The heaviest load the geocomposite would be required to support probably would be construction equipment used to place the cover soil and vegetation on the closed facility.

The design for the surface water-collector system is determined by an allowable flow rate divided by a required flow rate. Allowable rates for geocomposites are determined experimentally by exactly the same method as for geonets. The specific cross section used in the test procedure should replicate the intended design as closely as possible. For the required flow rate, Darcy's law or HELP[36,37] can be used. Then the design-by-function concept is used to determine the DR, or FS.

$$\text{DR} = \text{FS} = \frac{q_{\text{allowable}}}{q_{\text{required}}} \tag{26.15}$$

26.4.5 GAS COLLECTOR AND REMOVAL SYSTEMS

Degradation of solid waste materials in a landfill proceeds from aerobic to anaerobic decomposition very quickly, thereby generating gases that collect beneath the closure FML. Almost 98% of the gas produced is either carbon dioxide (CO_2) or methane (CH_4). Because CO_2 is heavier than air, it will move downward and be removed with the leachate. However, CH_4, representing about 50% of the generated gas, is lighter than air and, therefore, will move upward and collect at the bottom of the facility's "impermeable" FML. If the gas is not removed, it will produce a buildup of pressure on the FML from beneath.

In gas-collector systems, either a granular soil layer or a needle-punched nonwoven geotextile is placed directly beneath the FML or clay of a composite cap system. Gas compatibility and air transmissivity are the design factors that must be considered. Methane, the most predominant gas, should be compatible with most types of geotextiles including PET, PP, and PE.

The thickness design should be based on gas transmissivity tests. Since water has a viscosity that is 1000–10,000 times that of gas, q_{allow} for gas flow should compare very favorably with the results of a water transmissivity test. Alternatively, one could look directly at permeability coefficients where geotextile air flow is several orders of magnitude greater than the MTG-required values. In the test method, the geotextile specimen fits underneath a load bonnet. Then the load, equivalent to the cover soil, is added and gas is brought to the inside of the geotextile. The gas flows through the geotextile and into a shroud that goes on the outside of the flanges and registers on an air meter. The resulting applied stresses, gas pressures, and gas permeabilities are then recorded and, if necessary, converted into gas transmissivity. The allowable gas transmissivity is then divided by the required gas transmissivity to yield the DR, or FS.

Gas generation occurs over a period of 70–90 years, so gas-collector and removal systems must work for at least that long to avoid gas pressure on the underside of the cover.

Gas generation might also cause problems in "piggyback" landfills, landfills that have been built on top of one another. It is still unknown what happens to the gas generated in an old landfill after a new liner is placed on top of it. To minimize problems, the old landfill should have a uniform slope and possibly an accordian-pleated bottom cross section. Then the gas could escape from the underside and be collected from the high gradient side of the site.

As seen in Figure 26.30, the details of a gas collection system are quite intricate and yet very important to the proper functioning of the system.

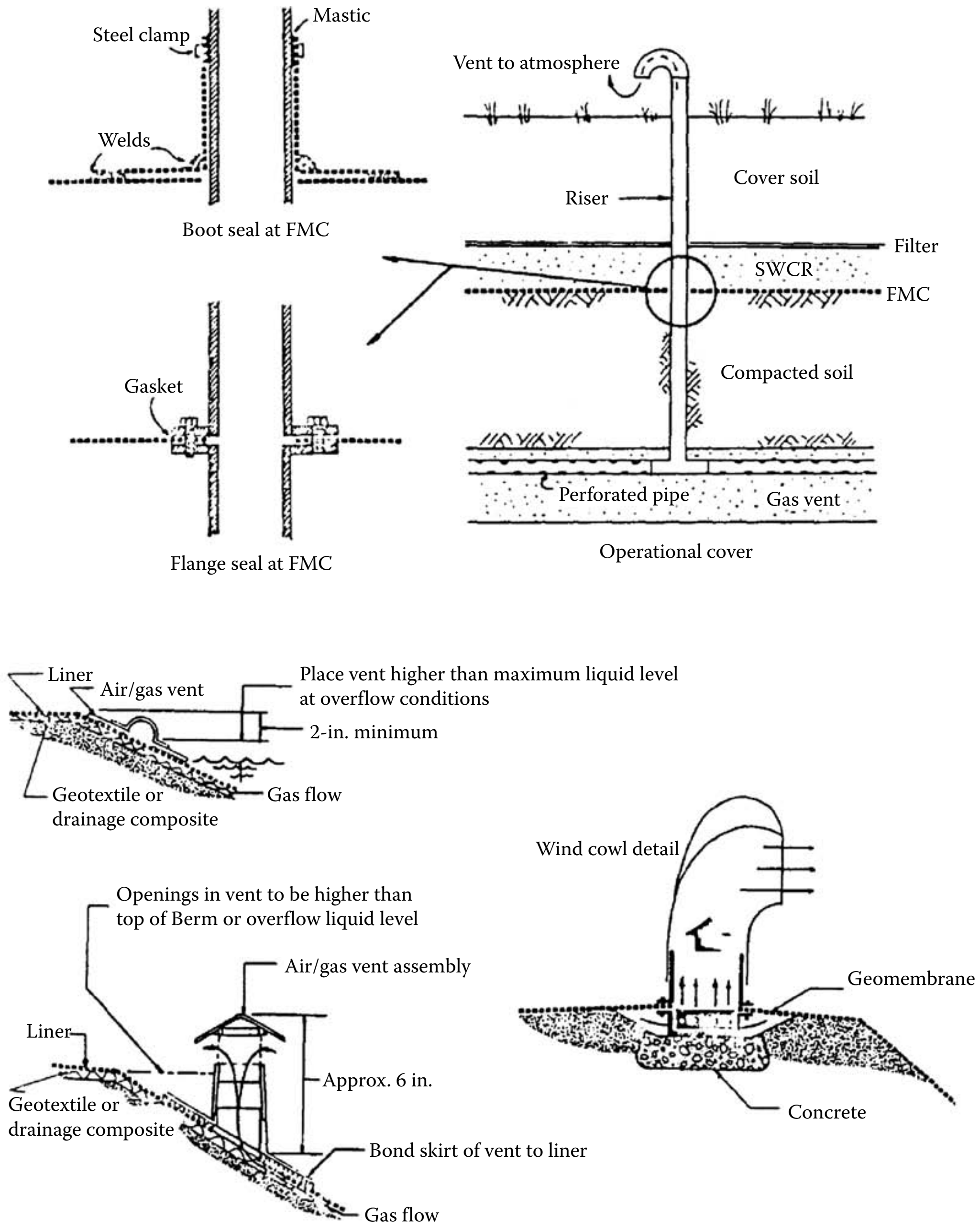


FIGURE 26.30 Miscellaneous details of a gas-collector system. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

26.5 SECURING A COMPLETED LANDFILL

This section describes the elements in a closure or cap system of a completed landfill, including flexible membrane caps (FMCs), SWCR systems, gas control layers, biotic barriers, and vegetative top covers. It also discusses infiltration, erosion control, and long-term aesthetic concerns associated with securing a completed landfill.

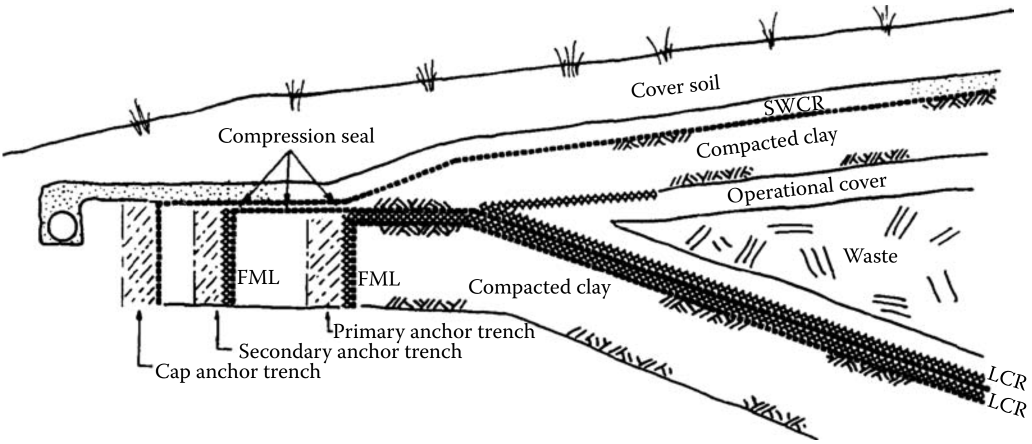


FIGURE 26.31 Typical geosynthetic cell profile. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

Figure 26.31 shows a typical landfill profile designed to meet U.S. EPA's MTG requirements.[38] The upper subprofile comprises the cap, or cover, and includes the required 2-ft vegetative top cover, 1-ft lateral drainage layer, and low-permeability cap of barrier soil (clay), which must be more than 2 ft thick. This three-tier system also includes an optional FMC and an optional gas control layer. The guidance requires a 40-mil thick FMC.

26.5.1 Flexible Membrane Caps

FMCs are placed over the low-permeable clay cap and beneath the SWCR system. FMCs function primarily in keeping surface water off the landfill and increasing the efficiency of the drainage layer. U.S. EPA leaves operators with the option of choosing the synthetic material for the FMC that will be most effective for site-specific conditions. In selecting materials, operators should keep in mind several distinctions between FMLs and FMCs. Unlike an FML, an FMC is usually not exposed to leachate; so chemical compatibility is not an issue. Membrane caps also have low normal stresses acting on them in comparison with FMLs, which generally carry the weight of the landfill. An advantage FMCs have over liners is that they are much easier to repair, because their proximity to the surface of the facility makes them more accessible. FMCs will, however, be subject to greater strains than FMLs due to settlement of the waste.

26.5.2 SWCR Systems

The SWCR system is built on top of the FMC. The purpose of the SWCR system is to prevent infiltration of surface water into the landfill by containing and systematically removing any liquid that collects within it. Actual design levels of surface water infiltration into the drainage layer can be calculated using the water balance equation or the HELP model.[36,37]

Errors in grading the perimeter of the cap often integrates (or cross-connects) the SWCR system with the secondary LDRS, resulting in a significant amount of water infiltrating the secondary detection system. This situation should be remedied as soon as possible if it occurs. Infiltration of surface water is a particular concern in nuclear and hazardous waste facilities, where gas vent stacks are found. A containment system should be designed to prevent water from entering the system through these vents.

In designing an SWCR system above an FMC, three issues must be considered[5]:

1. Cover stability.
2. Puncture resistance.
3. The ability of the closure system to withstand considerable stresses due to the impact of settlement.

26.5.2.1 Cover Stability

The stability of the FMC supporting the SWCR system can be affected by the materials used to construct the drainage layer and by the slope of the site. In some new facilities, the drainage layer is a geonet placed on top of the FMC, with the coefficient of friction between those two elements being as low as 8–10°. Such low friction could allow the cover to slide. One facility at the Meadowlands in New Jersey is constructed on a high mound having side slopes steeper than 2:1. To ensure adhesion of the membrane to the side slopes of the facility, a nonwoven geotextile was bonded to both sides of the FMC.

26.5.2.2 Puncture Resistance

FMCs must resist penetration by construction equipment, rocks, roots, and other natural phenomena. Traffic by operational equipment can cause serious tearing. A geotextile placed on top of or beneath a membrane increases its puncture resistance by 3 or 4 times. Remember, however, that a geotextile placed beneath the FMC and the clay layer will destroy the composite action between the two. This will lead to increased infiltration through penetrations in the FMC.

26.5.2.3 Impact of Settlement

The impact of settlement is a major concern in the design of the SWCR system. A number of facilities have settled 6 ft in a single year, and 40 ft or more over a period of years.[5] The Meadowlands site in New Jersey, for example, was built at a height of 95 ft, settled to 40 ft, and then was rebuilt to 135 ft. Uniform settlement can actually be beneficial by compressing the length of the FMC and reducing tensile strains. However, if waste does not settle uniformly, it can be caused by interior berms that separate waste cells.

In one current closure site in California, a waste transfer facility with an 18-ft wall is being built within a 30-ft trench on top of a 130-ft high landfill. The waste transfer facility will settle faster than the adjacent area, causing tension at the edge of the trench. Electronic extensometers are proposed at the tension points to check cracking strains in the clay cap and FMC.

Settlements can be estimated, although the margin for error is large. Secure commercial hazardous waste landfills have the smallest displacement, <1.5%. Displacements at new larger solid waste landfills can be estimated at 15%, while older, unregulated facilities with mixed wastes have settlements of up to 50%.

26.5.3 GAS CONTROL LAYER

Gas-collector systems are installed directly beneath the low-permeability clay cap in a hazardous waste landfill. Landfills dedicated to receiving only hazardous wastes are relatively new and gas has never been detected in these systems. It may take 40 years or more for gas to develop in a closed secure hazardous waste landfill facility. Because the long-term effects of gas generation are not known, and costs are minimal, U.S. EPA strongly recommends the use of gas-collector systems.

Figure 26.30 shows details of a gas vent pipe system. The two details at the top left of the illustration show close-ups of the boot seal and flange seals located directly at the interface of the SWCR system with the FMC. To keep the vent operating properly, the slope of the closure system should

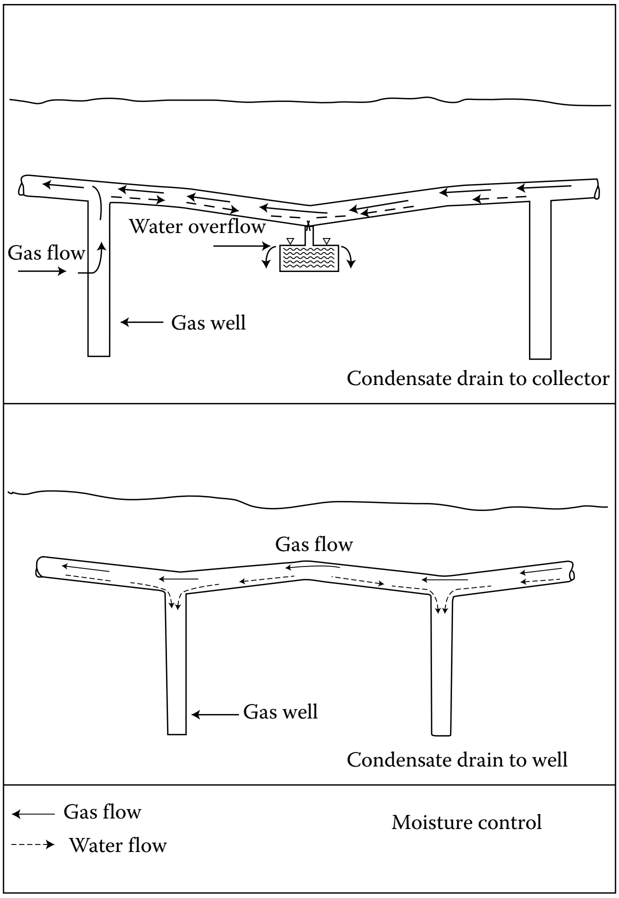


FIGURE 26.32 Water traps in a gas-collector system. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

never be less than 2%; 5–7% is preferable. A potential problem with gas-collector systems is that a gas venting pipe, if not properly maintained, can allow surface water to drain directly into the landfill waste.

Figure 26.32 illustrates two moisture control options in gas-collector systems. Gas-collector systems will tolerate a large amount of moisture before air transmissivity is affected. Condensates from the gas-collector layer that form beneath the clay and FMC can also be taken back into the waste, since most hazardous wastes are deposited very dry.

26.5.4 Biotic Barriers

A biotic barrier is a gravel and rock layer designed to prevent the intrusion of burrowing animals into the landfill area. This protection is primarily necessary around the cap but, in some cases, may also be needed at the bottom of the liner. Animals cannot generally penetrate an FMC, but they can widen an existing hole or tear the material where it has wrinkled.

Figure 26.33 shows the gravel filter and cobblestone components of the biotic barrier and their placement in the landfill system. The proposed 1-m thickness for a biotic barrier should effectively prevent penetration by all but the smallest insects. Note that the biotic barrier also serves as the surface water collection/drainage layer. Biotic barriers used in nuclear caps may be up to 14 ft thick

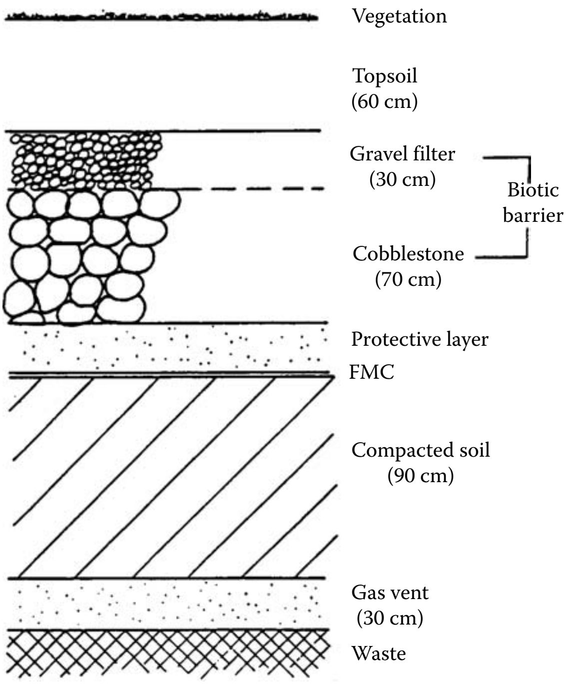


FIGURE 26.33 Optional biotic barrier layer. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

with rocks several feet in diameter. These barriers are designed to prevent disruption of the landfill by humans both now and in the future.

26.5.5 VEGETATIVE LAYER

The top layer in the landfill profile is the vegetative layer. In the short term, this layer prevents wind and water erosion, minimizes the percolation of surface water into the waste layer, and maximizes evapotranspiration, the loss of water from soil by evaporation and transpiration. The vegetative layer also functions in the long term to enhance aesthetics and to promote a self-sustaining ecosystem on top of the landfill. The latter is of primary importance because facilities may not be maintained for an indefinite period of time by either government or industry.

Erosion can seriously effect a landfill closure by disrupting the functioning of drainage layers and surface water and LCRSs. Heavy erosion could lead to the exposure of the waste itself. For this reason, it is important to predict the amount of erosion that will occur at a site and reinforce the facility accordingly. The Universal Soil Loss Equation shown below can be used to determine soil loss from water erosion[5]:

$$X = RKSLCP \tag{26.16}$$

where X is the soil loss, R is the rainfall erosion index, K is the soil erodibility index, S is the slope gradient factor, L is the slope length factor, C is the crop management factor, and P is the erosion control practice.

Figure 26.34 can be used to find the soil loss ratio due to the slope of the site as used in the Universal Soil Loss Equation. Loss from wind erosion can be determined by the following equation:

$$X' = I'K'C'L'V' \tag{26.17}$$

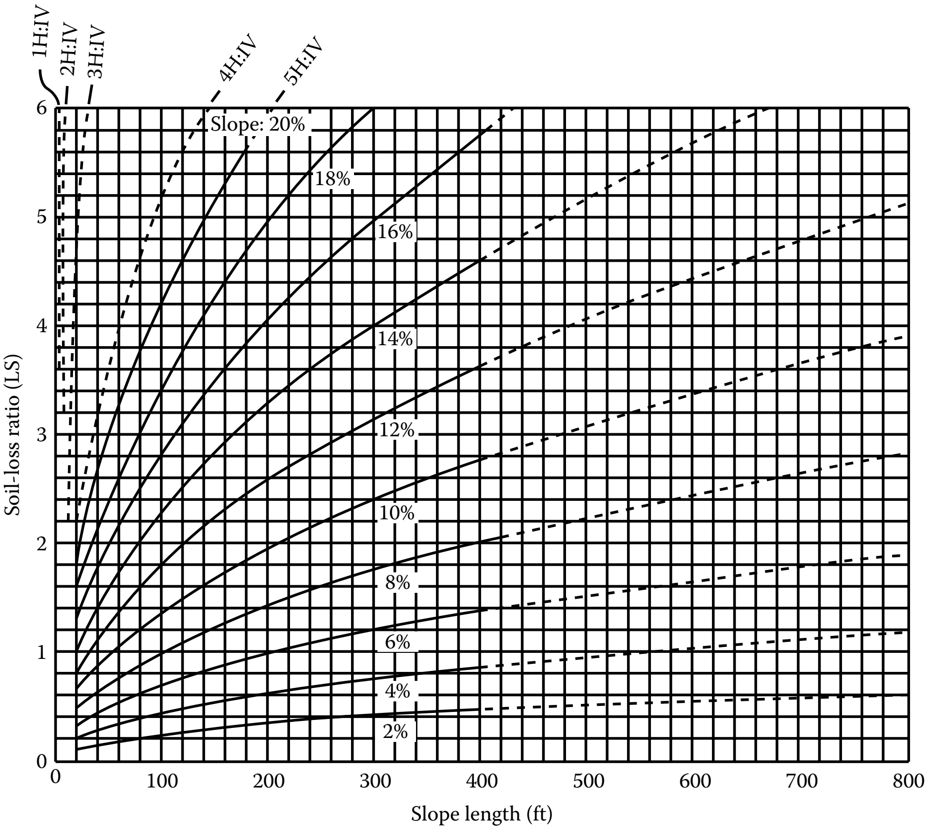


FIGURE 26.34 Soil erosion due to slope. (Adapted from U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.)

where X' is the annual wind erosion, I' is the field roughness factor, K' is the soil erodibility index, C' is the climate factor, L' is the field length factor, and V' is the vegetative cover factor. There are many problems in maintaining an agricultural layer on top of a landfill site, especially in arid or semiarid regions. An agricultural layer built on an SWCR system composed of well-drained stone and synthetic material may have trouble supporting crops of any kind because the soil moisture is removed. In arid regions, a continuous sprinkler system may be needed to maintain growth on top of the cap, even if the soil is sufficiently deep and fertile. A final problem involves landfills built on slopes greater than 3:1. Equipment necessary to plant and maintain crops cannot operate on steeper slopes.

Operators should contact their local agricultural extension agent or State Department of Transportation to find out what kinds of vegetation will grow under the conditions at the site. The impact of the SWCR system on the soil layer should also be studied before vegetation is chosen. Usually native grasses are the best choice because they are already adapted to the surrounding environment. Sometimes vegetation can overcome adverse conditions, however. At one site in the New Jersey Meadowlands, plants responded to excess surface water by anchoring to the underlying waste through holes in an FMC, creating a sturdy bond between surface plants and underlying material.

For sites on very arid land or on steep slopes, an armoring system, or hardened cap, may be more effective than a vegetative layer for securing a landfill. Operators should not depend on an agricultural layer for protection in areas where vegetation cannot survive. Many States allow asphalt caps as an alternative to vegetative covers. Some closures at industrial sites have involved constructing hardened cap "parking lots" on top of the cap membrane and clay layers. A chip seal layer over the asphalt prevents ultraviolet degradation of the pavement. These caps, however, need to be maintained and resealed every 5 years. At some sites, a fabric incorporated into the top of the asphalt minimizes cracking and water intrusion.

26.5.6 OTHER CONSIDERATIONS

Filter layers, frost penetration, and cap-liner connections are other factors to consider in designing the closure system for a hazardous waste landfill. Before using geotextiles for filter layers in closures, one should conduct pressure tests and clogging tests on the material. Freeze–thaw cycles probably have little effect on membranes, but their impact on clay is still not known. Because of this lack of knowledge, membrane and clay layers should be placed below the frost penetration layer. Finally, a cap membrane should not be welded to the primary FML. Differential settlement in the cap can put tension on the cap membrane. In such a situation, the seam could separate and increase the potential for integration of the surface water collection system into the LDS.

26.6 LINER COMPATIBILITY WITH WASTES

This section discusses chemical compatibility (resistance) of geosynthetic and natural liner materials with wastes and leachates. Even in a relatively inert environment, certain materials deteriorate over time when exposed to chemicals contained in both hazardous and nonhazardous leachate. It is important to anticipate the kind and quality of the leachate a site will generate and select liner materials accordingly. The chemical resistance of any FML materials, geonets, geotextiles, and pipe should be evaluated before installation.[39]

Chemical compatibility tests using U.S. EPA Method 9090[40] should always be performed for hazardous waste sites, but some municipal waste sites also contain hazardous, nondegradable materials. U.S. EPA conducted a 5-year study of the impact of municipal refuse on commercially available liner materials and found no evidence of deterioration within that period. However, in a current study of leachate quality in municipal landfills, the Agency has discovered some organic chemical constituents normally found in hazardous waste landfill facilities. Apparently, small quantities of household hazardous waste enter municipal sites or are disposed of as small quantity generator wastes. As a result of these findings, U.S. EPA developed a position on the need for chemical compatibility tests for thousands of municipal waste disposal sites.

In general, cover materials, including membranes and geosynthetics, do not need to be checked for chemical compatibility since these materials do not encounter leachates. Research data indicate that the predominant gases coming from municipal sites are methane, hydrogen, and carbon dioxide, although a few others may be emitted from household hazardous waste. These gases pass through cover materials by diffusion, and evidence to date indicates that they have caused no deterioration of membranes. Also, chemical compatibility of cover materials with gases has not been a major problem at hazardous waste facilities.

A primary objective of chemical compatibility testing is to ensure that liner materials will remain intact not just during a landfill's operation but also through the postclosure period, and preferably longer. It is difficult, however, to predict future chemical impacts. There is no guarantee that liner materials selected for a site today will be the same as materials manufactured 20 years from now. For example, the quality of basic resins has improved considerably over the last few years.

The wastes themselves also change over time. Tests should be performed to ensure that landfill leachate will not permeate the liner layer. U.S. EPA recommends a variety of physical property degradation tests, including a fingerprint program of thermogravimetric analysis (TGA), differential scanning calorimetric tests, and infrared analysis. Fingerprinting involves analyzing the molecular structure of the leachate components. Sometimes, a particularly aggressive leachate component can be identified by evaluating the fingerprint analysis tests after exposure of the membrane to the leachate.

26.6.1 EXPOSURE CHAMBER

The first area of concern in chemical compatibility testing is the exposure chamber used to hold the leachate and membranes being tested. The exposure chamber tank can be made of stainless steel, PE, glass, or a variety of other materials. Any geosynthetic liner material being considered must be tested for chemical compatibility with the leachate. Some leachates have caused rusting and deterioration of stainless steel tanks in the past, and if PE is being evaluated, the tank should be of another type of material to prevent competition between the tank material and the test specimen for aggressive agents in the leachate.

The conditions under which the material is tested are crucial. The top of the exposure chamber must be sealed and the tank should contain no free air space. A stirring mechanism in the tank keeps the leachate mixture homogeneous and a heater block keeps it at an elevated temperature as required for the test. Stress conditions of the material in the field should also be simulated as closely as possible. The original U.S. EPA Method 9090 test included a rack to hold specimens under stress conditions but was revised when some materials shrank in the leachate. Due to the hazardous nature of the material, testing should be performed in a contained environment and safety procedures should be rigorously followed.

In some cases, a sump at the waste management facility can be used as an exposure chamber if it is large enough. The designer of a new landfill site can design a slightly larger sump especially for this purpose. However, since the temperature of a sump is colder than room temperature (55°F instead of 72°F), the geosynthetics need to be exposed for a longer period of time. Instead of 120 days, the test might take 6 months to a year or longer.

26.6.2 REPRESENTATIVE LEACHATE

It is important that the sample being tested is representative of the leachate in the landfill. Leachate sampled directly from a sump is usually representative, but care must be taken not to mix it during removal. This will disturb the sample's homogeneity and may result in components separating out. Another problem is that municipal solid waste landfill leachate will start oxidizing as soon as it leaves the sump and should probably be sampled under an inert atmosphere.

A sampler should be familiar with the source of all the leachates at a site before removing a sample. If radioactive materials are present, extra care must be taken.

At some existing waste management facilities, operators have placed coupons of geosynthetic materials into sump areas to monitor leachate effects. Information gathered from this monitoring procedure provides an excellent database. Regular recording of data allows the operator to discover compatibility problems as they develop, rather than waiting until a landfill liner fails. If the coupon shows early signs of deterioration, the operator can respond immediately to potential problems in the facility.

26.6.3 COMPATIBILITY TESTING OF COMPONENTS GEOSYNTHETICS

U.S. EPA's Method 9090[40] can be used to evaluate all geosynthetic materials used in liner and LCRSs currently being designed. Method 9090 is used to predict the effects of leachate under field conditions and has been verified with limited field data. The test is performed by immersing a geosynthetic in a chemical environment for 120 days at two different temperatures: room and elevated temperature. Every 30 days, samples are removed and evaluated for changes in physical properties. Tests performed on FMLs are listed in Table 26.7. The results of any test should be cross-referenced to a second, corollary test to avoid errors due to the test itself or to the laboratory personnel.

Physical property tests on geotextiles and geonets must be designed to assess different uses, weights, and thicknesses of these materials, as well as construction methods used in the field. Some tests for geonets and geotextiles recommended by U.S. EPA are listed in Table 26.8.

TABLE 26.7
Compatibility Tests for FMLs

Name of Test
Hardness
Melt index
Extractibles
Volatile loss
Peel adhesion
Tear resistance
Specific gravity
Low temperature
Water absorption
Puncture resistance
Dimensional stability
Modulus of elasticity
Bonded seam strength
Hydrostatic resistance
Carbon black dispersion
Thickness, length, width
Tensile at yield and break
Environmental stress crack
Elongation at yield and break

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

TABLE 26.8
Compatibility Tests for Geonets

Name of Test
Puncture
Thickness
Permittivity
Transmissivity
Mass per unit area
Burst strength
Abrasive resistant
Percent open area
Ultraviolet resistivity
Grab tensile/elongation
Equivalent opening size
Hydrostatic bursting strength
Tearing strength (trapezoidal)
Compression behavior/crush strength

Source: U.S. EPA, *Requirements for Hazardous Waste Landfill Design, Construction, and Closure*, EPA/625/4–89/022, U.S. Environmental Protection Agency, Cincinnati, OH, August 1989.

Until recently, U.S. EPA recommended using 1.5 times the expected overburden pressure for in-plane transmissivity tests. Laboratory research, however, has revealed that creep and intrusion cause a loss of transmissivity; so the Agency has amended its recommendation to 2–3 times the overburden pressure. U.S. EPA also recommends that the geotextile or the geonet be aged in leachates, but that the actual test be performed with water. Performing the test with the leachate creates too great a risk of contamination to test equipment and personnel. The transmissivity test should be run for a minimum of 100 h. The test apparatus should be designed to simulate the field conditions of the actual cross section as closely as possible.

26.6.4 PIPES

The crushing strength of pipes should also be tested. There have been examples where pipes in landfills have actually collapsed and thus forced the site to stop operating. The ASTM D2412[41] is used to measure the strength of pipe materials.

26.6.5 NATURAL DRAINAGE MATERIALS

Natural drainage materials should be tested to ensure that they will not dissolve in the leachate or form a precipitant that might clog the system. ASTM D2434[42] will evaluate the ability of the materials to retain permeability characteristics, while ASTM D1883[43] tests for bearing ratio, or the ability of the material to support the waste unit.

26.6.6 INTERPRETING DATA

When liner material test data show the rate of change of the material to be nil over a period of time, then the membrane is probably not undergoing any chemical change. There have been instances, however, in which a material was tested for a year without change and then suddenly collapsed. For this reason, the longer the testing process can continue, the more reliable the data will be. When test data reveal a continuous rate of change, then the material is reacting with the leachate in some way. If the data show an initial continuous rate of change that then tapers off, new leachate may need to be added more often.

A designer should consult with experts to interpret data from chemical compatibility tests. To meet this need, U.S. EPA developed a software system called Flexible Membrane Liner Advisory Expert System (FLEX) to assist in evaluating test data. FLEX is an expert system that is based on data from many chemical compatibility tests and contains interpretations from experts in the field.

NOMENCLATURE

A	Area
c	Concentration of solute in effluent
c_o	Concentration of solute in leachate
C	Runoff coefficient
C	Crop management factor
C'	Climate factor
CU	Uniformity of the upstream particle sizes
d_{50}	50% size of upstream particles
D	Depth
D	Dielectric constant
D_R	Relative density of the upstream particles
DR	Design ratio
FS	Factor of safety
h	Height

H	Head
i	Hydraulic gradient
i	Infiltration rate
I	Average runoff intensity
I'	Field roughness factor
k	Hydraulic conductivity
K	Soil erodibility index
K'	Soil erodibility index
L	Length
L	Slope length factor
L'	Field length factor
L_f	Depth of soaked soil
n	Porosity
n_e	Effective porosity
n_o	Electrolyte concentration
O_{95}	95% opening size of geotextile
P	Erosion control practice
q	Flow rate per unit width for drainage
q'	Flow rate per unit area for filtration
Q	Flow rate
R	Rainfall erosion index
S	Slope gradient factor
S	Trough depth
t	Time
T	Thickness
v	Cation valence
V'	Vegetative cover factor
V_s	Seepage velocity
w	Width
X	Soil loss
X'	Annual wind erosion
θ	Transmissivity
Ψ	Transmissivity for drainage
Ψ'	Permittivity for filtration

ACRONYMS

ALR	Action leakage rate
ASTM	American Society for Testing and Materials
CPE	Chlorinated polyethylene
CQA	Construction quality assurance
CSPE	Chlorylsulfonated polyethylene
DR	Design ratio
DT	Destruct tests
EPDM	Ethylene propylene diene monomer
FLEX	Flexible Liner Evaluation Expert
FMC	Flexible membrane caps
FML	Flexible membrane liner
FS	Factor of safety
GCL	Geosynthetic clay liner
GM	Geomembrane

HDPE	High-density polyethylene
HELP	Hydrologic Evaluation Landfill Performance Model
HSWA	Hazardous and Solid Waste Amendment
LCRS	Leachate collection and removal system
LDCR	Leak detection, collection, and removal
LLDPE	Linear low-density polyethylene
MTG	Minimum technology guidance
MTR	Minimum technological requirements
NDT	Nondestruct tests
PA	Polyamide
PE	Polyethylene
PET	Polyester
PI	Plasticity index
PLCR	Primary leachate collection and removal
PP	Polypropylene
PVC	Polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
SLCR	Secondary leachate collection and removal
SWCR	Surface water collection and removal
TGA	Thermogravimetric analysis
TOT	Time of travel
USDA	U.S. Department of Agriculture
U.S. EPA	U.S. Environmental Protection Agency

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27 Kinetics and Case Histories of Activated Sludge Secondary Flotation Systems

Lawrence K. Wang, Daniel Guss, and Milos Krofta

CONTENTS

27.1 INTRODUCTION

27.1.1 SUMMARY

A description is given of a unique solution for the problems of overloaded conventional activated sludge systems. A high-rate dissolved air flotation (DAF) clarifier is applied in series between the aeration basin and secondary sedimentation in an activated sludge process to separate the living microorganisms before secondary sedimentation. This results in the following improvements in the existing wastewater treatment system:

a. Solids and hydraulic loadings on an overloaded secondary sedimentation are reduced for preventing sludge rising, increasing clarification efficiency, and saving construction cost on expansion of secondary sedimentation facilities.
b. Hydraulic loading on an aeration basin is reduced, thus increasing the retention time without increasing the aeration basin size. This is accomplished by reduced recycle sludge volume due to higher solids content in the recycled sludge.
c. Higher solids content of the wasted sludge represents cost saving and improved operation of sludge thickening, dewatering, and disposal.
d. The living microorganisms, separated by the DAF, are returned to the aeration basin quickly (in less than 15 min). The microorganisms stay in aerobic conditions at all times and are more active than comparable settled microorganisms. Microscopic examinations of settled and floated sludge are made to demonstrate this fact. The oxygen requirement for the mixed liquor suspended solids (MLSS) is also significantly reduced.
e. The problems of sludge rising and sludge bulking can be totally solved when using secondary flotation clarification.

This new concept is applied for improving the operation of an existing overloaded activated sludge plant, or for the expansion of the hydraulic capacity to handle additional wastewater flow.

A pioneering installation of a DAF clarifier (49 ft inside diameter) is described in detail. Pilot-scale results and full-scale design considerations are presented. The newly improved activated sludge process system with a secondary flotation clarifier allows a 50% increase in hydraulic loading to an existing waste treatment plant. Typical applications in treatment of industrial and combined wastewaters for solving sludge rising and bulking problems are introduced and critically discussed.

27.1.2 Problems of an Existing Activated Sludge Wastewater Treatment System

Activated sludge consists of biological flocs that are matrices of microorganisms, nonliving organics, and inorganic substances. The microorganisms include bacteria, fungi, protozoa (Sarcodina, Mastigophora, Sporozoa, Ciliata, and Suctoria), rotifers, viruses, and higher forms of animals such as insect larvae, worms, and crustaceans. The activated sludge process is one of the most common biological wastewater treatment processes, and can be defined as a suspended-growth system in which biological flocs are continuously circulated to come into contact and to oxidize the organic waste substances in the presence of oxygen and nutrients. The waste organic matter is aerobically converted to gaseous carbon dioxide, cell tissue of microorganisms ($C_5H_7NO_2$), and other simple soluble end products. Part of the microorganisms (i.e., activated sludge) are returned to the aeration basin in order to maintain a constant microbial population (i.e., constant MLSS). The wastewater is considered to be adequately treated when the excess microorganisms (i.e., excess waste sludge) and residual suspended solids are separated from the aqueous phase by clarification, and the clarified effluent meets the Federal and State Effluent Standards. The most common clarification used today is sedimentation clarification, which frequently has sludge bulking and sludge rising problems. Hydraulic overloading is another problem of an existing activated sludge wastewater treatment plant, which must serve a growing community.

27.1.3 Application of Secondary Flotation Clarification as an Engineering Solution

The recent and accelerating emphasis on water pollution control has necessitated the rapid development of improved biological waste treatment systems to aid in cost and energy savings. The use of secondary flotation clarification in place of or in assisting secondary sedimentation clarification in the activated sludge process system is one recent advancement in this basic process. The potential of this development, in terms of higher suspended solids and 5-day biochemical oxygen demand (BOD_5) removals from existing plants and expansion of hydraulic capacity at a significantly reduced cost, is expected to result in extremely rapid acceptance by municipalities and industries.

The primary distinguishing feature of the improved activated sludge treatment system is that high-rate DAF is the secondary clarifier for separation of suspended solids from the activated sludge aeration basin effluent, as opposed to secondary sedimentation alone in a conventional activated sludge system.

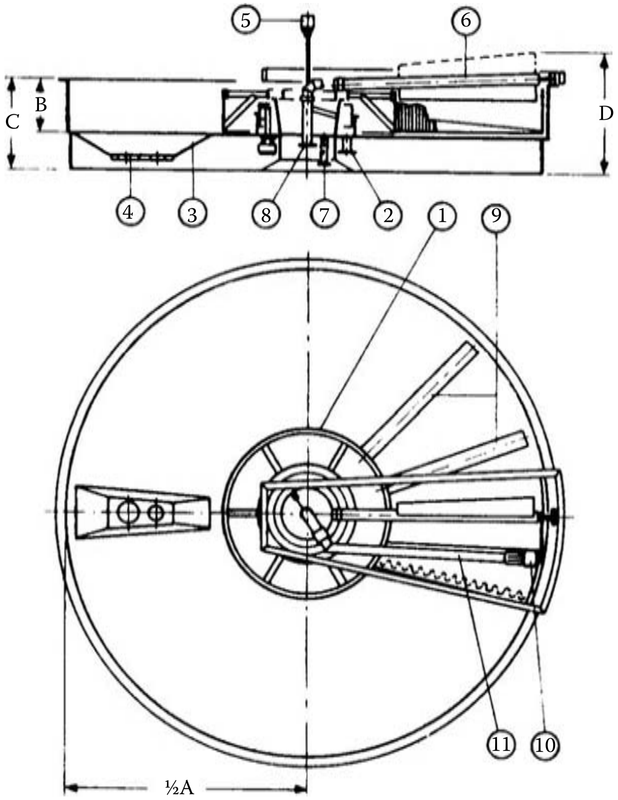
The concept of using flotation for water–solid separation is not new at all; many engineers have applied the flotation technology in sludge separation since the early 1920s. The major deterrent to flotation use in the municipal and industrial processes envisaged by these early practicing engineers was economics, with objections centering mainly around the cost of gas bubble generation and retention. Wang has reported the evolution of DAF clarifiers during the last 50 years.[1] The following progress has been made: (a) specific clarification load increased from 1.5 gpm (gallons per minute)/ft^2 (60 Lpm/m^2) to 3.5 gpm/ft^2 (140 Lpm/m^2) and for triple stacked unit to 10 gpm/ft^2 (420 Lpm/m^2); (b) the retention time of water in the flotation clarifier decreased from 30 to 3 min; (c) the largest unit size increased from 260 gpm (1000 Lpm) to 7900 gpm (30,000 Lpm) and for triple stacked units to 23,700 gpm (90,000 Lpm); (d) the size of modern DAF units is much smaller when treating the same hydraulic flow. It allows construction predominantly in stainless steel prefabricated for easy erection; (e) the smaller size and weight 120 lb/ft^2 (60 kg/m^2) allows installation on posts leaving free passage under the unit; therefore, it is easier to find available space for indoor installation and to construct inexpensive housing; (f) air dissolving is improved and now requires only 10 s retention time in the air dissolving tube instead of the previous 60 s, accordingly, this reduction in retention time results in smaller air dissolving tubes that are predominantly built from stainless steel; and (g) availability of excellent flocculating chemicals gives a high stability of operation and a high clarification degree.

In summary, modern DAF units with only 3 min of retention time can treat water and wastewater at an overflow rate of 3.5 gpm/ft^2 for a single unit, and up to 10.5 gpm/ft^2 for triple stacked units. Of course, the actual retention time used for DAF design will be higher when an engineering safety factor is applied. Figure 27.1 shows a typical DAF clarifier that will be explained in detail later.

The comparison between a DAF clarifier and a conventional sedimentation clarifier shows that (a) DAF floor space requirement is only 15% of the settler; (b) DAF volume requirement is only 5% of the settler; (c) the degrees of clarification of the both clarifiers are the same with the same flocculating chemical addition; (d) the operational cost of the DAF clarifier is slightly higher than that for the settler, but this is offset by considerably lower cost of the installation financing; and (e) DAF clarifiers are mainly prefabricated in stainless steel for erection cost reduction, corrosion control, better construction flexibility, and possible future changes, contrary to *in situ* constructed heavy large concrete sedimentation tanks. Ideally, for the design and construction of a new activated sludge wastewater treatment plant, it will be more cost-effective if secondary flotation is used instead of conventional secondary sedimentation.

27.1.4 Objectives of the Engineering Research and Documentations

The primary objective of this research, however, is to introduce the secondary flotation clarification concept that can be applied for improving treatment efficiency of an existing overloaded activated sludge plant, or for expansion of the existing plant's hydraulic capacity to handle additional wastewater flow. A commercially available high-rate DAF clarifier can be applied in series between the aeration basin and secondary sedimentation in a conventional activated sludge process to separate the living microorganisms before settling in the existing secondary sedimentation basins. This results in the following improvements in the existing plant: (a) solids and hydraulic loadings on an overloaded secondary sedimentation are reduced, resulting in increased clarification efficiency and saving of



A Diameter of supracell
B Depth of supracell tank
C Depth of supracell tank with bottom support
D Minimum overall height of supracell

1 Rotating center section
2 Clarified water outlet
3 Settled sludge sump
4 Settled sludge outlet
5 (KROFTA) rotary contact
6 (KROFTA) spiral scoop
7 Floated sludge outlet
8 Unclarified water inlet
9 Clarified water extraction pipes
10 Gear motor
11 Distribution duct

Type		Dimensions						Flow		
A ft	A mm	B in	B mm	C in	C mm	D in	D mm	m^3/min	US gpm	m^3/h
8	2400	23.5	600	33	850	45	1150	0.56	148	34
10	3200	23.5	600	33	850	49	1250	1.00	263	60
12	3900	25.5	650	35	900	51	1300	1.50	394	90
15	4500	25.5	650	37	950	57	1450	2.00	525	120
18	5500	25.5	650	37	950	58	1480	3.00	789	180
20	6100	25.5	650	37	950	61	1560	3.65	961	219
22	6700	25.5	650	37	950	62	1580	4.40	1160	264
24	7200	25.5	650	37	950	63	1600	5.08	1340	305
27	8100	25.5	650	37	950	67	1700	6.44	1695	386
30	9000	25.5	650	37	950	71	1820	7.95	2090	477
33	10,000	25.5	650	37	950	72	1840	9.80	2580	588
36	11,000	25.5	650	37	950	73	1860	11.87	3125	712
40	12,200	26	660	38	960	76	1920	14.60	3840	876
44	13,400	27	685	39	985	78	1980	17.60	4630	1056
49	14,800	27	685	39	985	82	2070	21.50	5650	1290
55	16,800	27	685	39	985	87	2200	27.70	7290	1662

FIGURE 27.1 Single-cell high-rate DAF system (Krofta Supracell).

construction cost on expansion of secondary sedimentation facilities; (b) a reduction in recycle sludge volume due to higher solids content in the recycled sludge reduces the hydraulic loading on an aeration basin, thus increasing the retention time without increasing the aeration basin size; (c) higher solids content in the waste sludge represents cost saving and improved operation of sludge thickening, dewatering, and disposal; (d) the living microorganisms, separated by the DAF, are returned to the aeration basin quickly (in less than 15 min) in aerobic condition and are more active than comparable settled microorganisms, and the oxygen requirement for the MLSS is also significantly reduced; and (e) the problems of sludge rising and sludge bulking, and/or hydraulic overloading, can be totally solved when using the secondary flotation clarification.

In Section 27.2, the principles of a DAF unit and the entire improved activated sludge wastewater treatment system are disclosed in detail. The economic use of secondary flotation in the improved system requires only a relatively inexpensive high-rate DAF cell that is commercially available. The consulting engineers should understand such principles for the selection of an appropriate DAF unit and for the optimization of the entire improved wastewater treatment system.

Section 27.3 introduces the improved activated sludge systems involving the use of either a DAF clarifier or a dissolved air flotation–filtration (DAFF) clarifier as the secondary flotation clarification unit.

Sections 27.4 through 27.6 describe the case history and operating experience. Both pilot-scale results and full-scale design considerations are presented. The new design involving simple addition of a secondary flotation clarifier prior to an existing secondary sedimentation clarifier allows a 50% increase in hydraulic loading to an existing waste treatment plant.

Section 27.7 discloses the common causes of sludge rising and sludge bulking and discusses other possible alternatives for biological process optimization.

Section 27.8 summarizes the feasibility and advantages of an improved biological wastewater treatment system involving the use of secondary flotation clarification.

27.2 DAF AND DAFF CLARIFIERS

27.2.1 Commercially Available DAF and DAFF Clarifiers for Biological Wastewater Treatment Systems

DAF is mainly used to float suspended and colloidal solids by decreasing their apparent density. The influent feed liquid can be raw water, wastewater, liquid sludge, or industrial process water.[1–37] A DAF clarifier can be either a continuous reactor or a sequencing batch reactor[1,28–30,37] when used in a biological wastewater treatment plant for primary clarification, secondary clarification, or sludge thickening. A combined DAFF clarifier is commonly called a DAFF clarifier. A DAFF clarifier is suitable for secondary clarification or tertiary clarification in a biological wastewater treatment system.[1] The shape of a DAF clarifier or a DAFF clarifier can be either circular or rectangular.

The flotation system consists of eight major components: a influent feed pump, air supply, a pressurizing pump, an air dissolving tube (retention tank), a friction valve, a flotation chamber, a spiral scoop, and an effluent extraction pipe. Figures 27.1 and 27.2 show a single cell and a double cell, respectively, of a high-rate DAF clarifier, which is commercially available from Krofta Engineering Corporation (KEC), Lenox, Massachusetts. It should be noted that there are many DAF/DAFF manufacturers and patented DAF/DAFF processes around the world, which are equally effective for either primary clarification or secondary in biological wastewater treatment plants (including an activated sludge wastewater plant).[1,28–43] A few selected major DAF and DAFF manufacturers are listed below:

a. Dongshin Engineering Corporation, Seoul, Korea
b. KEC, Massachusetts

1	Raw water collection tank
2	Supracell feed pump
3	Supracell inlet pipe (imbedded in ground)
4	Inlet compartment
5	Settled sludge sump
6	Settled sludge discharge
7	Clarified water outlet
8	Clarified water return for level control (1)
9	Level control in supracell with pneumatic sensor and clarified water discharge regulating valve
10	Pressure pump for recycling of clarified water to the air dissolving tubes
11	Air dissolving tubes
12	Supracell main tank
13	Spiral scoop for collection of the floated sludge
14	Floated sludge
15	Steel legs
16	Second elevated supracell in steel construction

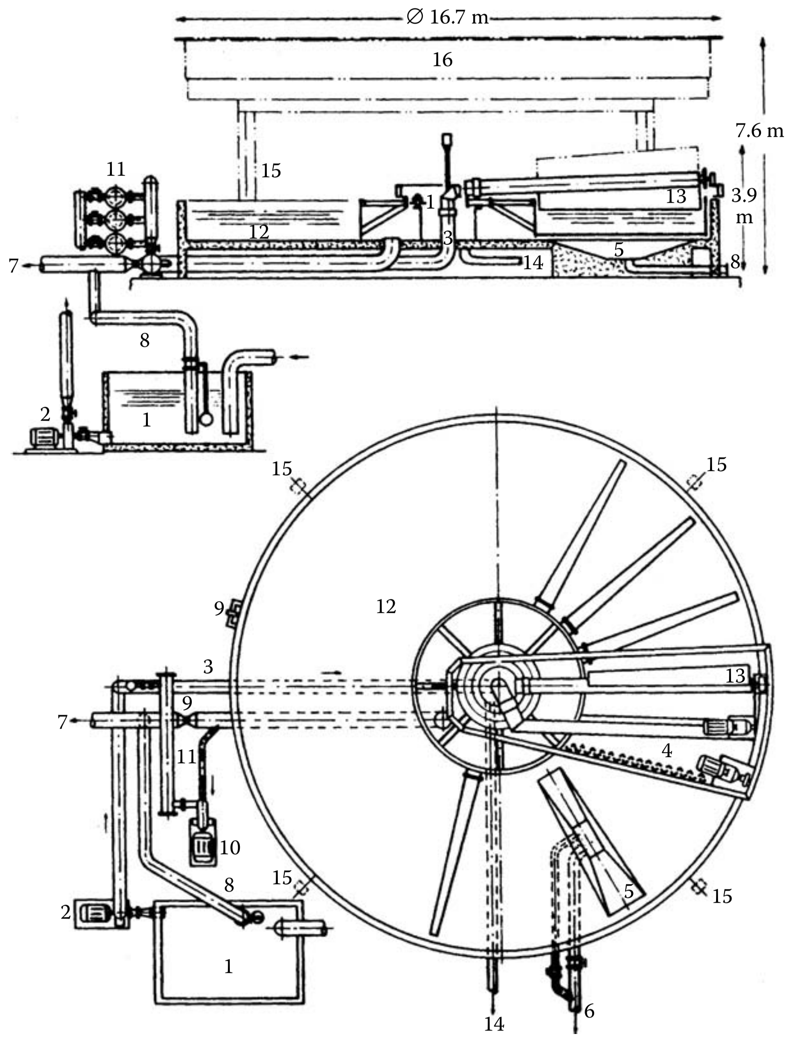


FIGURE 27.2 Double-cell high-rate DAF system (Krofta Supracell).

c. Austep Srl (Extant Environmental Solutions), Milan, Italy
d. MarTint Inc., Lexington, South Carolina
e. Siemens AG International, Schuhstrasse, Germany
f. Komline-Sanderson, Peapack, New Jersey
g. WesTech Engineering Inc., Salt Lake City, Utah
h. Praxair, Inc., Burr Ridge, Illinois
i. Degremont Technologies-Infilco, Richmond, Virginia
j. EIMCO Water Technologies, West Valley City, Utah
k. HI-Tech Environmental, Hoover, Alabama
l. Noram Engineering and Construction, Vancouver, BC, Canada
m. KWI North America Corporation, Massachusetts
n. Krofta Technologies, Massachusetts.

All DAFs are similar to each other in terms of theory, principles, design, operation, and secondary flotation performance. The authors select the circular DAF process equipment manufactured by KEC for the purpose of feasibility studies. The users should contact more than one major DAF and DAFF manufacturers for appropriate pilot plant demonstrations and cost comparisons. Rectangular DAF and DAFF clarifiers are as good as circular DAF and DAFF clarifiers.

It is seen from Figure 27.1 that the single circular DAF (Krofta Supracell) unit can be as large as 55 ft in diameter, handling a maximum flow of 7290 gpm (or 10.5 MGD, or 37.85 ML/d). However, for doubling the capacity vertically in order to save some land space, a second DAF can be installed on 4 legs over the bottom one, as shown in Figure 27.2. This second DAF is built in steel with steel supports. Three DAFs installed one over the other have also been built, and are all incorporated in lightweight housing.

A commercial DAF unit, such as Krofta Supracell, can be delivered fully prefabricated. Larger units are delivered in parts that are flanged together. Construction materials are painted or stainless steel. A tile or concrete tank is optional. Generally, no heavy foundation or support structure is needed for a single-cell unit as the total load factor when filled with water weighs <150 lb/ft^2, which is less than the load for a parking lot. A flat concrete ground pad is usually sufficient.

The following sections describe the operational procedures and the principles and special features of some selected major flotation components.

27.2.2 GENERAL OPERATIONAL DESCRIPTION OF DAF AND DAFF CLARIFIERS

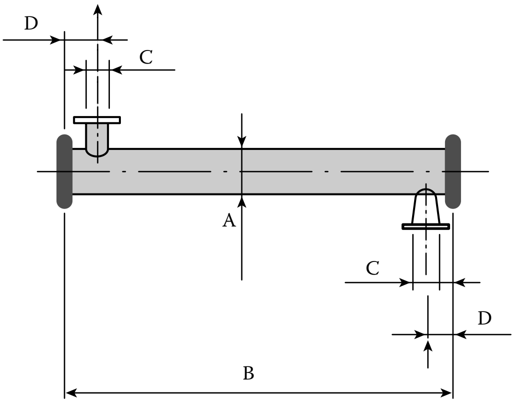
27.2.2.1 DAF and DAFF Clarifier Systems

The inlet, outlet, and sludge removal mechanisms are contained in the central rotating section. This central rotating section and the spiral scoop rotate around the tank at a speed synchronized with the flow (Figures 27.1 and 27.2).

Unclarified water, first passing through an air dissolving tube (Figures 27.3 and 27.4) and a friction valve (Figure 27.5), is released through a rotary joint in the center of the tank. It then passes into the distribution duct that moves backward with the same velocity as the forward incoming water. The settling and the flotation processes take place in the quiescent state in the flotation chamber.

The spiral scoop that is shown in Figures 27.6 and 27.7 as a part of the patented structure takes up the floated sludge, pouring it into the stationary center section where it is discharged by gravity for either recycling or disposal.

Clarified water is removed by effluent extraction pipes that are attached to the moving center section. The clarified water that normally contains <30 mg/L of suspended solids can be recycled in the process and/or sewered.



Dimensions of air dissolving tubes

Type	500	1000	1500	2000	2500	3000
Flow US gpm	132	263	395	526	658	789
A diam. inches	12″	12″	18″	18″	18″	18″
B feet inches	3′ 10″	6′ 8″	10′ 2″	6′ 8″	8′ 5″	10′ 2″
C diam. inches	2½″	6″	6″	6″	6″	6″
D inches	4″	6″	6″	6″	6″	6″

FIGURE 27.3 Dimensions of air dissolving tubes (air saturation tanks).

Wiper blades attached to the moving distribution duct scrape the bottom and the sides of the tank and discharge settled sludge into the built-in sump, for periodic purging. The variable speed gear motor drives the rotating elements and the scoop. Electrical current for the gear motor feeds from a rotary contact mounted on the central shaft.

According to Henry's law, the solubility of gas (such as air) in aqueous solution increases with increasing the pressure. The influent feed stream can be saturated at several times atmospheric pressure (45–85 psig) by a pressurizing pump. The pressurized feed stream is held at this high pressure for about 10 s in an air dissolving tube designed to provide efficient dissolution of air into the water or wastewater stream to be treated. The pressurized stream usually enters the air dissolving tube tangentially at one end and is discharged at the opposite end. During the short passage the water cycles inside the tube and passes repeatedly by an insert, fed by compressed air. Very thorough mixing under pressure then dissolves the air in the water. Because of the small diameter, the improved air dissolving tube does not require official testing and coding. The small dimensions allow an

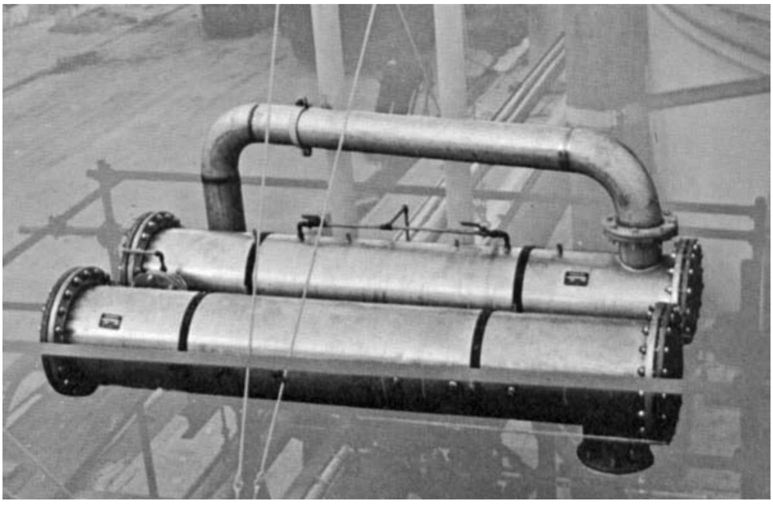


FIGURE 27.4 Typical models of air dissolving tubes (air saturation tanks).

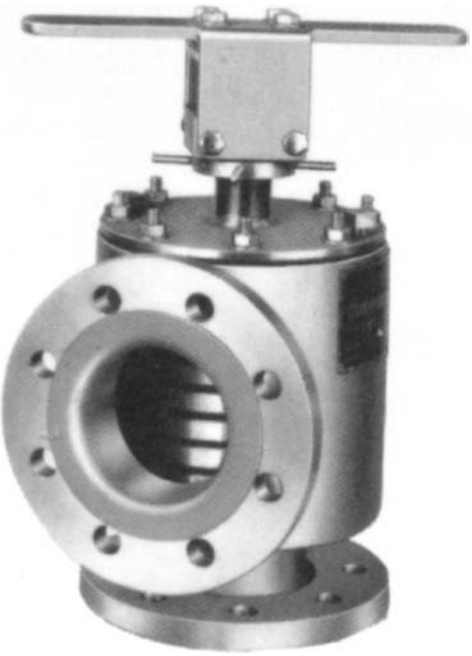


FIGURE 27.5 Friction valve (pressure release valve or pressure reduction valve) for pressure reduction and pressurized water release.

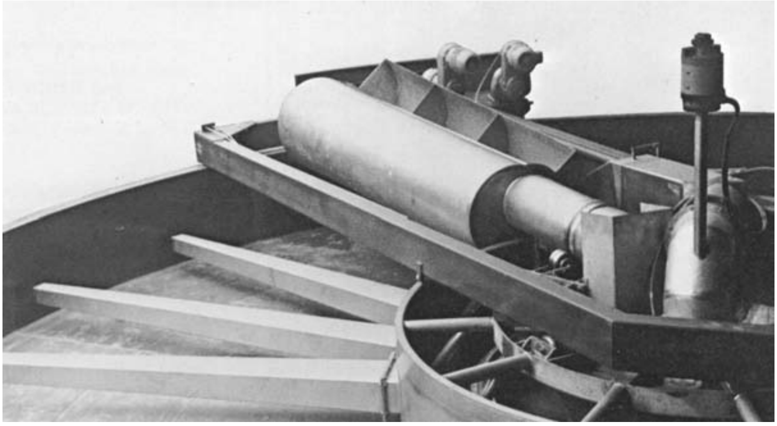
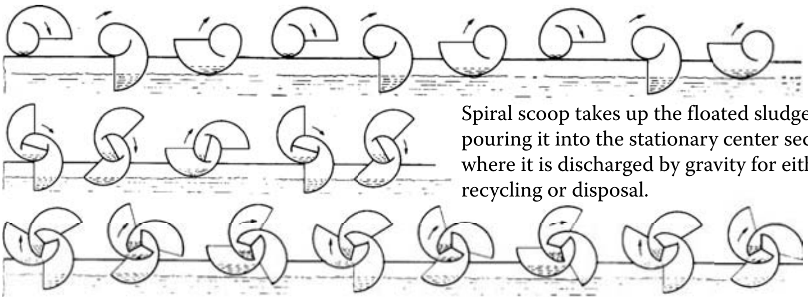


FIGURE 27.6 Spiral scoop (top) and effluent extraction pipes.



Spiral scoop takes up the floated sludge, pouring it into the stationary center section where it is discharged by gravity for either recycling or disposal.

FIGURE 27.7 Spiral scoop operations.

economical construction in stainless steel. Figure 27.3 introduces the dimensions of air dissolving tubes, and Figure 27.5 illustrates a typical model.

The pressurized water is decompressed in a friction valve (see Figure 27.3), where the liquid is forced through a narrow slot in a coil spring. High shear is produced and dissolved air is forced out of the solution.

From the air dissolving tube (through a friction valve), the water stream is released back to atmospheric pressure in the flotation chamber, as shown in Figures 27.8 through 27.10. Most of the pressure drop occurs after the friction valve (*note*: the friction valve is located in the transfer line between the air dissolving tube and flotation chamber shown in Figures 27.8 through 27.10), so that the turbulent effects of depressurization can be minimized. The sudden reduction in pressure in the flotation chamber results in the release of microscopic air bubbles (average diameter 80 μm or smaller), which attach themselves to suspended or colloidal particles in the process water in the flotation chamber. This results in agglomeration that, due to the entrained air, gives a net combined specific gravity less than that of water, and causes the flotation phenomenon. The vertical rising rate of air bubbles ranges between 0.5 and 2.0 ft/min. The floated materials rise to the surface of the flotation chamber to form a floated layer, which is carried away by a spiral scoop shown in Figure 27.6. Clarified water (effluent) is usually drawn off from the bottom of the flotation chamber through effluent extraction pipes (see Figure 27.6) and either recovered for reuse or discharged.

The unique, compact and efficient design of a circular DAF cell is made possible by using the principle of "zero velocity." As mentioned earlier, the influent distribution duct moves backward with the same velocity as the forward incoming water. The "zero velocity" quiescent state in the flotation chamber is thus created ideally for flotation.

The retention time in the flotation chambers is usually about 2.5–4 min depending on the characteristics of process water and the performance of a flotation unit. The process effectiveness depends on the attachment of air bubbles to the particles to be removed from the process water. The attraction between the air bubbles and particles is primarily a result of the particle surface charges and bubble-size distribution. The more uniform the distribution of water and microbubbles, the shallower the flotation unit can be. Generally, the depth of effective modern flotation units is only between 16 in. and 2 ft.

A DAFF clarifier's top portion is similar to a DAF clarifier, but its bottom portion is an automatic backwash filtration unit. The readers are referred to elsewhere for a detailed description of a DAFF clarifier.[41,43]

27.2.2.2 Spiral Scoops

Specially designed spiral scoops (see Figures 27.6 and 27.7) continuously remove the floated material and subsequently pour it into the stationary center section of a flotation chamber, where it is discharged by gravity for either recycling or disposal.

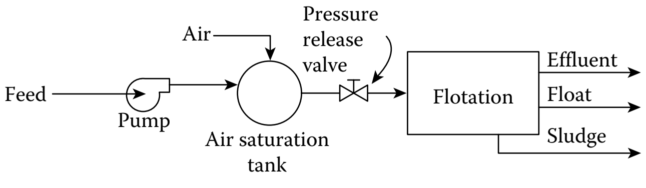


FIGURE 27.8 The DAF full-flow pressurization (total pressurization) system. [From WEF, *Sludge Thickening*, Manual of Practice No. FD-1, Water Environment Federation (formerly Water Pollution Control Federation), Washington, DC, 1980, pp. 33–66. With permission.]

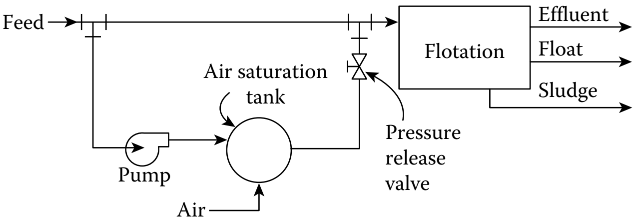


FIGURE 27.9 The DAF partial flow pressurization (partial pressurization) system. [From WEF, *Sludge Thickening*, Manual of Practice No. FD-1, Water Environment Federation (formerly Water Pollution Control Federation), Washington, DC, 1980, pp. 33–66. With permission.]

The surface sludge layer can in certain cases attain a thickness of many inches and can be relatively stable for a short period. The layer thickens with time, but undue delays in removal will cause a release of particulates back to the liquid.

27.2.2.3 Flotation System Configurations

There are three common flotation system configurations: (a) full-flow pressurization; (b) partial flow pressurization without effluent recycle; and (c) recycle flow pressurization, which have been graphically illustrated in Figures 27.8 through 27.10, respectively.

In the full-flow pressurization system (Figure 27.8), the entire influent feed stream is pressurized by a pressurizing pump and held in the air dissolving tube. The system is usually applicable to the feed stream with suspended solids exceeding 800 mg/L in concentration, and is not susceptible to the shearing effects caused by the pressurizing pump and the high pressure drop at the friction valve. It is occasionally used for separating some discrete fibers and particles that require a high volume of air bubbles. It is particularly feasible for solid–water separation where suspended solids will flocculate rapidly with the addition of chemical coagulants in the inlet compartment in the presence of the released air. The air bubbles may become entrapped within the floc particles, resulting in a strong air-to-solids bond and thus in a highly efficient separation process.

In the partial flow pressurization without effluent recycle system (Figure 27.9), only about 30–50% of the influent feed stream is pressurized by a high-pressure pump and held in the air dissolving tube. The remaining portion of the influent stream is fed by gravity or a low-pressure pump to the inlet compartment of the flotation chamber where it mixes with the pressurized portion of the influent stream. Materials with low specific gravity can be removed with the partial flow pressurization system. This system is again not recommended to be used when the suspended solids are susceptible to the shearing effects of the pressurizing pump and the high pressure drop at the friction valve. It is generally employed in applications where the suspended solids concentrations are low, resulting in lower air requirement and, in turn, lower operation and maintenance costs.

In the recycle flow pressurization system (Figure 27.10), a portion (15–50%) of the clarified effluent from the flotation chamber is recycled, pressurized, and semisaturated with air in the air dissolving tube. The recycled flow is mixed with the unpressurized main influent stream just before admission to the flotation chamber, with the result that the air bubbles come out of aqueous phase in contact with suspended particulate matter at the inlet compartment of the flotation chamber. The system is usually employed in applications where preliminary chemical addition and flocculation are necessary and ahead of flotation. It eliminates the problems with shearing the flocculated particles since only the clarified effluent passes through the pressurizing pump and the friction valve. It should be noted, however, that the increased hydraulic flow on the flotation chamber due to the flow recirculation must be taken into account in the flotation chamber design.

While all the aforementioned three system configurations can be used for sludge (or fiber) separation, only the recycle flow pressurization system is recommended for water purification or wastewater treatment.

27.3 THE IMPROVED BIOLOGICAL TREATMENT SYSTEM

27.3.1 General Principles and Process Description

Activated sludge is a continuous flow, biological treatment process characterized by a suspension of aerobic microorganisms, maintained in a relatively homogeneous state by the mixing and turbulence induced by aeration. The microorganisms are used to oxidize soluble and colloidal organics to CO_2 and H_2O in the presence of molecular oxygen. The process is generally but not always preceded by a primary sedimentation clarifier. The mixture of microorganisms and wastewater formed in the aeration basins, called mixed liquor, is transferred to gravity clarifiers for liquid–solid separation. The major portion of the microorganisms settling out in the clarifiers can be recycled to the aeration basins to be mixed with incoming wastewater, while the excess, which constitutes the waste sludge, is sent to the sludge-handling facilities. The rate and concentration of activated sludge returned to the

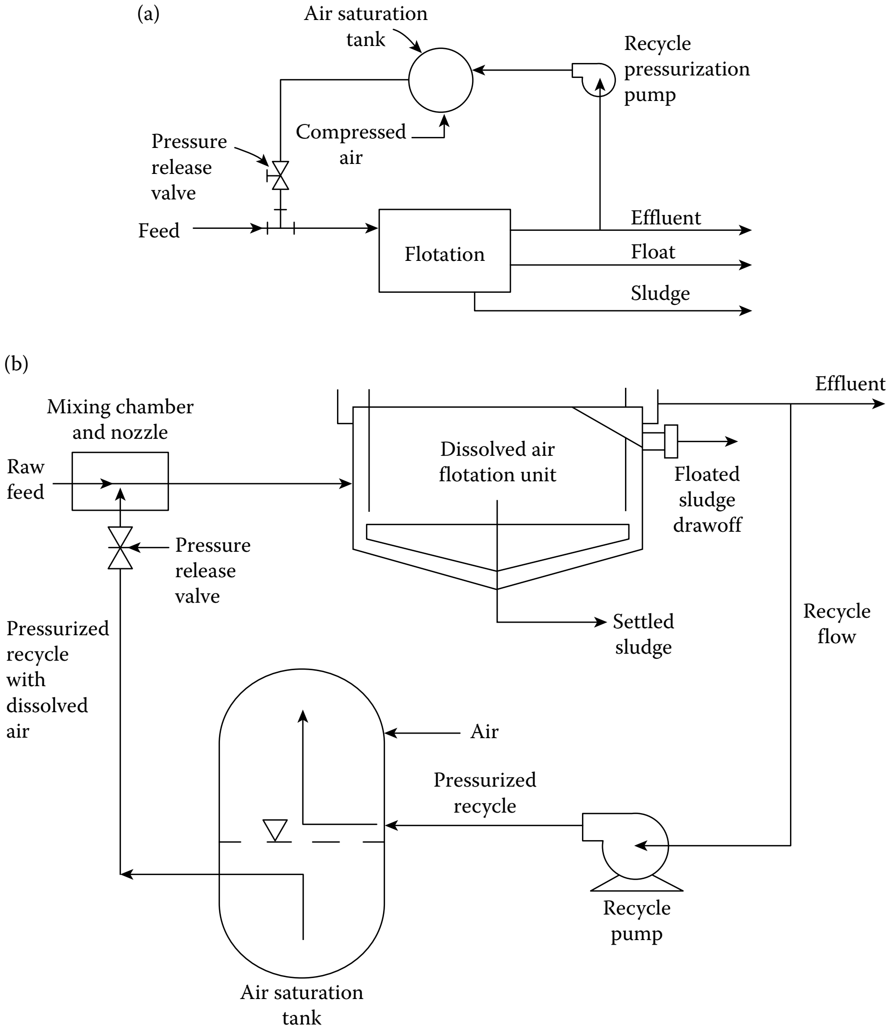


FIGURE 27.10 (a) DAF recycled flow pressurization (recycle pressurization) system, (b) flow schematic, and (c) control valves. *Note:* B = ball valve; P = pressure gauge; R = rotameter; C = check valve; H = high pressure reducer; G = gate valve; T = temperature gauge; S = selenoid valve [From WEF, *Sludge Thickening*, Manual of Practice No. FD-1, Water Environment Federation (formerly Water Pollution Control Federation), Washington, DC, 1980, pp. 33–66. With permission.]

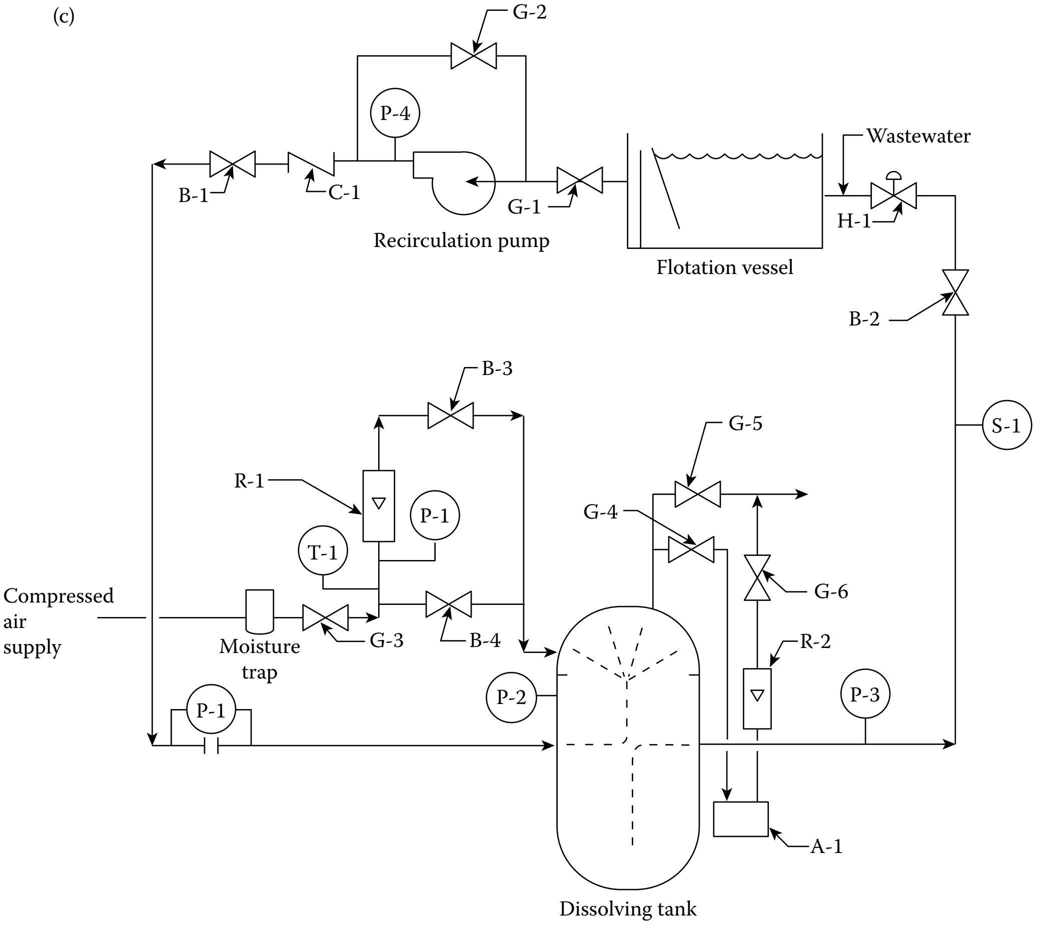


FIGURE 27.10 Continued.

aeration basins determine the MLSS level developed and maintained in the basins. During the oxidation process, a certain amount of the organic material is synthesized into new cells, some of which then undergoes auto-oxidation (self-oxidation or endogenous respiration) in the aeration basins, the remainder forming net growth or excess sludge. Oxygen is required in the process to support the oxidation and synthesis reactions. Volatile compounds are driven off to a certain extent in the aeration process. Metals will also be partially removed, with accumulation in the sludge. Activated sludge systems are classified as high rate, conventional, or extended aeration (low rate) based on the organic loading. In the conventional activated sludge plant, the wastewater is commonly aerated for a period of 4–8 h (based on average daily flow) in a plug-flow hydraulic mode. Either surface or submerged aeration systems can be employed to transfer oxygen from air to wastewater.

A partial listing of design criteria for the conventional activated sludge process is summarized as follows:

a. Volumetric loading = 25–50 lb BOD_5/day/1000 ft^3.
b. Aeration detention time = 4–8 h (based on average daily flow).
c. MLSS = 1500–4500 mg/L.
d. Food-to-microorganisms ratio, $F/M = 0.25–0.5$ lb BOD_5/day/lb MLVSS, where MLVSS = mixed liquor volatile suspended solids.
e. Air requirement = 800–1500 standard ft^3/lb BOD_5 removed.
f. Mean cell residence time = 5–10 days.

27.3.2 GENERAL KINETICS OF THE ACTIVATED SLUDGE WASTEWATER TREATMENT SYSTEM

The success of an activated sludge process in producing a high-quality effluent depends on the continuous growth of biological flocs having a good separating characteristic.[44–46] The growth of biological flocs is accompanied by the organic substrate removal. The rate of microbial growth and the rate of substrate utilization are interrelated. If one assumes that the Michaelis–Menten enzymatic kinetics can be applied to the substrate utilization by microorganisms in the process, then

$$\begin{aligned} U &= \frac{\mathrm{d}S/\mathrm{d}t}{X}, \\ U &= \frac{k_\mathrm{m}S}{K_\mathrm{s}+S}, \\ U &= \frac{Q(S_0 - S)}{VX}, \\ U &= \frac{(F/M)E}{100}, \end{aligned} \tag{27.1}$$

in which U is the specific substrate (i.e., soluble organics) utilization rate, change of soluble substrate concentration per unit time per unit microbial concentration; S is the the substrate concentration in solutions, mass per unit volume; X is the microbial concentration (VSS) in the reactor, mass per unit volume; k_m is the maximum rate of specific substrate utilization, time^{-1}; K_s is the Michaelis–Menten constant, or half velocity coefficient being numerically equal to the substrate concentration when $U = k_\mathrm{m}/2$, mass per unit volume; S_0 is the initial substrate concentration, mass per unit volume (mg/L); Q is the volumetric wastewater flow rate, volume per unit time; V is the reactor volume; F/M is the food-to-microorganism ratio $= S_0/TX$; T is the hydraulic detention time of the reactor V/Q; and E is the process efficiency $= 100(S_0 - S)/S_0$.

The readers are referred to the Nomenclature section for details about the units.

Biological growth is the result of the coupled synthesis–endogenous respiration reactions. The net result can be expressed as

$$\begin{aligned} u &= \frac{\mathrm{d}X/\mathrm{d}t}{X}, \\ u &= YU - b, \end{aligned} \tag{27.2}$$

in which u is the net specific growth rate, the change of microbial concentration per unit time per unit microbial concentration, time^{-1}; Y is the growth yield coefficient, mass microbial growth per unit mass substrate utilized; and b is the endogenous or decay coefficient, time^{-1}.

27.3.3 PROCESS-SPECIFIC KINETICS OF THE CONVENTIONAL ACTIVATED SLUDGE PROCESS SYSTEMS WITH SLUDGE RECYCLE

There are four conventional activated sludge process schemes: (a) complete-mix reactor with sludge recycle; (b) complete-mix reactor without sludge recycle; (c) plug-flow reactor with sludge recycle; and (d) plug-flow reactor without sludge recycle. These process schemes are described elsewhere in detail.[38] This report introduces only the conventional system using complete-mix reactor with sludge recycle for the purpose of comparison between a conventional system and an improved system using secondary flotation clarification.

In the conventional activated sludge process with biological sludge recycled from the final sedimentation clarifier, shown in Figure 27.11, the mean cell residence time or sludge retention time is

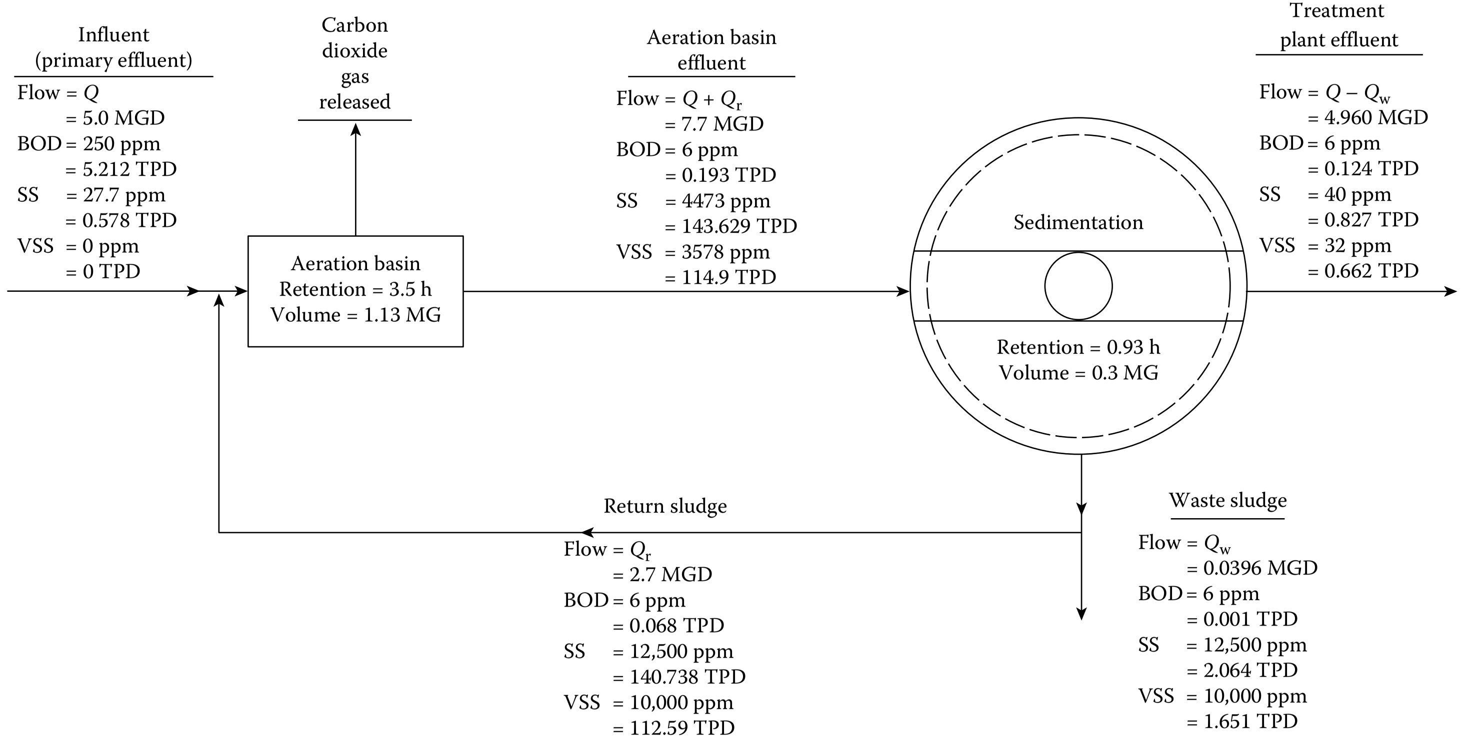


FIGURE 27.11 The conventional activated sludge process system before the installation of a secondary flotation clarifier (example). *Note:* 1 MGD = 0.0438 m^3/s; 1 ppm = 1 mg/L; 1 TPD = 37.8 kg/h.

longer than the hydraulic retention time. When sludge wasting is accomplished from the recycle line, the sludge retention time is calculated as

$$T_c = \frac{VX}{[Q_w X_r + (Q - Q_w)X_e]}, \tag{27.3}$$

in which T_c is the sludge retention time, day; Q_w is the wasted sludge flow rate, volume per unit time; X_r is the return sludge concentration, mass per unit volume; and X_e is the sludge concentration in the treated effluent from the final sedimentation clarifier.

Assuming that X_e is very small, Equation 27.3 can be rewritten as

$$Q_w = \frac{VX}{T_c X_r}. \tag{27.4}$$

By writing the mass balance equation for "sludge" in the entire system, as shown in Figure 27.11, and assuming X_0 is in negligible amounts (X_0 is the sludge concentration in the primary effluent), one can obtain

$$V\frac{\mathrm{d}X}{\mathrm{d}t} = (YUX - bX)V - [Q_w X_r + (Q - Q_w)X_e], \tag{27.5}$$

where $V(\mathrm{d}X/\mathrm{d}t)$ is the rate of change of microorganism concentration in the bioreactor; $(YUX - bX)$ V is the net rate of microorganism growth in the bioreactor; and $[Q_w X_r + (Q - Q_w)X_e]$ is the rate of microorganism outflow from the reactor.

Making use of Equation 27.3 and considering steady-state conditions, Equation 27.5 can be simplified and rearranged to yield

$$\frac{1}{T_c} = u = YU - b, \tag{27.6}$$

in which both $1/T$ and u are termed the net specific growth rate. The following are the working equations of substrate (S), MLSS concentration (X), and aeration volume (V) for the sludge recycle model:

$$S = \frac{[K_s(1 + bT_c)]}{[T_s(Yk_m - b) - 1]}, \tag{27.7}$$

$$X = \frac{[T_c Y(S_0 - S)]}{[T(1 + bT_c)]}, \tag{27.8}$$

$$V = \frac{[YQT_c(S_0 - S)]}{[X(1 + bT_c)]}. \tag{27.9}$$

It is important to know from Equation 27.7 that the performance of a complete mix with recycle system does not depend on hydraulic retention time. For a specific wastewater, a biological culture, and a particular set of environmental conditions, all coefficients K_s, b, Y, and k_m become constant. It is apparent from Equation 27.7 that the system performance is a function of mean cell residence time.

A typical overloaded complex-mix activated sludge treatment plant is graphically illustrated in Figure 27.11 in detail. The treatment plant treats 5.0 MGD (million gallons per day) of settled sewage having a BOD_5 of 250 mg/L. The plant effluent consistently contains over 40 mg/L of total suspended solids (TSS) and about 6 mg/L of soluble BOD_5. The effluent TSS violates the effluent standard because of the overloaded existing secondary sedimentation clarifier. Assume that the following field conditions are applicable:

a. Wastewater temperature = 200°C.
b. Return sludge concentration = 12,500 mg/L TSS.

c. Volatile suspended solids (VSS) = 0.8 TSS.
d. Mean cell residence time $T_c = 10$ days.
e. Growth yield coefficient $Y = 0.65$ lb cells per lb of BOD_5 utilized.
f. Endogenous or decay coefficient $b = 0.1\ \text{day}^{-1}$.
g. Waste contains adequate nitrogen and phosphorus and other necessary trace nutrients for biological growth.
h. Aeration basin volume $V = 1{,}130{,}000$ gallons.
i. Sedimentation clarifier volume = 300,000 gallons.

The process conditions of the existing system will be

a. MLSS $X = 4375$ mg/L.
b. Hydraulic detention time of aeration basin = 3.5 h.
c. Hydraulic detention time of the secondary sedimentation clarifier = 0.935 h.
d. Return sludge flow $Q_r = 2.7$ MGD.
e. Sludge production rate $(\mathrm{d}X/\mathrm{d}t) = 3300$ lb VSS/day = 4125 lb TSS/day.
f. Waste sludge flow $Q_w = 0.04$ MGD.
g. Specific substrate (soluble BOD_5) utilization rate $U = 0.31\ \text{day}^{-1}$.

27.3.4 Specific Kinetics of the Improved Activated Sludge Process Using Secondary Flotation

Figure 27.12 shows the improved activated sludge process in which a new secondary flotation is applied in series between the aeration basin and the final sedimentation clarifier for increasing the overall treatment performance and hydraulic capacity of an originally overloaded existing plant.

A microbial mass balance equation can be established for the improved system as shown in Figure 27.12:

$$V\frac{\mathrm{d}X}{\mathrm{d}t} = (YUX - bX)V - [Q_{w1}X_r + Q_{w2}X_{w2} + (Q - Q_{w1} - Q_{w2})X_e], \tag{27.10}$$

where $V(\mathrm{d}X/\mathrm{d}t)$ is the rate of change of microorganism concentration in the reactor; $(YUX - bX)V$ is the net rate of microorganism growth in the bioreactor; $[Q_{w1}X_r + Q_{w2}X_{w2} + (Q - Q_{w1} - Q_{w2})X_e]$ is the rate of microorganism outflow from the bioreactor; Q_{w1} is the flow rate of waste sludge from secondary flotation, volume per unit time; $X_{w1} = X_r$ is the concentration of waste sludge (float) from secondary flotation, mass per unit volume; Q_{w2} is the flow rate of waste sludge from the existing final sedimentation clarifier, volume per unit time; X_{w2} is the concentration of waste sludge from the existing final sedimentation clarifier, mass per unit volume.

The sludge retention time (T_c) can be calculated as

$$T_c = \frac{VX}{[Q_{w1}X_r + Q_{w2}X_{w2}\,(Q - Q_{w1} - Q_{w2})X_e]}. \tag{27.11}$$

Assuming that the sludge concentration in the treated plant effluent (X_e) is very low, Equation 27.11 can be rewritten as

$$T_c = \frac{VX}{(Q_{w1}X_r + Q_{w2}X_{w2})}. \tag{27.12}$$

Again making use of Equations 27.1, 27.2, and 27.11 and considering steady-state conditions, Equation 27.11 can also be simplified and rearranged to yield Equation 27.6. It is, therefore, concluded that the design equation of the net specific growth rate (u or $1/T_c$) for the conventional activated sludge system is identical to that for the improved activated sludge system. The numerical

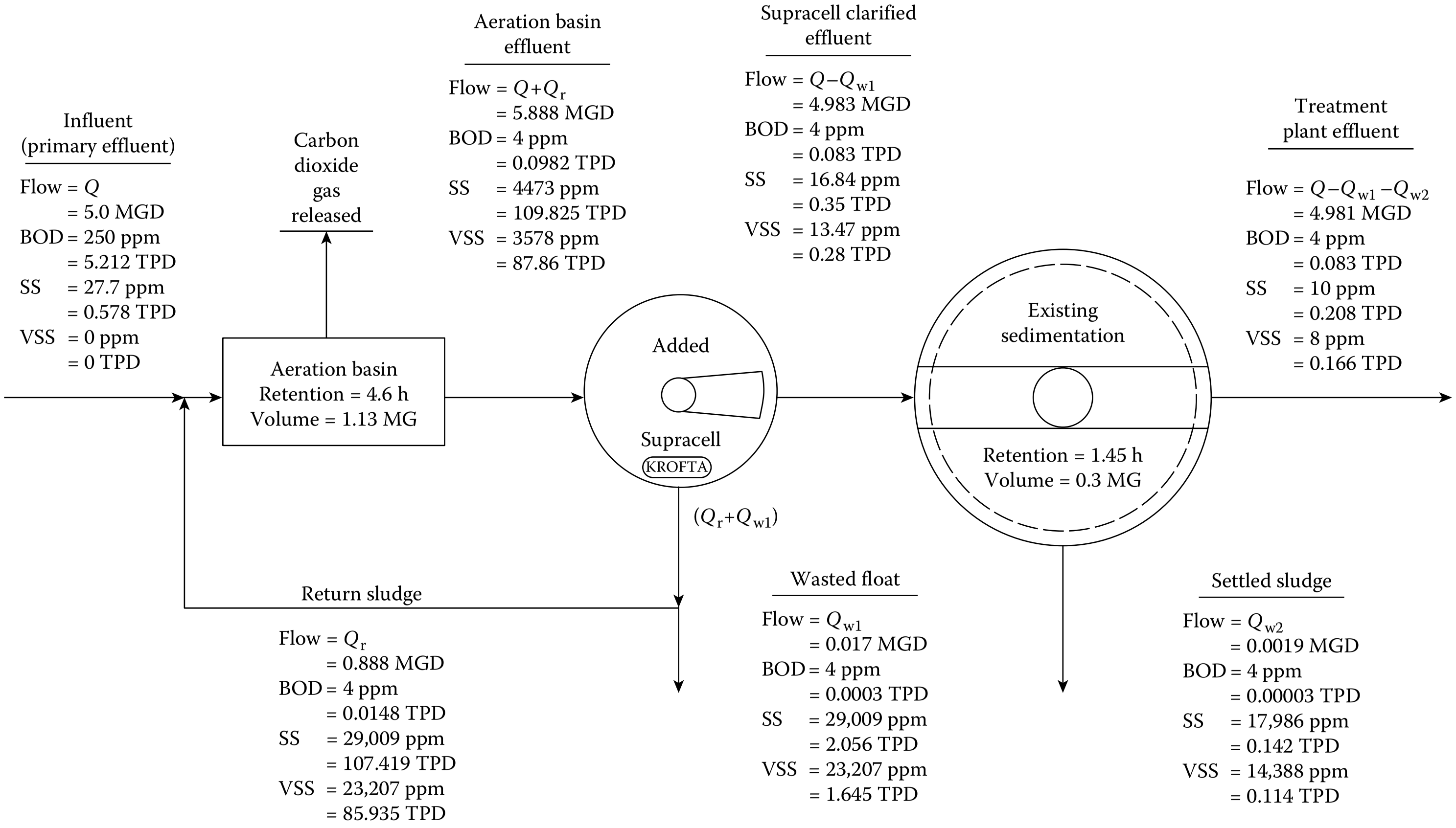


FIGURE 27.12 Improved activated sludge system with the installation of a secondary flotation clarifier (example). *Note:* 1 MGD = 0.0438 m^3/s; 1 ppm-1 mg/L; 1 TPD = 37.8 kg/h.

values of the two net specific growth rates, however, are different. Figure 27.13 shows the specific substrate utilization rate versus the limiting substrate concentration for the two activated sludge systems considered. Both systems use identical biological flocs; naturally the maximum specific substrate utilization rates (k_m) of the two systems are the same. The living biological flocs, separated by a secondary flotation clarifier, are returned to the aeration basin quickly (in less than 15 min), and thus stay in aerobic conditions at all times. Accordingly, the returned sludge (i.e., biological flocs) from secondary flotation (Figure 27.12) is more active (in terms of lower K_s value in Figure 27.13) than the comparable settled sludge from conventional secondary sedimentation (Figure 27.11). According to Equation 27.1, the improved activated sludge system (Figure 27.12) having a relatively lower K_s value (Figure 27.13) will definitely have a higher specific substrate utilization rate (U), signifying a higher biological treatment efficiency.

Microscopic examinations of floated sludge from secondary flotation and settled sludge from secondary sedimentation have been made to further demonstrate the aforementioned facts. Unstained samples of floated and settled sludge showed a marked difference in the number and viability of free-swimming and stalked ciliates (protozoa). Settled sludge contained only a few stationary cells (noted in 100 microscopic fields); floated sludge contained about 200 times more motile protozoan cells. Since protozoa are an integral and very important segment of the biological community, flotation is a desirable follow-up to the provision of dissolved oxygen (DO) within an aeration basin.

The equation of the net specific growth rate (Equation 27.6) holds true for both conventional and improved systems. The latter, having a comparatively higher specific substrate utilization rate (U), has a higher net specific growth rate (u) and requires less mean cell residence time (T_c) provided that the growth yield coefficient (Y) and the decay coefficient (b) of the floated sludge and the settled sludge are assumed to be the same.

The mean hydraulic retention time (T) can be determined by Equation 27.13, regardless of the types of treatment system used:

$$T = \sum_{i=1}^{n} \frac{V_i}{Q}. \tag{27.13}$$

For example, the mean hydraulic retention time for the entire improved activated sludge system can be expressed as

$$T = \frac{V_p + V + V_f + V_s}{Q}, \tag{27.14}$$

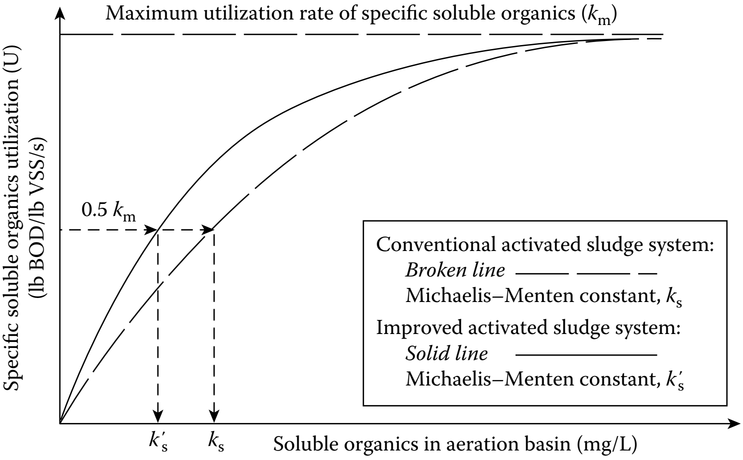


FIGURE 27.13 Specific soluble organics utilization rate versus the limiting soluble organic concentration.

where V_p is the volume of the primary clarifier, V is the volume of the aeration basin, V_f is the volume of secondary flotation, V_s is the volume of final sedimentation, and Q is the total wastewater flow to the wastewater treatment system.

For the secondary sedimentation alone, the mean hydraulic retention time is expressed as

$$T = \frac{V_s}{Q - Q_{w1}}. \tag{27.15}$$

For the aeration basin alone, the mean hydraulic retention time is expressed as

$$T = \frac{V}{Q + Q_r}. \tag{27.16}$$

A typical overloaded conventional complete-mix activated sludge treatment plant (shown in Figure 27.11) has been described in Section 27.3.3. The same conventional treatment plant can be improved by the addition of a secondary flotation clarifier (shown in Figure 27.12). Some advantages of the improved activated sludge system are mathematically presented below.

The hydraulic detention time of the secondary sedimentation of the original overloaded conventional system can be calculated as

$$T = \frac{V_s}{Q} = 0.935 \text{ h}$$

(see Figure 27.11) in comparison with Equation 27.15 for the improved activated sludge system. It is seen that the hydraulic loading of the original overloaded secondary sedimentation can be significantly reduced by a parameter of Q_{w1}; thus saving of construction cost on expansion of any secondary sedimentation facilities is expected. With the addition of a small secondary flotation clarifier (such as a Krofta Supracell with a detention time of 3 min), the detention time of the sedimentation clarifier can be increased by 55% (i.e., from 0.935 to 1.45 h), as shown in Figures 27.11 and 27.12.

The hydraulic detention time of the conventional system's aeration basin is also expressed by Equation 27.16. However, the return sludge flow (Q_r) of the improved activated sludge system is only about 33% (0.888/2.7 = 0.33) of the conventional activated sludge system, assuming the TSS concentrations (i.e., consistencies) of floated sludge and settled sludge are 2.8% and 1.25%, respectively. Accordingly, the hydraulic loading of an aeration basin can be reduced significantly by a secondary flotation addition (Krofta Supracell or an equivalent DAF from another manufacturer) to increase the hydraulic retention time (from 3.5 to 4.6 h or a 31% increase) without actually increasing the size of the aeration tank.

The higher solids content (X_{w1}) of the waste sludge produced from the improved activated sludge system, shown in Figure 27.12, represents another cost saving and the improved operation of sludge thickening, dewatering, and disposal. The waste sludge produced from the improved system will be

0.0170 MGD at 29,009 mg/L, and
0.0019 MGD at 17,986 mg/L, or a combined
0.0189 MGD at 27,900 mg/L.

The comparable conventional activated sludge system (Figure 27.11), on the other hand, generates 0.0396 MGD of waste sludge with a concentration of 12,500 mg/L. The sludge treatment cost of an improved system will, therefore, be reduced to one half due to a reduction in sludge flow and an increase in sludge consistency.

The most important fact is that both the effluent TSS (X_e) and effluent soluble BOD_5 (S) of the improved wastewater treatment system will meet the governmental effluent standards.

27.4 CASE HISTORY: A PETROCHEMICAL CORPORATION IN TEXAS

Many pilot-scale and full-scale trials involving the use of secondary flotation (Krofta Supracell) in activated sludge treatment plants were conducted by KEC and Lenox Institute of Water Technology (LIWT) (formerly Lenox Institute for Research). Only partial operational data are selected for presentation in this chapter. The readers are encouraged to contact the authors for details. In the illustration of each case history, the true names of the company and its resident engineer involved are omitted for the protection of the Company's privacy.

The first example plant is a petrochemical manufacturing facility with an existing conventional activated sludge process. The waste loading was projected to increase when plant production increases in late 1981. In facing the loading increases the plant needed to meet the present State discharge limits and more stringent limits expected in the future. Mechanical breakdown of the secondary sedimentation clarifier or extremely high hydraulic loads due to sudden rainstorms in the past caused severe problems with high sludge loading, rising sludge, bulking sludge, and poor water quality. Figure 27.11 shows the conventional treatment plant before using a Krofta Supracell as an intermediate secondary flotation unit.

Full-scale trials with the secondary flotation clarifier were conducted in summer 1980, with excellent pilot results in solids removal, sludge consistency, and water clarity. Table 27.1 documents partial operational data. The following are the conclusions drawn from the investigation:

a. *TSS loading*: TSS loadings of 111–175 lb/day/ft^2 were maintained while still maintaining an acceptable quality of clarified water (125–475 mg/L of SS or 94–98% of TSS removal). Here 1 mg/L = 1 ppm. Improvement in water quality could be obtained with lower TSS loadings (60–77 lb/day/ft^2). At a loading of 60 lb/day/ft^2, and with chemical addition, very clean water (with <20 mg/L of TSS) was obtained.
b. *Chemical treatment*: Acceptable operation was obtained without chemical aids. It is recommended, however, that the aids be available for full-scale operation. A small chemical addition dosage of cationic polymer (Pearl River Chemical 560 or equivalent) in the 10–20 mg/L range may be desirable for good sludge compaction and improvement in the overall clarification. Larger doses in the range up to 100 mg/L of cationic polymer gave exceptionally clear water. This chemical dose would be used in those cases when the cleanest possible water must be obtained (i.e., breakdown of the existing settling unit).
c. *Aeration system*: The demonstration plant was operated in the "full-flow pressurization" mode (Figure 27.8) in which all of the incoming water plus dilution water is pumped through the air dissolving tube. For power savings in the large installations, only the recycled water would be aerated (i.e., the recycle flow pressurization system would be used; see Figure 27.10). This will not change the amount of air available for flotation, as the clarified water is a more effective absorption medium than the incoming water. If the raw incoming water is pumped into the unit with a low-shearing-type pump, or by gravity flow, less shearing and breakup of the flocs would be expected in the larger unit than was experienced in the demonstration plant.
d. *Settled material*: The great majority of the incoming solids floated; however, some settled material was observed in the bottom purge. For the full-scale unit, an automatic timed purge valve is installed, opening a few seconds every 0.5–1 h. The bottom purge goes directly to the existing sedimentation clarifier. This purge keeps the secondary flotation unit continuously clean, avoiding any buildup on the bottom, which could occur during operation over a period of days or weeks.
e. *Sizing for full-scale unit*: (An example) Normal secondary flotation influent flow from the aeration basin is estimated to be 2000 gpm of discharged water plus the recycled sludge volume. At normal solids loading of 4000 mg/L from the aeration basin and minimum floated sludge consistency of 2.2%, the total normal hydraulic loading on the secondary

TABLE 27.1
Operational Data of a Petrochemical Plant in Texas

Test Runs	Raw TSS (mg/L)	Raw TSS (lb/day/ft²)	Influent TSS (mg/L)	Clarified TSS (mg/L)	TSS Removal (%)	Float TSS (%)	Raw Flow (gpm)	Clarified Flow (gpm)	Sludge Flow (gpm)	Recycle Flow (gpm)	Total Flow (gpm)	Polymer Addition (mg/L)
1	8305	121	3620	143	98.3	2.8	12.2	10.5	2.2	16.4	28.6	None
2	8480	175	5105	125	98.5	2.4	17.2	12.6	2.4	10.6	28.7	None
3	8410	130	5015	160	98.1	2.5	12.9	7.6	5.3	9.0	21.9	None
4	8130	113	4280	235	97.1	2.3	11.6	7.4	4.2	11.0	22.6	None
5	8070	112	4240	153	98.1	2.2	11.6	7.4	4.2	10.8	22.4	None
6	8680	122	4070	190	97.8	2.5	11.8	7.6	4.2	14.0	25.8	None
7	8890	129	4320	475	94.6	2.6	12.1	8.0	4.1	14.3	26.4	None
8	9080	132	4970	460	94.9	2.6	12.1	8.0	4.1	11.0	23.1	None
9	9030	137	5180	375	95.8	2.5	12.7	8.5	4.2	10.1	22.8	None
10	8740	114	4650	180	97.9	2.3	10.9	8.4	2.5	9.9	20.8	49
11	8760	111	5060	280	96.8	2.1	10.6	8.1	2.5	8.2	19.0	49
12	8550	77	3060	115	98.6	2.2	7.5	5.4	2.1	13.9	21.4	49
13	8530	73	3330	120	98.6	1.9	7.4	5.5	1.9	12.0	19.4	70
14	8630	73	3190	145	98.3	3.1	7.1	6.0	1.1	12.7	19.8	70
15	8530	60	1800	0	(100)	3.7	5.9	4.3	1.6	22.0	27.9	100

[a] Polymer used was Pearl River Chemical 560 cationic cost at residual TSS of 10 mg/L = $.0006/1000 gallons.

[b] All suspended solids testing was done in the field, using procedures as outlined in Standard Methods.[47] Particle size retention of the glass fiber filter pad used was 0.3 μm.

[c] Supracell DAF operation parameters: air dissolving tube pressure 60 psi, compressed air 70 psi, scoop speed 6 rpm, rotometer 10 SCFH (standard ft³/h), water temp. 81°F, pH of water 7.1. diameter of Supracell DAF was 4 ft.

[d] Supracell DAF influent is a mixture of raw wastewater and recycle flow.

[e] TSS percent removal is calculated based on the equation: 100(Raw TSS–Clarified TSS)/Raw TSS.

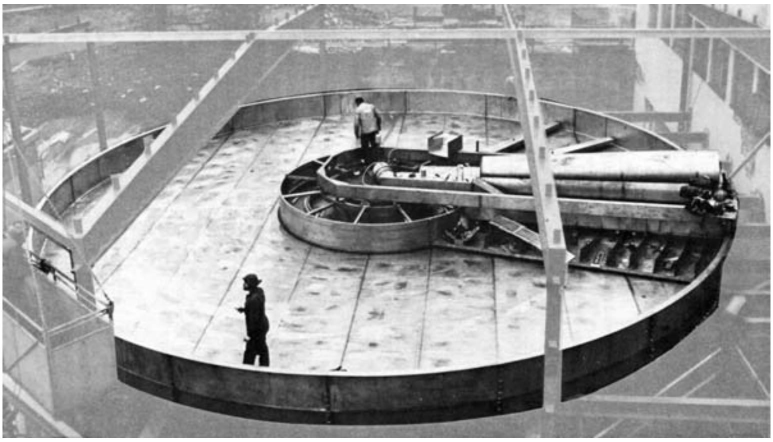


FIGURE 27.14 A 49-ft diameter DAF (Krofta Supracell) clarifier with a flow capacity of US 5650 gpm or 21.5 m^3/min.

> flotation unit is estimated at ~2400 gpm; a 49-ft-diameter circular dissolved flotation unit (such as a Krofta Supracell) would have a TSS loading under normal conditions of 60 lb/day/ft^2. During a rainstorm both TSS and hydraulic loadings would be significantly increased. If the solids concentration is increased to 6000 mg/L, the load would increase by ~65%. If both conditions occur together, the loading may go as high as 160 lb/day/ft^2, which is near the highest rate run in the demonstration plant. The 49-ft secondary flotation unit would be the best choice giving the possibility for excellent clarification under normal conditions and acceptable operation under the worst expected loadings.

Based on the test results, improvements in the hydraulic characteristics of the plant alone are very attractive, with the Krofta Supracell clarifier in a secondary flotation position (see Figure 27.12).

The plant installed a 49-ft diameter Krofta Supracell clarifier (Figure 27.14) for startup in late 1981. In addition to the hydraulic improvements, improved microbial activity increased the performance of the treatment plant. The trials had demonstrated that under normal operating conditions, the secondary flotation produced the same clarity as the existing settling unit, thus giving that unit 100% backup. Under overload conditions that were caused by rainstorms or mechanical breakdown in sludge wasting, etc., the secondary flotation unit cushioned the shock of heavy TSS loading by removing 90% of the TSS. The total project cost was far less than comparable expansion of the aeration basin and the secondary sedimentation clarifier and used less power.[31]

27.5 CASE HISTORY: A MUNICIPAL EFFLUENT TREATMENT PLANT IN HALTERN, GERMANY

The Municipal Effluent Treatment Plant in Haltern, Germany, has been designed for a wastewater capacity generated from 37,000 population units. The influent flow approximately ranges from 310 m^3/h in dry weather to 626 m^3/h in rainy weather. It is an activated sludge wastewater treatment plant treating about 1000 kg BOD_5 per day. The total volume of aeration basins is 1180 m^3. Currently, both solid loading and hydraulic loading of this plant are high; the plant engineers are actively seeking feasible solutions from both technical and economical viewpoints.

Many pilot plant operations have been conducted by KEC through Krofta Apparatebau G.M.B.H., Germany, under direct supervision of Mrs Elisabeth Hurst-Gaul, Manager. The use of a Krofta Supracell DAF clarifier for secondary clarification in the activated sludge treatment plant has been concluded to be feasible. This chapter summarizes the results of her investigation.

The pilot plant for demonstration had a diameter of 6 ft (i.e., 1.8 m), designed for a hydraulic capacity of 12 m^3/h and operated as a recycle flow pressurization system (Figure 27.10). The maximum pump pressure was 4.0 bars and only atmospheric air at the suction of the pump was used. The Supracell DAF pilot plant was installed between the aeration tank and the secondary sedimentation tank. A centrifugal pump was used to feed the aeration tank effluent to the pilot plant. The Supracell DAF effluent was discharged into the existing sedimentation tank; the floated sludge from Supracell DAF was partially returned to the aeration tank, and partially wasted, as shown in Figure 27.12.

Table 27.2 highlights some of the operational data. It can be seen from the table that the Supracell DAF effluent (to be discharged into a subsequent existing sedimentation tank) was fully aerated with an oxygen content of 6.2–7.4 mg/L. The DO in the floated sludge was above 3 mg/L except the first two runs when the Supracell DAF pilot plant was just started. The settleable solids in the clarified Supracell DAF effluent, in most cases, were below 1 mg/L. It is interesting to see that the sludge volume index (SVI) of the Supracell DAF influent (i.e., the aeration tank effluent) originally was in the range of 95–150. After DAF treatment, the SVI of the floated sludge was in the range of 28–48. The overall Supracell DAF treatment efficiency can be judged by the total solids of the influent, the clarified effluent, and the float. Table 27.2 indicates that in all cases, the treatment efficiency was between 92% and 99% in terms of total solids removal, and the float consistency was between 2% and 3.5%, which could be further concentrated if desired.

Additional investigations were conducted for the comparison of the original conventional system using only secondary sedimentation and the improved system using an intermediate secondary flotation. It was observed that the effluent of the Supracell DAF clarifier contained 6–7 mg/L of DO, whereas the effluent of the sedimentation clarifier only contained about 2 mg/L of DO. Average characteristics of the settled sludge from an existing sedimentation clarifier and the floated sludge from the Supracell DAF clarifier are presented below:

a. The sedimentation clarifier settled sludge
   DO = 0.56 mg/L
   Total solids = 4780 mg/L
   Solids volume = 492 mL/L
   SVI = 103 mL/g
b. The Supracell DAF clarifier floated sludge
   DO = 2.5 mg/L
   Total solids = 26000 mg/L
   Solids volume = 95.4 mL/L
   SVI = 37 mL/g.

It can be seen that comparatively the floated sludge will have higher DO content, higher total solids consistency, less sludge volume, and a much lower SVI. In conclusion, the quality of the floated sludges is better than that of settled sludges.

It should be noted, however, that the Supracell DAF pilot plant installed between the existing aeration basin and the sedimentation clarifier was fed by a centrifugal pump. Although the total solids and suspended solids of the Supracell DAF were extremely low, the turbidity was high. The problem of high effluent turbidity was later solved by feeding the Supracell DAF with a nonshearing screw pump, or simply by gravity.

27.6 CASE HISTORY: A PAPER COMPANY IN HOUSTON, TEXAS

A conventional activated sludge treatment plant in Houston, Texas, is heavily overloaded. KEC and the LIWT evaluated the flotation characteristics of MLSS in the Krofta Supracell

TABLE 27.2

Operational Data of a Municipal Effluent Treatment Plant in Haltern, Germany

	Flows (m^3/h)	Oxygen (mg/L)			Settleable (mL/L)			SVI (mL/g)		SS Volatility (%)			Total Solid (mg/L)		
Test Runs	Influent	Influent	Effluent	Float	Influent	Effluent	Float	Influent	Float	Influent	Effluent	Float	Influent	Effluent	Float
1	1440	2.7	7.2	1.5	225	2.0	980	107	48	99	75	69	2100	100	20,400
2	684	2.9	7.0	1.8	225	1.5	970	109	47	—	67	62	2070	150	20,800
3	342	3.8	6.8	—	270	0.3	998	114	39	62	50	74	2370	50	25,700
4	288	4.5	—	—	260	0.5	998	96	28	67	—	—	2700	25	35,400
5	306	7.8	—	—	260	0	—	—	—	—	—	—	—	—	—
6	396	2.7	—	—	200	0	999	95	30	61	—	77	1900	—	33,200
7	396	6.5	—	—	—	—	—	—	—	—	80	—	—	—	—
8	216	1.0	6.2	—	210	0.1	990	102	32	—	—	—	2050	40	31,400
9	234	7.5	7.4	3.8	225	—	990	132	39	73	68	65	1700	19	25,200
10	331	3.5	7.0	3.2	240	—	999	126	35	66	59	79	1900	8	28,800
11	324	2.8	7.2	3.1	270	0.1	1000	150	36	60	64	68	1800	8	28,000

[a] Temperature of wastewater and floated sludge = 16–19°C.

[b] pH of the Supracell DAF influent = 7.3–8.1; pH of Supracell DAF effluent = 7.2–7.6.

[c] Recycle flow pressurization system.

[d] Scoop operation for float collection = 4.1–5.2 rpm.

[e] Depth of float collected by the scoop = 7.5–9 in. from the surface.

[f] Carrier operation = 5–7.3 min/rev.

[g] Air supple = 0.5–0.8 m^3/h.

[h] Pressure of compressed air to the air dissolving tube = 5.4–5.8 bars.

high-rate DAF clarifier. “The mixed liquor was the effluent of the aeration basin, or the influent of Supracell DAF.

The 4-ft-circular Supracell DAF was used for this testing. The flotation area is 10 ft^2. Maximum hydraulic loading is 30 U.S. gpm. The unit was set up adjacent to the aeration basin at the waste treatment plant. A small sump pump was used to pump mixed liquor to the Supracell DAF.

The pilot trial was segmented into three different test runs. Test 1: full-flow pressurization without chemical treatment. Test 2: full-flow pressurization with chemical treatment. Test 3: recycle flow pressurization with chemical treatment. Testing was limited to 4 days (a total of 22 operational hours). Table 27.3 summarizes the experimental conditions of the three test series.

All flow rates through the Supracell DAF were measured by time/volume measurements. The polymer feed pump was supplied by KEC/LIWT. The polymer feed rate was also checked by time/volume measurement.

During operation, samples of all flows were taken for suspended solids analysis. These tests were performed by a qualified local analytical laboratory. Procedures for this analysis were as outlined in standard methods.[47] Glass fiber filter pads with a particle size retention of 1.2 μm were used.

Table 27.4 documents the operational data generated from this investigation. The data show that a solids capture of 93% was obtained at a flow rate of ~2.2 gpm/ft^2. The percent capture was remarkably uniform for all flow rates and chemical treatments. Sludge consistency of 0.8–1.2% was

TABLE 27.3
Operational Conditions of a Paper Company in Texas

Test 1	DAF full-flow pressurization without chemical treatment
	Operational time = September 16, 17, and 18, 1981
	Average sludge flow rates = 4.2 gpm
	Average raw wastewater suspended solids = 1930 mg/L
	Average clarified water = 129 mg/L
	Average sludge consistency = 0.8790%
	Solids loadings = 58 lb/day/ft^2
Test 2	DAF full-flow pressurization with chemical treatment
	Average chemical dosage = 58 mg/L (Pearl River 560)
	Operational time = September 18, 1981
	Average total flow rate = 22.3 gpm
	Average sludge flow rate = 2.5 gpm
	Average raw wastewater suspended solids = 1781 mg/L
	Average clarified water suspended solids = 131 mg/L
	Average solids consistency = 1.2%
	Solids loading = 48 lb/day/ft^2
Test 3	DAF recycle flow pressurization with chemical treatment
	Average chemical dosage = 1547 mg/L (Pearl River 560)
	Operational time = September 18, 21, 22, 1981
	Average total flow rates = 21 gpm
	Average sludge flow rate = 3.0 gpm
	Percent recycle flow = 34%
	Average raw wastewater suspended solids = 1778 mg/L
	Average clarified water suspended solids = 121 mg/L
	Average sludge consistency = 1.4%
	Solids loading = 29 lb/day/ft^2

TABLE 27.4
Operational Data of a Paper Company in Texas

Test No. (See Table 27.3)	Sampling Time	Total Flow (gpm)	Float Flow (gpm)	Clarified Flow (gpm)	Recycle Flow (%)	Influent TSS (mg/L)	Float TSS (%)	Effluent TSS (mg/L)	SS Removal (%)	Chemical Dosage (mg/L)
1	11:30	24.5	3.5	21.0	0	2140	0.82	100	95	None
1	12:00	23.0	2.0	19.0	0	1760	0.74	150	92	None
1	12:30	10.0	2.4	6.9	0	1840	0.86	120	94	None
1	1:00	9.5	3.0	6.5	0	2160	0.74	132	94	None
1	2:30	21.2	3.7	17.5	0	1920	0.88	126	93	None
1	3:00	17.5	3.2	14.2	0	2140	1.13	164	92	None
1	3:30	23.0	3.5	19.2	0	1946	1.23	140	93	None
1	4:15	32.3	9.0	23.3	0	1960	0.76	112	94	None
1	4:45	30.0	9.0	21.0	0	1810	0.83	140	92	None
1	4:30	Not recorded			0	1980	0.75	132	93	None
1	7:10	25.4	2.4	23.0	0	1830	0.83	128	93	None
1	7:30	Not recorded			0	1760	0.92	108	94	None
1	7:45	Not recorded			0	1840	0.75	126	93	None
2	8:05	25.0	3.6	21.4	0	1870	0.96	154	92	51
2	8:30	25.0	3.6	21.4	0	1710	1.10	122	93	51
2	8:50	25.0	3.6	21.4	0	1920	1.30	142	93	51
2	9:06	19.0	1.9	17.0	0	1830	1.50	128	93	67
2	9:27	21.0	2.0	19.0	0	1760	0.96	132	92	60
2	10:02	21.6	2.3	19.3	0	1615	1.10	112	93	58
2	10:27	21.6	2.3	19.3	0	1810	1.30	126	93	65
3	11:47	34.0	2.7	21.3	29	1740	1.50	132	92	37
3	12:05	34.0	2.7	21.3	29	1710	1.40	106	94	37
3	12:21	34.0	2.7	21.3	29	1780	1.40	132	93	37
3	3:35	20.8	6.75	8.0	29	1810	1.30	112	94	4227
3	4:00	20.8	6.75	8.0	29	1690	1.40	108	94	1920

continued

TABLE 27.4 (continued)

Test No. (See Table 27.3)	Sampling Time	Total Flow (gpm)	Float Flow (gpm)	Clarified Flow (gpm)	Recycle Flow (%)	Influent TSS (mg/L)	Float TSS (%)	Effluent TSS (mg/L)	SS Removal (%)	Chemical Dosage (mg/L)
3	4:30	17.7	2.30	9.4	34	1840	1.70	94	95	4500
3	5:00	20.4	4.00	11.4	30	1820	1.50	116	94	738
3	5:30	19.4	2.60	10.8	31	1740	1.30	128	93	738
3	9:45	20.5	2.50	12.0	41	1860	0.98	106	94	None
3	11:00	20.5	1.60	12.7	41	1740	1.50	114	93	1100
3	11:15	22.0	1.60	14.4	38	1820	1.50	96	95	960
3	11:30	22.0	1.60	14.4	38	1760	1.30	118	93	960
3	11:45	Not recorded				1840	1.30	126	93	None
3	12:35	18.7	1.70	11.4	43	1810	1.30	104	94	1210
3	2:30	22.2	2.30	13.0	45	1760	1.40	112	94	649
3	3:05	23.0	2.40	14.4	37	1780	1.50	124	93	95

[a] Polymer used = Pearl River Chemical 560, cationic.

[b] Approximate cost of polymer = USD0.08 per pound.

obtained without chemical addition, and up to 1.5% with cost-effective chemical addition. It is expected that in a full-scale unit with proper flocculation, the goal of 2% or more could be met. Originally, the sludge was difficult to thicken. This was traced to the nature of the microbes. The spiral scoop of Supracell DAF could remove the low consistency sludge easily, and the sludge quantity removed could be controlled by adjustment of the level in the DAF clarifier.

27.7 DISCUSSIONS

The most common operational difficulties encountered in the conventional activated sludge treatment plant are rising sludge and bulking sludge, resulting in high suspended solids and BOD_5 in the plant effluent. This report discloses the common causes and efficient remedies.

The common cause of rising sludge is biological denitrification, in which nitrites and nitrates in the wastewater are converted to nitrogen gas.[38,44–46,48] When enough nitrogen gas is formed, and trapped in the sludge mass, the sludge in the conventional secondary sedimentation clarifier becomes buoyant and floats to the surface. This phenomenon is termed biological flotation.[1,28,29]

Rising sludge can also be caused by internal solids overloading and hydraulic overloading to the secondary sedimentation. Poor sedimentation clarifier design and operation in terms of flow-through velocity, weir design, and so on are also possible causes.

Sludge bulking is another phenomenon that often occurs in activated sludge plants whereby the sludge occupies excessive volumes and will not settle rapidly.

There are two principal types of sludge bulking problems: (a) the growth of filamentous organisms and (b) the formation of swelling biological flocs through the addition of bound water to the cells to the extent that their density is reduced.

Possible causes of sludge bulking include (a) absence of certain necessary trace elements in wastewater; (b) wide fluctuations in wastewater pH; (c) limited DO in the aeration tank; (d) inadequate F/M ratio; (e) inadequate mean cell residence time T_c; (f) inadequate return sludge pumping rate; (g) internal plant overloading; and (h) poor sedimentation clarifier operation.

The problems of sludge rising and sludge bulking, when serious, cannot be overcome easily. If rising and bulking conditions continue to persist after all the aforementioned factors have been checked, a critical investigation of the behavior of the aeration basin and the secondary sedimentation clarifier should be made. It is possible that the design is at fault, and either changes or expansions must be made in facilities.

Expansion of the existing aeration basins and secondary sedimentation clarifiers is costly and sometimes unaffordable. The easiest facility change will be addition of a secondary flotation unit, such as a Krofta Supracell or its equivalent, as shown in Figure 27.12.

The secondary sludge in the secondary flotation clarifier is floating; thus sludge rising is no longer a problem, and in fact, becomes a big plus.

Rapid changes (within hours) in many operational parameters, such as nutrients, F/M ratio, pH, DO, and so on, are detrimental to the performance of conventional activated sludge wastewater treatment systems. Under these conditions, production of filamentous fungi, which are the major cause of sludge bulking, is almost unavoidable. Fungi can tolerate an environment with a relatively low pH. Also they have a low nitrogen requirement and need only about one-half as much as bacteria. The ability of the filamentous fungi to survive and function under low pH and nutrient-limiting conditions makes them very important in biological treatment of certain industrial wastewaters and combined wastewaters with fluctuating characteristics. Sludge bulking is almost an expected phenomenon. Any filamentous living or nonliving substances will have poor settleability but excellent floatability. The selection of secondary flotation instead of conventional secondary sedimentation for sludge separation appears to be an ideal solution. Therefore, for a brand new activated sludge treatment plant treating industrial or combined wastewater, DAF clarifiers should be considered as a replacement of secondary sedimentation clarifiers.

For an existing conventional activated sludge treatment plant having a fungi problem, installing a DAF clarifier between the existing aeration basin and the final sedimentation clarifier (shown in Figure 27.12) will be the remedy.

The state-of-the-art method for controlling sludge bulking in an emergency situation is chemical oxidation by chlorine or hydrogen peroxide. Although chemical oxidation is effective in controlling sludge bulking caused by the growth of filamentous fungi, it is ineffective when sludge bulking is due to lightweight biological flocs containing bound water. Therefore, chemical oxidation is only a temporary solution to the fungi problem. Secondary flotation using a high-rate DAF, on the other hand, is a permanent solution to the sludge bulking problem caused by both filamentous substances and bound water.

The aeration/suffocation sequence resulting from the exclusive use of a secondary sedimentation clarifier by practically all facility designers since 1914 is contraproductive and harmful; it constitutes a shock: several inches below the surface of a settling unit there is practically no DO. In the practical operation of an efficient activated sludge treatment plant, the change in DO should not exceed 0.5 mg/L. Effluent coming from the aeration basin, maintained at about 2.0 mg/L DO, is depleted of DO within minutes after the mixed liquor enters the secondary sedimentation clarifier; the oxygen-requiring microorganisms cannot recover instantly from the shock resulting from such a tremendous change, and the recovery is bound to take up valuable retention time in the aeration basin. (The aeration basin with spare retention time capacity is a rare exception.) The addition of secondary flotation can return aerobic biological solids to the aeration basin and allow the more settleable solids to collect in the existing secondary settling units. An efficient DAF clarifier can gather the biological solids within 3 min and concentrate them to 2% or over in consistency, coincidentally reducing the return flow into the aeration basin since the consistency of sludge from settling often is only about 1%; and this could provide additional (*note*: frequently badly needed) retention time in the activated sludge treatment plant's aeration basin.

Section 27.3 presents the kinetic and material balance equations showing how the retention times of the existing aeration basin and the secondary sedimentation clarifier can be significantly increased and how the excess solids loading to the existing secondary sedimentation clarifier can be reduced by connecting a DAF secondary flotation clarifier (small in dimension) in series between the aeration basin and the secondary sedimentation clarifier, as shown in Figure 27.12. It should be noted that for the improved activated sludge wastewater treatment system (see Figure 27.12), the waste sludge settled in the final sedimentation (Q_{w2}) having a low consistency (~1–2% solids) can also be returned to the aeration basin when desired.

Another alternative involves the addition of a secondary flotation clarifier that parallels the existing secondary sedimentation clarifier in a conventional existing activated sludge wastewater treatment plant.

The use of secondary flotation as the sole secondary clarification unit in a brand new activated sludge wastewater treatment plant should also be considered by modern environmental engineers. It has been practiced in Italy[24] and West Germany.[47] The use of flotation for treatment of water, wastewater, and sludge is a well-established technology.[1–26,28,29,36–38,41,49–53] It has been applied for some 36 years or more in highly civilized countries with highest treatment requirements and therefore cannot be considered an innovative process. The use of secondary flotation as a secondary clarification unit in an activated sludge treatment plant, however, is still an innovative approach; the risk of using the unit is extremely low. A reference list documenting the DAF being used around the world can be found of elsewhere.[1,28,36,41,42]

When considering significant cost saving, flotation technology has a high potential as a substitute for sedimentation technology. One of the largest wastewater installations designed for the use of primary flotation instead of conventional primary sedimentation is the Sand Island Wastewater Treatment Plant in Honolulu, Hawaii.[46] Both primary flotation and secondary flotation can be used in other types of biological treatment processes, such as trickling filter, rotating biological contactors, and so on.[1,28,29]

27.8 SUMMARY AND CONCLUSIONS

Both DAF and DAFF clarifiers can be used for secondary flotation clarification in an activated sludge wastewater treatment plant. The Krofta Supracell is a high-rate DAF clarifier. This unique DAF clarifier has minimum water volume (<18 inch water depth), low cost, and flexibility in application due to the small size and has been very successfully applied for in-process and secondary flotation in industrial and municipal applications. It should be noted, however, that there are many reputable DAF/DAFF manufacturers and patented DAF/DAFF processes around the world, which are equally effective for either primary clarification or secondary clarification in biological wastewater treatment plants (including an activated sludge wastewater plant).[1,28–40] A few selected major DAF and DAFF manufacturers are listed below: (a) Dongshin Engineering Corporation, Seoul, Korea; (b) KEC, Massachusetts; (c) Austep Srl (Extant Environmental Solutions), Milan, MI, Italy; (d) MarTint Inc., Lexington, South Carolina; (e) Siemens AG International, Schuhstrasse, Germany; (f) Komline-Sanderson, Peapack, New Jersey; (g) WesTech Engineering Inc., Salt Lake City, Utah, (h) Praxair, Inc., Burr Ridge, Illinois; (i) Degremont Technologies-Infilco, Richmond, Virginia; (j) EIMCO Water Technologies, West Valley City, Utah; (k) HI-Tech Environmental, Hoover, Alabama; (l) Noram Engineering and Construction, Vancouver, BC, Canada; (m) KWI North America Corporation, Massachusetts; and (n) Krofta Technologies, Massachusetts.

The DAF/DAFF has the following advantages when used to separate biological solids from activated sludge mixed liquor[54]:

a. Sludge consistency for the floated biological sludge is about 3 times higher than the comparable settled sludge. This fact has been recognized for years in the use of flotation thickeners for the waste sludge. The spiral scoop and level control may give a wide range of control in sludge concentration.
b. The DAF/DAFF floated sludge is aerobic. There is far less kill of the biological community due to anaerobic shock. This has been demonstrated in field comparisons using both floated and settled sludge.
c. The aerobic DAF/DAFF floated sludge is returned to the aeration basin in 8–15 min versus hours for the conventional activated sludge process using the secondary sedimentation clarifier.
d. Clarified water from a properly operated and sized DAF unit is comparable in quality to settled effluent. This has been demonstrated in field pilot trials. When a settling unit already exists in the process, the practice is to undersize the DAF and install it in series with the existing settling unit. The DAF is then the workhorse or “harvester” and the settling unit is the final “polisher” for the effluent. The problems of high solids loading, high hydraulic loading, sludge rising, and/or sludge bulking in the existing conventional activated sludge treatment plants can then be solved.
e. The small size of the DAF greatly simplifies the adjustments to the process due to short cycle time, and the cleanup and/or maintenance.
f. Capital cost of DAF is definitely lower than conventional sedimentation clarifiers or comparable basin expansion.
g. Stainless steel and/or prefabricated construction is economically feasible.

In summary, although the present conventional activated sludge process has been in use for many decades, there is still a lot of room for improvement. One big area of weakness of the conventional process is the secondary sedimentation clarifier that gives low-consistency sludge, shocks the living biota by holding them for long periods in anaerobic conditions, and has problems of sludge rising, sludge bulking, and so on. The use of a high-rate DAF unit in series before the final sedimentation clarifier solves these deficiencies of the conventional activated sludge process. The net results are lower solids loading to the existing sedimentation clarifier, higher hydraulic capacity and retention time of the aeration tank, easier concentration of waste sludge, more active recycled sludge, better effluent quality, and lower wastewater treatment costs. Besides, there will be no sludge rising or sludge bulking problems.

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ABBREVIATIONS

BOD	Biochemical oxygen demand
BOD_5	5-day biochemical oxygen demand
DO	Dissolved oxygen
EFF	Effluent
FLOAT	Floated sludge or scum
gpm	Gallons per minute
INF	Influent
KEC	Krofta Engineering Corporation
LIWT	Lenox Institute of Water Technology
Lpm	Liters per minute
MGD	Million gallons per day
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
NTIS	National Technical Information Service
ppm	Parts per million
SVI	Sludge volume index
TPD	Tons per day
TSS	Total suspended solids
VSS	Volatile suspended solids

NOMENCLATURE

b	Endogenous or decay coefficient, time^{-1} (s^{-1})
E	Process efficiency in terms of soluble organics removal = $100(S_0 - S)/S_0(\%)$
F/M	Food-to-microorganism ratio = S_0/TX (s^{-1})
k_m	Maximum rate of specific soluble organics utilization, time^{-1} (s^{-1})

K_s	Michaelis–Menten constant, or half velocity coefficient being numerically equal to the soluble organics concentration when $U = 0.5k_m$, mass per unit volume (mg/L)
Q	Volumetric wastewater flow rate, volume per unit time (ft^3/s or m^3/s)
Q_w	Wasted sludge flow rate, volume per unit time (ft^3/s or m^3/s)
Q_{w1}	Flow rate of waste sludge from secondary flotation, volume per unit time (ft^3/s or m^3/s)
Q_{w2}	Flow rate of waste sludge from the existing secondary sedimentation clarifier, volume per unit time (ft^3/s or m^3/s)
S	Soluble organics (i.e., substrate) concentration in wastewater, mass per unit volume (mg/L)
S_0	Initial soluble organic (i.e., substrate) concentration, mass per unit volume (mg/L)
t	Time (s)
u	Net specific growth rate, the change of microbial concentration per unit time per unit microbial concentration, $time^{-1}$ (s^{-1})
U	Specific soluble organics (i.e., substrate) utilization rate, the change of soluble organics concentration per unit time per unit microbial concentration (s^{-1})
V	Biological reactor volume (ft^3 or m^3)
V_f	Volume of the secondary flotation clarifier (ft^3 or m^3)
V_p	Volume of the primary clarifier (ft^3 or m^3)
V_s	Volume of the secondary sedimentation clarifier (ft^3 or m^3)
X	Microbial concentration (i.e., VSS) in the biological reactor, mass per unit volume (mg/L)
X_e	Sludge concentration in the treated effluent from the final clarifier, mass per unit volume (mg/L)
X_0	Sludge concentration in the primary effluent, mass per unit volume (mg/L)
X_r	Return sludge concentration, mass per unit volume (mg/L)
X_{w1}	Concentration of waste sludge (i.e., float) from secondary flotation, mass per unit volume (mg/L)
X_{w2}	Concentration of waste sludge from the existing secondary sedimentation clarifier, mass per unit volume (mg/L)
Y	Growth yield coefficient, mass microbial growth per unit mass substrate utilized (dimensionless)
T	Hydraulic detention time of the biological reactor = V/Q (s)
T_c	Mean cell residence time, or sludge retention time, time (s)

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28 Management and Treatment of Acid Pickling Wastes Containing Heavy Metals

Lawrence K. Wang, Veysel Eroglu, and Ferruh Erturk

CONTENTS

28.1 INTRODUCTION

28.1.1 METAL FINISHING INDUSTRY

Metal industries use substantial quantities of water in processes such as metal finishing and galvanized pipe manufacturing in order to produce corrosion-resistant products. Effluent wastewaters from such processes contain toxic substances, metal acids, alkalis, and other substances that must be treated, such as detergents, oil, and grease. These effluents may cause interference with biological treatment processes at sewage treatment plants. In the case when the effluents are to be discharged directly to a watercourse, treatment requirements will be more stringent and costly.[1–8]

28.1.2 ACID PICKLING AND ACID CLEANING OF METAL SURFACE

Laser cutting, welding, and hot working leave a discolored oxidized layer or scale on the surface of the worked steel. This must be removed in order to perform many of the surface finishing processes. The acid pickling process is used to remove the oxide or scale of metals and corrosion products, in which acids or acid mixtures are used.

Acid cleaning is also used for removing inorganic contaminant not removable by other primary cleaning solutions. Acid cleaning has its limitations in that it is difficult to handle because of its corrosiveness and is not applicable to all steels. Hydrogen embrittlement becomes a problem for some alloys and high-carbon steels. The hydrogen from the acid reacts with the surface and makes it brittle and crack. Because of its high reactivity to treatable steels, acid concentrations and solution temperatures must be kept under control to ensure desired pickling rates.

Technically speaking, acid pickling is a treatment of metallic surfaces that is done to remove impurities, stains, rust, or scale with a solution called pickle liquor, containing strong mineral acids, before subsequent processing, such as extrusion, rolling, painting, galvanizing, or plating with tin or chromium. The two acids commonly used are hydrochloric acid and sulfuric acid.

28.1.3 PICKLING LIQUOR AND WASTE PICKLING LIQUOR

The most common acid used for pickling is sulfuric acid. Other acids such as hydrochloric, phosphoric, hydrofluoric, or nitric acids are also used individually or as mixtures. Sulfuric or hydrochloric acids are used for pickling carbon steels, and phosphoric, nitric, and hydrofluoric acids are used together with sulfuric acid for stainless steel. Water is used in pickling and rinsing. The quantity of water used can vary from <100 to 3000 L/ton, depending on whether once-through or recycle systems are used.[1,2]

Carbon steel is pickled usually by either sulfuric acid or hydrochloric acid. At one time, sulfuric acid was the pickling agent of choice for picklers running integrated steel works.[1] Hydrochloric acid is chosen in more modern lines when bright surfaces, low energy consumption, reduced overpickling, and the total recovery of the pickling agent from the waste pickle liquor are desired.

The spent pickling liquor is called waste pickling liquor (WPL), which must be properly treated for disposal or reuse. Wastewaters from pickling include acidic rinse waters, metallic salts, and waste acid. WPL is considered a hazardous waste by the U.S. Environmental Protection Agency (U.S. EPA).

28.1.4 ACID PICKLING OPERATION

Pickle solutions that are used in the removal of metal oxides or scales and corrosion products are acids or acid mixtures.

Depending on the product being pickled, the acid pickling operation can be a batch or continuous process. In continuous strip pickling, more water is required for several operations such as the uncoilers, looping pit, and coilers. In the case of pickling hot rolled coils, the coils are transported to the pickling line. In the uncoiler section, the coil is fed through a pit containing water for washing off the surface dirt and then fed through the pickling line.

28.1.5 WPL TREATMENT AND RECYCLE

Lime or alkaline substances are used to neutralize the waste pickle liquor. In addition, 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solids (TSS), oil and grease (O&G), ammonium nitrogen (NH_4^+-N), pH, cyanides, fish toxicity, and several relevant metal ions such as cadmium (Cd^{2+}), iron (Fe^{2+}), zinc (Zn^{2+}), nickel (Ni^{2+}), copper (Cu^{2+}), and chromate (Cr^{6+}) have to be reduced below the maximum allowable limits.

Some acid pickling plants, particularly those using hydrochloric acid, operate acid recovery plants where the mineral acid is boiled away from the iron salts, but there still remains a large volume of highly acid ferrous sulfate or ferrous chloride to be disposed of. Since the 1960s, total hydrochloric acid regeneration processes have reached widespread acceptance.[5] The by-product of nitric acid pickling is marketable to a couple of secondary industries including fertilizers.

28.2 PICKLING PROCESS REACTIONS AND WPL CHARACTERISTICS

28.2.1 WPL Generation

During the application of the pickling process in the finishing of steel, in which steel sheets are immersed in a heated bath of acid (sulfuric, hydrochloric, phosphoric, etc.), scales (metallic oxides) are chemically removed from the metal surface. The pickling process can be a batch or continuous process. In these processes, water is used in pickling and rinsing operations. In continuous pickling, wet fume scrubbing systems are also used. The effluent water from the pickling tanks, which is called the waste pickle liquor (WPL), consists of spent acid and iron salts. Waste hydrochloric liquor contains 0.5–1% free hydrochloric acid and 10% dissolved iron, and the production of WPL is approximately 1 kg free hydrochloric acid and 10 kg dissolved iron per ton of steel pickled.[2] In waste sulfuric acid pickle liquor, the free acid and dissolved iron content are approximately 8% each, resulting in 10 kg each of free sulfuric and dissolved iron per ton of steel pickled. WPL may also contain other metal ions, sulfates, chlorides, lubricants, and hydrocarbons. Rinse water, which contains smaller concentrations of the above contaminants, ranges in quantities from 200 to 2000 L/ton. Fume scrubber water requirements range from 10 to 200 L/ton.[2]

In hot rolling processes, pickling is used for further processing to obtain the surface finish and proper mechanical properties of a product. In the case of pickling hot rolled coils, the coil is fed through a pit containing water for washing off surface dirt and then fed through the pickling line. In the pickling section, the coil strip comes in contact with the pickle liquor (sulfuric or hydrochloric acid). Wastewater sources are processor water, waste pickle liquor, and rinse water.

In the case of batch pickling, the product is dipped into a pickling tank and then rinsed in a series of tanks. The quantity of wastewater discharged from a batch process is less than that from continuous operation. The wastewater is usually treated by neutralization and sedimentation.

28.2.2 Sulfuric Acid Pickling Reaction

In sulfuric acid pickling, ferrous sulfate is formed from the reaction of iron oxides with sulfuric acid:

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O. \tag{28.1}$$

The ferrous sulfate that is formed in the above reaction is either monohydrate or heptahydrate ($FeSO_4 \cdot 7H_2O$).

28.2.3 Hydrochloric Acid Pickling Reactions

During the hot forming or heat treating of steel, oxygen from the air reacts with the iron to form iron oxides or scale on the surface of the steel. This scale must be removed before the iron is subsequently shaped or coated. One method of removing this scale is pickling with hydrochloric acid.[5]

Pickling is conducted by continuous, semicontinuous, or batch modes depending on the form of metal processed. In developing a National Emission Standard for the steel pickling industry, U.S.

EPA recently surveyed the industry and produced a background information document containing detailed information concerning the various processes in the industry, pollution control devices, and emissions.[5]

When iron oxides dissolve in hydrochloric acid, ferrous chloride is formed according to the following reactions:

$$Fe_2O_3 + Fe + 6HCl \rightarrow 3FeCl_2 + 3H_2O, \tag{28.2}$$

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O. \tag{28.3}$$

Since Fe_3O_4 is $Fe_2O_3{\cdot}FeO$, the reaction for Fe_3O_4 is the sum of the two reactions. Some of the base metal is consumed in the above reaction as well as in the following reaction:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2. \tag{28.4}$$

An inhibitor is usually added to lessen the acid's attack on the base metal while permitting it to act on the iron oxides. The rate of pickling increases with the temperature and concentration of HCl. As pickling continues, HCl is depleted and ferrous chloride builds up in the pickling liquid to a point where pickling is no longer effective. At this point, the old liquid is discharged and the pickling tank is replenished with fresh acid. Typical HCl concentrations in a batch pickling process are 12 wt% for a fresh solution and 4 wt% before acid replenishment. At these concentrations, the concentration of HCl in the vapor phase increases rapidly with temperature.[5]

28.3 TREATMENT OF WPLs AND CLEANING WASTES

28.3.1 Treatment, Disposal, or Recycle

Through the late 1980s, spent pickle liquor was traditionally land disposed by steel manufacturers after lime neutralization. The lime neutralization process raises the pH of the spent acid and makes heavy metals in the sludge less likely to leach into the environment. Today, however, some of the spent pickle liquor can be recycled or regenerated on-site by steel manufacturers.[5]

The treated wastewater effluents, in general, can be either discharged to a watercourse or a public sewer system. In the former case, the treatment requirements will be more stringent.

The waste pickle liquor, rinse water discharges, and fume scrubber effluent can be combined in an equalization tank for subsequent treatment. Basically, three methods are used to treat the WPL:

1. Neutralization and clarification [sedimentation or dissolved air flotation (DAF)]
2. Crystallization of ferric sulfates and regeneration of the acid
3. Deep-well disposal.

The most commonly used methods are the first two.

28.3.2 Neutralization and Clarification (Sedimentation or DAF)

In old plants, neutralization and sedimentation are applied to the treatment of wastewaters in general, including WPL. A typical treatment system for continuous pickling water is shown in Figure 28.1.[1,3] In an integrated steel mill, a central wastewater treatment system is used to treat wastewater from pickling lines, cold rolling mills, and coating lines.

The pickling wastewater has a low pH and contains dissolved iron and other metals. The blowdown and dumps from the cold rolling mill solutions, which may contain up to 8% oil, are collected in emulsion-breaking tanks in which the emulsions are broken by heat and acid. The oil is then

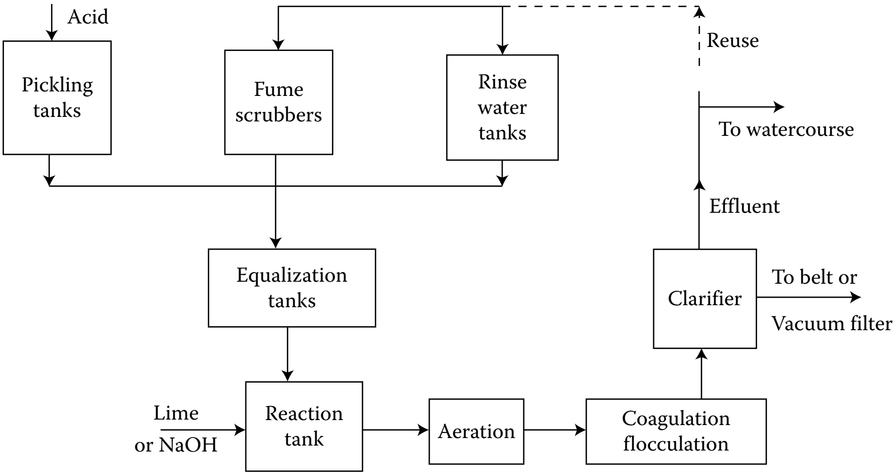

FIGURE 28.1 Typical treatment system for pickling. (From Eroglu, V. and Erturk, F., in *Handbook of Industrial Waste Treatment*, Wang, L.K. and Wang, M.H.S., Eds, Marcel Dekker, New York, 1991, pp. 293–306; Eroglu, V., Topacik, D., and Ozturk, I., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989. With permission.)

skimmed, and the water phase containing 200–300 mg/L of oils is treated together with the wastewaters from pickling, cold rolling, and coating lines. The combined wastewater flows to a settling and skimming tank where solids and oil are removed. The effluent from the settling/skimming tank is then treated in a series of settling tanks where chemicals (coagulants and/or lime) and air are added to oxidize the remaining iron to ferric ions (Fe^{3+}), to further break the oil emulsions and neutralize the excess acid in the wastewater. The effluent from the mixing tanks then enters a flocculator/clarifier system, the overflow from the clarifier is discharged, and the settled sludge is pumped to a dewatering system consisting of centrifuges, belt, or vacuum filters. The dewatered sludge is disposed and the water phase returned to the clarifier effluent.

The clarifier shown in Figure 28.1 can be either a sedimentation clarifier, a DAF clarifier, or a dissolved air flotation-filtration (DAFF) clarifier, depending on the space availability, pretreatment requirements, effluent limitations, and costs.[6–11] Modern pickling plants use DAF or DAFF for more cost-effective clarification or more efficient clarification, respectively.

28.3.3 CRYSTALLIZATION AND REGENERATION

The use of lime or other alkaline substances to neutralize acid is quite costly, especially when large capacities are involved. Also there are potential values in the acids and ferrous ion, and therefore, recovery of these substances will not only reduce the pollution load, but their sale or reuse will represent a profit to the industry.

Crystallization is one of the treatment methods for sulfuric acid waste pickle liquor. Thus, it is possible to decrease the pollution load and at the same time recover various hydrates of $FeSO_4$. The crystallization of $FeSO_4$ depends on the characteristics of the water and acid, and solubility of $FeSO_4$. The solubility of ferrous sulfate as a function of temperature and sulfuric acid concentration is shown in Figure 28.2.[4] In this figure, $FeSO_4 \cdot 7H_2O$ is dominant in region A, $FeSO_4 \cdot 4H_2O$ in region B, and $FeSO_4 \cdot H_2O$ in region C.

The crystallization of ferrous sulfate as heptahydrate is commonly used today. The concentration of iron in the acid bath is approximately 80 g/L as Fe^{3+}. The crystallization of $FeSO_4 \cdot 7H_2O$ is achieved by cooling the acid waters in heat exchangers or evaporation under vacuum after pickling.

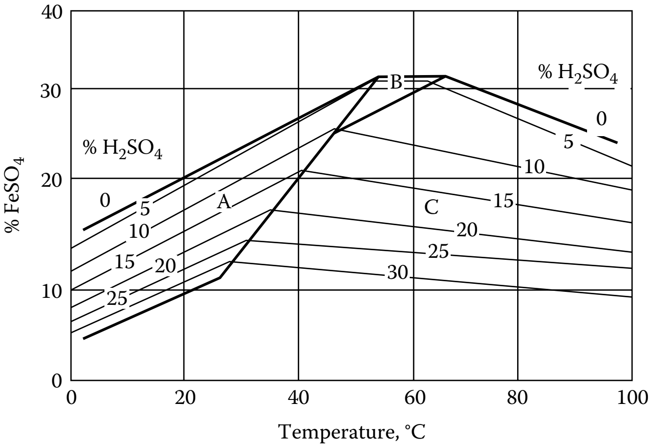

FIGURE 28.2 Solubility of ferrous sulfate $FeSO_4$ as a function of temperature and sulfuric acid concentration. (From Eroglu, V. and Erturk, F., in *Handbook of Industrial Waste Treatment*, Wang, L.K. and Wang, M.H.S., Eds, Marcel Dekker, New York, 1991, pp. 293–306; Eroglu, V., Topacik, D., and Ozturk, I., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989. With permission.)

Make-up acid must be added to the bath. During countercurrent cooling, the acid bath waste passes through two to three crystallization tanks and is cooled down between 0°C and 5°C. The crystallized ferric sulfates are recovered by centrifuging. A typical flow diagram of $FeSO_4 \cdot 7H_2O$ crystallization is shown in Figure 28.3.

The WPL is sprayed above a cyclone crystallizer, and air is blown from the bottom countercurrent to the liquid. A packing material is also present in order to increase the area of contact between the air and the liquid. The acid wastewaters are then cooled, and the $FeSO_4 \cdot 7H_2O$ crystals are recovered by centrifuging.

In the Ruthner process,[1] the WPL is first concentrated in an evaporator. The concentrate is then pumped to a reactor where it is combined with hydrochloric acid gas, in which ferrous chloride and sulfuric acid are formed. The sulfuric acid is then separated by centrifuging. The ferrous chloride

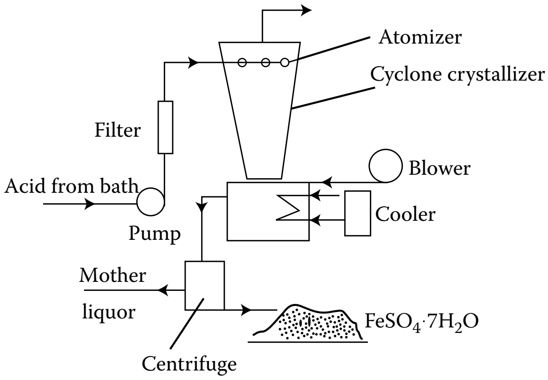

FIGURE 28.3 Flow diagram of ferrous sulfate $FeSO_4 \cdot 7H_2O$ crystallization. (From Eroglu, V. and Erturk, F., in *Handbook of Industrial Waste Treatment*, Wang, L.K. and Wang, M.H.S., Eds, Marcel Dekker, New York, 1991, pp. 293–306; Eroglu, V., Topacik, D., and Ozturk, I., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989. With permission.)

goes to a roaster in which it is converted to ferric oxide. The gases liberated from the roaster and the acid from the centrifuge go to a degassing chamber, and the sulfuric acid is removed and returned to the pickling process, or can be sold. The remaining gases from the degasser are passed through an absorption system and then reused in the reaction chamber.

In the Lurgi process[1] that was developed in Germany, hydrochloric acid is recovered from the WPL. The acid is regenerated in a fluidized bed. During pickling with HCl, the acid circulates between a pickling tank and a storage tank and the acid reacts with the iron oxide scale from the steel producing ferric chloride, resulting in increasing concentration of dissolved iron and decreasing concentration of acid.

In the Lurgi system,[1] the acid level in the pickling liquor stays constant at about 10%. A continuous bleed stream is removed from the system at the same rate as it is pickled. The bleed stream, or spent pickle, is fed to a pre-evaporator and heated with gases from the regeneration reactor. Concentrated liquor from the pre-evaporator then enters the lower part of the reactor containing 13% acid and 20% ferrous chloride. The reactor contains a fluidized bed of sand and is fired by oil or gas to maintain an operating temperature of about 800°C. The reaction products leave from the top of the reactor. The ferric oxide is removed by a cyclone, and the hot gases enter the pre-evaporator. The overhead from the evaporator, which is at a temperature of about 120°C, contains water vapor, HCl, combustion products, and also some HCl that vaporizes directly from the plant liquor that enters the system. The gas mixture from the pre-evaporator enters the bottom of the adiabatic absorption tower, where HCl is absorbed by another bleed stream of the pickle liquor, and thus the regenerated acid is placed back in the pickle liquor circuit. The regenerated acid contains 12% acid and about 70 g/L of iron. The unabsorbed gases move to a condenser.

28.4 TREATMENT OF WASTEWATER FROM ACID PICKLING TANKS IN A GALVANIZED PIPE MANUFACTURING FACTORY USING SULFURIC ACID

28.4.1 General Description

This study was conducted at Cayirova Boru Sanayii AS (a galvanized pipe manufacturing factory) in Gebze, Kocaeli, Turkey.[1,3] At this plant, batch pickling is applied. During the manufacturing process, the pipes are immersed in an acid bath that contains 25% sulfuric acid at 80°C and then prepared for the galvanization process by passing through cold water, hot water, and flux baths. The purpose of a cold water bath is to clean the acid from the surface of the pipes following pickling. A hot bath is applied in order to dry and prevent water and acid from entering a flux bath. The purpose of the flux bath, in which ammonium zinc chloride (NH_4ZnCl_3) is used, is to prepare a suitable surface for galvanization and prevent oxidation of the pipe. The flow diagram of the baths is shown in Figure 28.4.

Acid bath wastewaters are usually discharged once a week. The average flow rate of these wastewaters is 4 m^3/h, with a maximum of 8 m^3/h. The hot and cold water baths are discharged once every 15 days. The quantities and flow rates of these wastewaters are shown in Table 28.1.[1,3]

28.4.2 Characteristics of Wastewaters

Wastewater characteristics must be known in order to select a suitable treatment system. For this purpose, the wastewater samples taken from the sources were analyzed to determine various parameters. Also, the quantities of chemicals (NaOH) required for neutralization and settling characteristics were determined. These were made separately for continuous and batch discharges. Since the system is to be designed according to the continuous discharge of wastewaters from the batch system to the treatment plant, "mixed wastewater" was prepared in quantities proportional to the flow rates. The quantity of NaOH required for 1000 mL of mixed wastewater is shown in Table 28.2.[1,3]

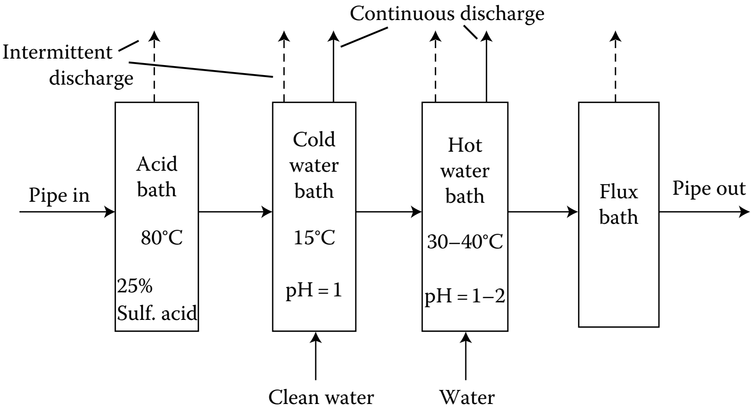

FIGURE 28.4 Flow diagram showing sources of wastewaters in the galvanized pipe manufacturing process. (From Eroglu, V. and Erturk, F., in *Handbook of Industrial Waste Treatment*, Wang, L.K. and Wang, M.H.S., Eds, Marcel Dekker, New York, 1991, pp. 293–306; Eroglu, V., Topacik, D., and Ozturk, I., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989. With permission.)

TABLE 28.1
Types and Quantities of Wastewaters in Acid and Flux Baths

Wastewater Source	Average	Maximum
Continuous discharge from hot and cold water baths	4 m^3/h	6 m^3/h
Intermittent discharge (once every 7 days)	15 m^3	15 m^3
Cold water bath (once every 15 days)	15 m^3	15 m^3
Hot water bath (every 15 days)	15 m^3	15 m^3
Flux bath	5 m^3	5 m^3

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.2
Quantities of Wastewater Required for 1000 mL "Mixed Wastewater"

Units	Flow Rate (m^3/2 months)	Quantity of NaOH Required for 1000 mL
Continuous discharge	8640	971
Acid bath	129	14.5
Cold water bath	60	6.8
Hot water bath	60	6.8
Flux bath	5	0.56
Total	8894	1000

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.3
Experimental Results for Continuous Discharge

Parameter	Unit	Original Sample	After Neutralization and Separation
Total iron	mg/L	5980	350
Chromate	mg/L	0	0
Lead	mg/L	0	0
COD	mg/L	350	20
Zinc	mg/L	0	0
pH	—	1.6	8.0
Color	—	—	Greenish

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

Since the continuous discharge quantities are much larger compared to batch discharges, they were analyzed separately. The wastewaters from continuous discharge were neutralized with 2 N NaOH. The results are given in Table 28.3.[1,3] The settling characteristics of the continuous discharge wastewaters are shown in Table 28.4.[1,3] The experimental results from the "mixed wastewaters," the quantities of which were shown in Table 28.2, are given in Table 28.5.[1,3] The settling characteristics of the mixed wastewaters are shown in Table 28.6.[3]

Neutralization can also be carried out by a combination of NaOH and lime. Experiments were conducted in order to determine the optimum combination of NaOH and lime. For this purpose, various quantities of lime were added to 1 L of mixed wastewater, and then the amount of NaOH required was determined to obtain a pH of 8.5. The results are shown in Table 28.7.[3]

As can be seen from Table 28.7, the required dosage of NaOH does not increase significantly when the limb dosage is more than 20 g/1000 mL. The mixed wastewater, which was treated with the dosages of lime and NaOH shown in Table 28.7, was then aerated for 15 min after the pH reached 8.5. After aeration, it was allowed to settle for a period of 30–120 min. An analysis of the clear phase after settling is shown in Table 28.8.[3] The wastewater was treated with 15 g/L of lime

TABLE 28.4
Settling Characteristics of Continuous Discharge Wastewaters

Time	Volume of Clear Phase (mL/L)
15 min	20
30 min	50
1.0 h	90
2.5 h	240
3.5 h	400
4.5 h	460
5.5 h	500
20 h	720

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.5
Experimental Results for Mixed Wastewater Samples

Parameter	Original Sample	After Neutralization and Separation in Clear Phase
Total iron, mg/L	6100	300
Sulfate, mg/L	19,000	16,000
Chromate, mg/L	0	0
Lead, mg/L	0	0
Zinc, mg/L	15	0
COD, mg/L	360	15
pH	0.7	8.5

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.6
Settling Characteristics of Mixed Wastewaters

Time	Volume of Clear Phase (mL/L)
30 min	40
1 h	100
2.5 h	220
3.5 h	350
4.5 h	410
53 h	460
20 h	700

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.7
Quantities of Sodium Hydroxide Required for Different Quantities of Lime to Obtain a pH of 8.5

I 10 g Lime		II 20 g Lime		III 26 g Lime		IV 32 g Lime	
pH	NaOH Added (mL)	pH	NaOH Added (mL)	pH	NaOH Added (mL)	pH	NaOH Added (mL)
3.4	0	6.8	0	7.1	0	7.4	0
6.5	20	7.4	8	7.6	4	7.6	4
7.4	28	8.4	16	7.9	12	8.6	12
8.0	30	8.5	17.2	8.6	15.2		
8.5	32						

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.8
Analysis of Mixed Wastewater after Neutralization, Aeration, and Clarification

		Lime + NaOH (g)			
Parameter (mg/L)	**Settling Time (min)**	**10**	**20**	**26**	**32**
Iron	30	125	30	5	0
	120	0	0	0	0
Sulfate	30	5750	5759	5000	3000
	120	5750	5750	5000	2750
Settlable matter	30	120	280	320	440
	120	400	520	410	480

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

TABLE 28.9
Analysis of Wastewater after Neutralization, Aeration, and Clarification

Parameter	Concentration (mg/L)
COD	0
Total iron	0
Zinc	0
Sulfate	2100

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

and NaOH to attain a pH of 8.5, aerated for 1 h, mixed for 23 h, and an additional hour was allowed for clarification. The analysis of the clear clarifier effluent is shown in Table 28.9.[1,3]

28.4.3 TREATMENT METHODS

As was indicated in the previous section, the concentration of iron in the mixed wastewaters ranged from 5980 to 6100 mg/L; its pH was 0.7 and zinc concentration was 15 μg/L. Since these wastewaters come only from acid baths and not from other processes of the plant, parameters such as cadmium and fluoride are not encountered. The discharge standards for the metal industry effluents set by the Turkish Water Pollution Control Regulation (Official Gazette, Table 15.7, September 4, 1988) are shown in Table 28.10.[1]

The experiments conducted on wastewaters, the results of which were shown in the previous section, indicated that neutralization/aeration/settling gave satisfactory results. The sludge formed must be disposed after dewatering in a filter press, a horizontal belt filter, or a centrifuge. An equalization tank is required in order to compensate for the effects of intermittent discharges. The treated wastewater can then be recycled to be used in the process or discharged to the river. The flow diagram of the selected system is shown in Figure 28.5.

TABLE 28.10
Effluent Standards for Metal Industry Wastewaters in Turkey

Parameter	2-h Composite Sample (mg/L, except pH)
COD	200
Suspended solids	125
Oil and grease	20
Ammonium nitrogen	400
Cd	0.1
Fe	3
Flouride	50
Zn	5
Fish toxicity	10
pH, units	6–9

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

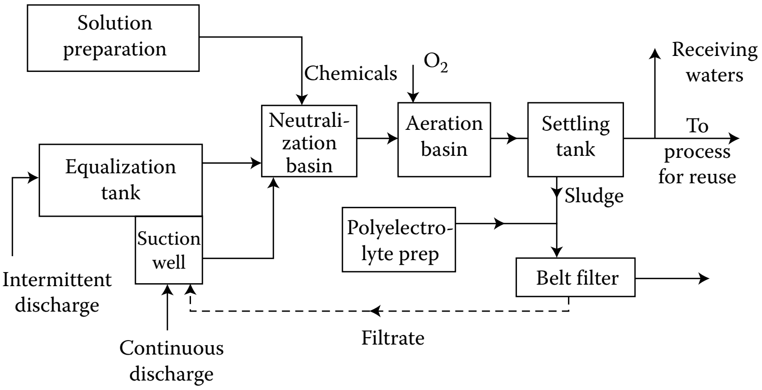

FIGURE 28.5 Flow diagram of the selected treatment system. (From Eroglu, V. and Erturk, F., in *Handbook of Industrial Waste Treatment*, Wang, L.K. and Wang, M.H.S., Eds, Marcel Dekker, New York, 1991, pp. 293–306; Eroglu, V., Topacik, D., and Ozturk, I., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989. With permission.)

28.5 MANAGEMENT AND TREATMENT OF WASTEWATER AND AIR EMISSIONS FROM ACID PICKLING TANKS USING HYDROCHLORIC ACID

28.5.1 Environmental Management at Steel/Iron Hydrochloric Acid Pickling Plants

Hydrochloric acid aerosols are produced and released into the air during the pickling process as HCl volatilizes, and steam and hydrogen gas with entrained acid fumes rise from the surface of the pickling tank and from the pickled material as it is transferred from the pickling tank to the rinse tank. Pickling and rinse tanks are covered and the acid fumes are generally collected and treated by control devices (e.g., packed tower scrubbers) to remove HCl. Emissions from many batch operations are uncontrolled. Pickling is sometimes accomplished in vertical spray towers. In this process, all the HCl in the pickling solution produces hydrochloric acid aerosols that are also used. Acid storage tanks and loading and unloading operations are also potential sources of HCl emissions. Uncontrolled HCl emissions from a storage tank may be of the order of 0.07–0.4 tons per year (tpy) of HCl per tank, depending on the tank size and usage. For each million ton of steel processed at continuous coil or push–pull coil model facilities, storage tank losses are estimated to amount to 0.39 tpy. For other types of pickling facilities, storage tank losses are estimated to be about 11.19 tpy of HCl per million ton of steel processed.

The U.S. EPA guidance for acid storage tanks can be applicable to storage tanks used in conjunction with the pickling process and may be extended to apply to the pickling process itself.[6] For storage tanks, one applies the amount of hydrochloric acid aerosol generated from a tank under average 19 capacity and other conditions to the manufacturing threshold and multiplies that by the number of times the tank has been drawn down and refilled. The amount of acid aerosol manufactured during the pickling process can be similarly determined by the amount of HCl generated from the pickling tanks during the processing of a certain amount of material and scaling up that figure to apply to all the material processed by the same process and under the same conditions. The amount of hydrochloric acid aerosols lost from the pickling tanks counts toward the material released to air unless the aerosol is collected and removed before exiting the stack. The hydrochloric acid aerosol collected in a scrubber is converted to the nonaerosol form, not reportable; the hydrochloric acid aerosol removed by the scrubber is considered to have been treated for destruction.

Hydrochloric acid may be recovered from the WPL in an acid regeneration process. This process has the potential for emitting significant amounts of hydrochloric acid aerosols. The annual capacities of 10 acid regeneration plants surveyed by the U.S. EPA[5] ranged from 3.2 to 39.8 million gallons (MG) per year for a single facility. The spray roasting acid regeneration process is the dominant one presently employed. One older facility used a fluidized bed roasting process.

In the spray roasting acid regeneration process, WPL at 2–4% HCl comes into contact with hot flue gas from the spray roaster that vaporizes some of the water in the WPL. The WPL then becomes concentrated pickling liquor (CPL). The CPL is then sprayed on the spray roaster where ferrous chloride in the droplets falling through the rising hot gases reacts with oxygen and water to form ferric oxide and HCl,

$$2\mathrm{FeCl_2} + [\mathrm{O}] + 2\mathrm{H_2O} \rightarrow \mathrm{Fe_2O_3} + 4\mathrm{HCl}. \tag{28.5}$$

Flue gas containing HCl goes to a venturi preconcentrator and an absorption column. There, the generated acid contains approximately 18% HCl by weight. Emissions from acid regeneration plants range from about 1 to more than 10 tpy from existing facilities with and without pollution control devices (controlled and uncontrolled facilities).

Acid regeneration plants have storage tanks for spent and regenerated acid and these tanks are potential sources of HCl emissions. Emission estimates for uncontrolled and controlled storage tanks at acid regeneration facilities are 0.0126 and 0.008 tpy per 1000 gallons of storage capacity, respectively.

Acid recovery systems are used to recover the free acid in the WPL. They are not employed in larger facilities because they recover only 2–4% free HCl from the spent acid, but leave the $\mathrm{FeCl_2}$ in the solution that must be processed or disposed of separately. These acid recovery systems are generally closed-loop processes that do not emit HCl. In their survey, U.S. EPA compiled data from different types of pickling operations and their estimated emissions.[5] This information is reproduced in Table 28.11.

In order to estimate emissions from pickling facilities, U.S. EPA developed 17 model plants to represent five types of pickling operations and one acid regeneration process.[12] The model plants include one or more size variation for each process model. The model plants were developed from information obtained from a survey of steel pickling operations and control technologies. U.S. EPA estimated emission rates for model facilities. Using these emission rates and the production and hours of operation for the model pickling plants, emission factors were calculated. These appear in Table 28.12.

TABLE 28.11
Annual Emission Estimates from Steel Pickling Operations

Type of Facility	Number of Facilities	Number of Operations	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)
Continuous coil	36	64	22,820	2640
Push–pull coil	19	22	815	29
Continuous tube	20	55	6524	4252
Batch	4	11	100	52
Acid regeneration	26	59	2632	1943
Storage tanks	10	13	5662	393
	99	369 (estimated)	41	24

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

Note: Mg = million grams.

TABLE 28.12
Air Emissions and Emission Factors for Model Pickling Plants

Type of Facility	Production (tpy)[a]	Hours of Operation (h)	Uncontrolled HCl Emissions (lb/h)	Control Efficiency (%)	Emission Factor (lb HCl/tons Processed)[b] (U)	(C)
Continuous coil (S)	450,000	6300	111	93	1.6	0.1
Continuous coil (M)	1,000,000	6300	179	92	1.1	0.1
Continuous coil (L)	2,700,000	7000	347	92	0.9	0.1
Push–pull coil (S)	300,000	5000	12	98	0.2	0.0
Push–pull coil (M)	550,000	4400	27	98	0.2	0.0
Push–pull coil (L)	1,300,000	8760	42	95	0.3	0.0
Continuous rod/wire (S)	10,000	5100	46	98	23.5	0.5
Continuous rod/wire (M)	55,000	7800	119	84	16.9	2.7
Continuous rod/wire (L)	215,000	7200	413		13.8	
Continuous tube (S)	80,000	6400	73	95	5.8	0.3
Continuous tube (L)	420,000	6700	312	95	5.0	0.2
Batch (S)	15,000	4400	16	94	4.7	0.3
Batch (M)	75,000	4600	65	90	4.0	0.4
Batch (L)	170,000	5700	147	81	4.9	0.9
Acid regeneration (S)	4	8200	7	98	14,350.0	287.0
Acid regeneration (M)	13.5	7700	28	98	15,970.4	319.4
Acid regeneration (L)	30	8760	1064	98.5	310,688.0	4660.3

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

[a] The production for acid regeneration facilities is in units of million gallons per year.

[b] The emission factor units for acid regeneration facilities is in units of lb of HCl per million gallons of HCl produced.

S: small; M: medium; L: large; U: uncontrolled; C: controlled.

A National Emission Standard for Hazardous Air Pollutants (NESHAP) for new and existing hydrochloric acid process steel pickling lines and HCl regeneration plants pursuant to Section 112 of the Clean Air Act as amended in November 1990 has been proposed (62 FR 49051, September 18, 1997). The purpose of this rulemaking is to reduce emissions of HCl by about 8360 megagrams per year.

28.5.2 MANUFACTURING PLANT OF STAINLESS STEEL PIPES AND FITTINGS: A CASE HISTORY

28.5.2.1 Manufacturing Process

This stainless steel pipes and fittings manufacturing plant is located in the United States and produces stainless steel pipes of various diameters and lengths and custom-made pipe fittings.[13] It operates over 6240 h/yr to produce nearly 30 million pounds of pipe annually.

Raw materials used by the plant include coil and sheet metal stock, solvent-based marking ink, and protective plastic end caps. The two major operations in this plant, pipe and fitting formation and acid pickling, are described in this section.

28.5.2.1.1 Pipe and Fitting Formation

Stainless steel coil and sheet stock is unloaded and stored outdoors under protective cover. As it is needed, the coil stock is moved indoors by a forklift to one of six automatic tube mills where the sides of unrolled metal strips are curled up to form a continuous, cylindrical pipe. The seam of the resulting pipe is fused in an electric in-line welding operation. An abrasive saw is used to cut the continuously formed pipe to specified lengths; sections of poorly welded pipe are cut away.

Stainless steel sheet stock is used to form custom products such as tees, elbows, and reducers. The sheets are cut with a band saw or plasma torch into smaller pieces and custom formed into final product shapes using various forming and bending equipments.

All pipes and fittings are hardened in electric induction or gas annealing furnaces. After annealing, the pipes are water spray quenched or quenched in a water-filled tank outdoors, depending on their size.

The roughened ends of the pipe are manually deburred with an air grinder. Then the pipes are straightened as necessary and transported to the acid pickling process.

28.5.2.1.2 Acid Pickling

All pipes and fittings are transported to the pickling process in which an overhead crane is used to lower them into an acidic pickle liquor solution that chemically cleans and etches the black oxide surface layer resulting in a clean, rust-resistant pipe.

Each pipe is rinsed with water in one of two rinse tanks and is then mounted on a wash rack and manually sprayed with water in a second rinsing operation. After the pipes dry, they are labeled with a solvent-based ink spray jet and protective plastic caps are hammered onto the ends. The finished products are stored outdoors until they are shipped to customers.

28.5.2.2 Waste Minimization and Pollution Prevention

This plant has already implemented the following techniques to manage and minimize its wastes:

1. The polymer previously used by this plant as a flocculent in the on-site wastewater treatment system has been replaced by magnesium hydroxide in order to reduce the volume of sludge generated and shipped off-site.
2. An acid regeneration system has been installed to regenerate spent pickle liquor for reuse on-site.

The type of waste currently generated by the plant, the source of the waste, the waste management method, the quantity of the waste, and the annual waste management cost for each waste

TABLE 28.13
Summary of Current Waste Generation

Waste Generated	Source of Waste	Waste Management Method	Annual Quantity Generated (lb/yr)	Annual Waste Management Cost
Packaging and protective barrier waste	Receipt and storage of raw materials	Shipped to municipal landfill	7500	\$0[a]
Leaked and spent lubricating oil	Machining	Shipped to fuels blending program	8540	5980
Spent abrasive saw blades	Cutting of pipe	Shipped to municipal landfill	5200	0[a]
Stainless steel scrap	Machining and cutting of pipe	Sold to scrap recycler	700,000	−164,300 (net revenue received)
Oxidized metal flakes and metal dust	Annealing, deburring, and cutting	Shipped to special landfill	30,000	15,810
Quench water	Quenching of pipes following annealing	Sewered to POTW	49,800	40
Damaged plastic end caps	Packaging of finished product	Shipped to municipal landfill	130	0[a]
Pickling rinse water	Acid pickling of product	Treated in on-site WWTP; sewered to POTW	84,598,000	89,100
Wastewater treatment sludge	On-site treatment of wastewater	Shipped to hazardous waste landfill	1,560,000	265,370
Miscellaneous solid waste	Various plant operations	Shipped to municipal landfill	135,000 cu ft[b]	26,990

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

[a] Included in annual waste management cost for miscellaneous solid waste.

[b] Includes specific quantities given for packaging and protective barrier waste, spend abrasive saw blades, and damaged plastic end caps. The majority of this waste stream is cardboard waste.

stream identified are given in Figure 28.6 and Table 28.13. Acid pickling appears to be one of many stainless steel products' manufacturing operations according to Figure 28.6. However, from Table 28.13, the importance of pickling rinse water treatment is clearly identified.[12] The toxic waste sludge disposal is the highest, while the miscellaneous solid waste disposal cost is ranked the third.

Table 28.14 shows the opportunities for pollution prevention that the U.S. EPA recommended for the plant.[12] The opportunity, the type of waste, the possible waste reduction and associated savings, and the implementation cost along with the simple payback time are given in the table. The quantities of waste currently generated by the plant and possible waste reduction depend on the production level of the plant. All values should be considered in that context.

It should be noted that the financial savings of the opportunities result from the need for less raw material and from reduced present and future costs associated with waste management. Other savings not quantifiable by this study include a wide variety of possible future costs related to changing emission standards, liability, and employee health. It should also be noted that the savings given for each pollution prevention opportunity reflect the savings achievable when implementing each opportunity independently and do not reflect duplication of savings that would result when the opportunities are implemented in a package.

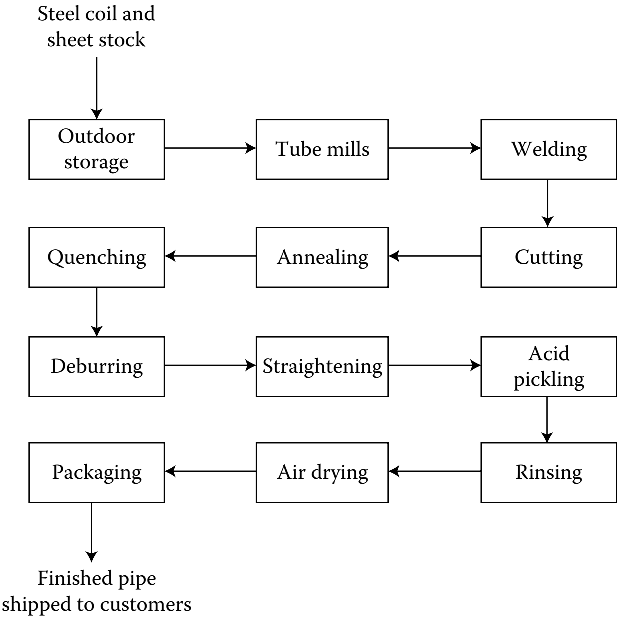

FIGURE 28.6 Flow diagram of a typical stainless steel products manufacturing plant involving acid pickling operation. (From Eroglu, V. and Erturk, F., in *Handbook of Industrial Waste Treatment*, Wang, L.K. and Wang, M.H.S., Eds, Marcel Dekker, New York, 1991, pp. 293–306; Eroglu, V., Topacik, D., and Ozturk, I., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989. With permission.)

28.5.2.3 Regeneration of WPL and Bright Dipping Liquors

Acid cleaning, or pickling, is often used to remove contaminants from the workpiece using an acid. Acid pickling is used to remove oxides (rust), scale, or tarnish as well as to neutralize any base remaining on the parts. Acid pickling uses aqueous solutions of sulfuric, hydrochloric, phosphoric, and/or nitric acids. For instance, most carbon steel is pickled in sulfuric or hydrochloric acids although hydrochloric acid can embrittle certain types of steel and is used only in specific applications. In the pickling process, the workpiece generally passes from the pickling bath through a series of rinses and then onto plating. Acid pickling is similar to acid cleaning, but is more commonly used to remove the scale from semifinished mill products, whereas acid cleaning is usually used for near-final preparation of metal surfaces prior to finishing.

28.5.2.3.1 Copper and Alloys

As described earlier, straight electrolytic recovery is highly effective on many copper pickling and milling solutions including sulfuric acid, cupric chloride, and ammonium chloride solutions. Generally, solutions based on hydrogen peroxide are best regenerated by crystallization and removal of copper sulfate, with the crystals sold as by-products or redissolved for further treatment by electrolytic metal recovery.[14,15]

Highly concentrated bright dipping nitric/sulfuric acids are a difficult challenge for regeneration because of the small quantities (5–25 gallons) used and the high dragout losses. Regeneration is possible by distillation of nitric acid and removal of copper salts; however, the economics are usually not favorable.

28.5.2.3.2 Sulfuric and Hydrochloric Acids

Both sulfuric and hydrochloric acids are used commonly for cleaning steel. Sulfuric acid can be regenerated by crystallizing ferrous sulfate. Hydrochloric acid can be recovered by distilling off the

TABLE 28.14
Summary of Recommended Pollution Prevention Opportunities

	Annual Waste Reduction					
Pollution Prevention Opportunity	**Waste Reduced**	**Quantity (lb/yr)**	**Percent**	**Net Annual Savings**	**Implementation Cost**	**Simple Payback (yr)**
Install a propane-fired sludge drying oven to reduce the volume and weight of the sludge that is generated in the on-site wastewater treatment system and shipped off-site	Wastewater treatment sludge	928,200	60	$141,150	$66,200	0.5
Utilize a trash compactor to reduce the volume of municipal trash shipped off-site, thereby reducing disposal costs.	Miscellaneous solid waste	0[a]	0	12,810	15,000	1.2
Remove the poor quality length of each coil of raw material prior to forming in the mills. Current practice is for the entire length of raw material to undergo the normal forming and welding operations, regardless of the quality. The current procedure leads to unnecessary expenditures of welding gases, worker labor, and energy	n/a	—	—	9300	0	0
Automate the addition of caustic to the wastewater treated in the on-site wastewater treatment plant in order to reduce caustic purchases and reduce labor costs	n/a	—	—	12,620	12,600	1.0

Source: U.S. EPA, *Steel Pickling*, U.S. Environmental Protection Agency, Washington, DC, June 2008. Available at http://www.epa.gov/tri/TWebHelp/WebHelp/hcl_section_3_1_4_steel_pickling.htm

[a] A significant volume reduction would occur.

acid and leaving behind iron oxide. These techniques have been used for many years in large facilities. The economics of these processes, however, usually are not favorable for smaller facilities.[14,15]

Waste pickle liquors from these operations can often be of use to sanitary waste treatment systems for phosphate control and sludge conditioning. Some industrial firms can use spent process waste from pickling operation. Iron in the waste is used as a coagulant in wastewater treatment systems.[14,15]

28.5.2.4 Engineering Calculations for Determination of Hydrochloric Acid Requirements

By submerging steel in acid, two main reactions take place. Both if hydrogen chloride is used both produce ferrous chloride.

$$\mathrm{FeO + 2HCl \rightarrow FeCl_2 + H_2O}, \tag{28.3}$$

$$\mathrm{Fe + 2HCl \rightarrow FeCl_2 + H_2}. \tag{28.4}$$

Equation 28.4 shows the chemical reaction where the acid reacts with the base metal (the steel under the scale). This reaction (Equation 28.4) is quite slow and produces hydrogen gas as a by-product, which accounts for the bubbling and foaming in the tank. The ferrous chloride produced is the by-product that can be sold for cost recovery.

Another reaction shown by Equation 28.3 is where the acid reacts with the scale (FeO) itself. This reaction is much faster than the first and it produces both ferrous chloride and water as the by-products.

It is in the plant's interest to discourage the Equation 28.4 reaction from taking place, since the plant is only interested in removing the scale. This is carried out by leaving the steel in the acid until it is absolutely necessary to remove the scale and by adding a chemical (inhibitor) to the acid, which inhibits this reaction to the minimum.

By applying the chemistry indicated by Equations 28.3 and 28.4, an environmental engineer can calculate the acid requirement to pickle 1 ton of steel, assuming an average iron loss of 0.35% that is typical for pickling strip steel:

$$\mathrm{FeO} + 2\mathrm{HCl} \rightarrow \mathrm{FeCl_2} + \mathrm{H_2O}, \tag{28.3}$$

$$(72) + (73) \rightarrow (127) + (18).$$

73 lb of hydrogen chloride (not acid) are required to react with 56 lb of iron in the scale. Since 1 ton (2000 lb) of steel has 0.35% of iron to be removed as scale, which is

$$(2000 \times 0.35)/100 = 7\,\mathrm{lb},$$

it follows that if 56 lb of Fe require 73 lb of HCl, then 7 lb of Fe require

$$(73 \times 7)/56 = 9.13\,\mathrm{lb\ of\ HCl\ (pure\ chemical).}$$

The hydrochloric acid commercially available is shipped at 32 lb of HCl (gas) per 100 lb of an aqueous (in water) solution (32% concentration or 20° Be); it follows then that if 32 lb of HCl are dissolved in 100 lb of a solution, then 9 lb of HCl are dissolved in

$$(100 \times 9.13)/32 = 28.5\,\mathrm{lb\ of\ a\ solution.}$$

One gallon of 32% HCl acid weighs approximately 9.7 lb; therefore, the required volume of 32% HCl acid solution is calculated by the following equation:

$$(28.5)/9.7 = 2.94\ \mathrm{gallons\ of\ 32\%\ HCl\ acid.}$$

The above equation constitutes the theoretical or stoichiometric amount of liquid hydrochloric acid needed to pickle 1 ton of steel. "Stoichiometric" means as per chemical formula, using absolutely pure materials with no losses.[16] In practice, it is not possible to use up all the acid in the pickle tank if pickling is to be complete in any acceptable time. Depending on the pickling equipment, between 70% and 80% of the free acid will be used up in dissolving the scale, and 20–30% will remain as "free" acid in the spent pickle liquor.[16]

Accordingly, between 3.6 and 4.2 gallons of 32% hydrochloric acid are needed to pickle 1 ton of steel (assuming that the iron loss is 0.35%).

28.5.2.5 Engineering Calculations for Determination of Ferrous Chloride Recovered

The amount of ferrous chloride produced as a by-product during the pickling of 1 ton of steel can also be determined in the same manner.[16] Since molecular weight 56 is equal to 7 lb in the formula ratio, molecular weight 127 is equal to

$$(7 \times 127)/56 = 15.88\,\mathrm{lb\ of\ FeCl_2\ are\ produced\ per\ ton\ of\ steel\ pickled.}$$

The molecular weight of water is 18. Therefore,

$$(7 \times 18)/18 = 2.25 \text{ lb of water are produced per ton of steel pickled.}$$

28.6 SUMMARY

1. The basic unit operations/processes required for treating the acid pickling wastewater are (a) neutralization with NaOH and/or lime to increase the pH and (b) physicochemical methods, such as chemical coagulation, precipitation, clarification (sedimentation or DAF), and filtration to remove BOD_5, COD, and iron.
2. The iron present in the wastewater appears in the form of ferrous ion (Fe^{2+}), which is soluble in water and can be recovered as a by-product.
3. Ferrous ion can be removed either by oxidation to ferric (Fe^{3+}) or by crystallization.
4. Sulfuric acid, hydrochloric acid, and other acids, individually or in combination, can be used for acid pickling of metals, although sulfuric and hydrochloric acids are used commonly for cleaning steel.
5. Sulfuric acid can be regenerated by crystallizing ferrous sulfate.
6. Hydrochloric acid can be recovered by distilling off the acid and leaving behind iron oxide.
7. In the hydrochloric acid pickling process, ferrous chloride can also be recovered as a by-product.
8. Waste minimization and pollution prevention are very important for saving overall manufacturing cost in a steel product manufacturing plant.
9. Treatment of pickling wastewater by neutralization/aeration/clarification gave satisfactory results. The sludge formed must be disposed of after dewatering in a filter press, in a horizontal belt filter, or in a centrifuge. An equalization tank is required in order to compensate for the effects of intermittent discharges. The treated wastewater can be recycled for it to be used in the process or discharged to the river.
10. Either a sedimentation clarifier or a DAF clarifier, or a DAFF, can be used for clarification of the pickling wastewater.[17]
11. Both air emission control and sludge disposal are extremely important in a steel acid pickling plant.[18–20]

In a steel product manufacturing plant involving acid pickling operation, disposal of hazardous metal sludge is the most expensive engineering task, and treatment of pickling liquor and rinse water is the second most expensive engineering task.

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29 Recycling and Disposal of Hazardous Solid Wastes Containing Heavy Metals and Other Toxic Substances

Lawrence K. Wang

CONTENTS

29.1 INTRODUCTION

The disposal of electrical and electronic wastes around the world has not been very satisfactory. The rapid evolution of electrical, electronic, information, and communication technologies leads to an increased production of such wastes in the future. It is our ideal objective that we do not dispose of electrical and electronic wastes together with municipal solid wastes (MSWs). We should try our best to create separate disposal paths for electrical and electronic wastes. Some electrical and electronic wastes contain hazardous, but recyclable components, in particular metals. These can be recovered at a justifiable expense only if the appliances are collected separately and treated by suitable processes. In addition, there are often problematic legal and managerial issues on waste labeling, handling, packaging, transportation, and disposition. Different countries have established their national policies to solve the problems of hazardous wastes and universal wastes.[1–11]

29.2 HANDLING, MANAGEMENT, AND DISPOSAL OF ELECTRICAL AND ELECTRONIC WASTES: THE SWITZERLAND EXPERIENCE

Each country establishes its own ordinance on the handling, disposal, and general management of electrical and electronic wastes. The Swiss government has established the Ordinance on Return, Taking Back, and Disposal of Electrical and Electronic Appliances (ORDEA), which forms the legal framework allowing the industrial and commercial sectors to establish tailored and efficient return and recycling schemes.[4] Switzerland's Ordinance takes into account the regulations on cooperation between the country's Federal Council and private sectors that the Parliament has included in the revised Law relating to the Protection of the Environment. Their ORDEA came into force on July 1, 1998. Its provisions are short and primarily regulate the following:

1. Users of electrical and electronic appliances must bring worn-out appliances back to the manufacturers, importers, or dealers or to specialized disposal firms.
2. Manufacturers, importers, and dealers of electrical and electronic appliances are obliged to take back worn-out appliances.
3. Worn-out appliances must be recycled or finally disposed of in an environmentally sound way, by the most technically up-to-date means. The ORDEA also contains criteria for the environmentally sound disposal of worn-out appliances.
4. Anyone who accepts appliances for disposal in Switzerland requires a permit. Export of appliances for disposal must be authorized by the government.

Switzerland's authorities and economic sector are working closely together to implement the ORDEA. A uniform enforcement practice and substantial input from the companies are important prerequisites for success, to which their present guidelines will contribute.

29.3 HANDLING, MANAGEMENT, AND DISPOSAL OF ELECTRICAL AND ELECTRONIC WASTES: THE U.S. EXPERIENCE

In the United States, electrical and electronic appliances, when old and considered to be wastes, are sent to sanitary landfill sites for dismantling, separation, resource recovery, and disposal. Commercial companies are getting formed for the waste handling, packaging, transportation, resource recovery, and disposition operations, aiming at profit-making.[1–3,5–11]

Fluorescent lamps, fluorescent lamp ballasts, batteries, pesticides, mercury-containing thermostats, and other mercury-containing equipment are being singled out for special consideration. Specifically, these electrical and electronic wastes outfall into a regulated category called "universal wastes" in the United States.

By a strict definition, these electrical and electronic wastes are hazardous. Fluorescent lamps contain mercury, and almost all fluorescents fail the U.S. Environmental Protection Agency (U.S. EPA) toxicity test for hazardous wastes. Fluorescent lamp ballasts manufactured in the mid-1980s contain polychorinated biphenyls (PCBs), a carcinogen; most of these ballasts are still in service. Batteries can contain any of a number of hazardous materials, including cadmium (nickel–cadmium batteries), the explosive lithium (lithium–ion batteries), and lead (lead–acid batteries). Some of the household nonrechargeable batteries still in use also contain mercury, although mercury has been phased out of the batteries that are in wide circulation.

In the United States, the Universal Waste Regulations have so far streamlined the hazardous waste management standards for the above U.S. Federal universal wastes (batteries, pesticides, thermostats, and lamps). The regulations govern the collection and management of these widely generated wastes. This facilitates environmentally sound collection and increases the proper recycling or treatment of the universal wastes mentioned above.

These U.S. regulations have eased the regulatory burden on American retail stores and others that wish to collect or generate these wastes. In addition, these regulations also facilitate programs developed to reduce the quantity of these wastes going to MSW landfills or combustors. They also ensure that the wastes subject to this system will go to appropriate treatment or recycling facilities pursuant to the full hazardous waste regulatory controls.

According to a strict reading of the characteristics established by the U.S. EPA and the State environmental agencies, all of these items are hazardous wastes when disposed of, and should therefore be subject to the whole onerous spectrum of handling, transportation, and disposal requirements that have been established for toxins, carcinogens, mutagens, explosives, and other wastes that are threatening to health and the environment.

But batteries and fluorescents are generated by almost every company, and every household, in the country (hence the name “universal”). If they were defined as a hazardous waste, that would make practically every company and every household in the United States a hazardous waste generator, with the accompanying burden of reporting, record keeping, handling, and management requirements (not to mention outrageous waste management costs). The State and Federal agencies would be flooded with mountains of paper work and information to track, sort, store, and ultimately throw away.

Recognizing that the full hazardous waste approach would be overkill for batteries and fluorescents, the U.S. EPA created the “universal waste” regulatory category in the mid-1990s, and it has been adopted since then by almost all states. The universal waste requirements are straightforward. First, batteries and fluorescents are banned from disposal in landfills and incinerators. But, as long as they are handled, packed, and transported in a way that prevents their breakage and possible release to the environment, and are recycled through a licensed facility, they are exempt from definition and regulation as a hazardous waste. Instead, they are subject to a much less onerous (and much less costly) set of requirements specifically crafted to ensure their convenient, but safe, management, transportation, and ultimate disposition.

Fluorescents and batteries need to be handled and packaged in a way that prevents breakage and potential release of hazardous materials on a site and throughout the chain of custody to the ultimate disposition facility. A commercial company can provide packaging for all types of fluorescents (4′ and 8′ straight tubes, U-tubes, and others) to be delivered to a receiver. Straightforward handling and packaging procedures will prevent spills and breakage and their associated cleanup costs.

Handling and packaging needs for batteries are different. Batteries need to be handled and packed to prevent short-circuits and minimize transportation costs. Again, a commercial company can provide appropriate packaging materials and instructions designed to minimize handling requirements and costs and eliminate possible liabilities associated with mispackaged materials.

The universal waste transportation requirements are not onerous. Because they are not defined as hazardous wastes, universal wastes in the United States do not need to be accompanied by a hazardous waste manifest, or shipped by a hazardous waste transporter. Even so, transportation is where many generators lose money and where many recyclers make their margins.

The problem with transporting universal wastes is their volume. Fluorescents are too light to make a cost-effective load. A generator rarely generates a truckload, which leaves the generator at the mercy of less-than-load freight rates, or even higher oncall or “convenience” rates charged by some shippers and recyclers. Batteries are the opposite—too heavy and too bulky to cube out an efficiently loaded box trailer.

There are several possible solutions. If both electronic wastes and universal wastes are handled at the same time, they may be on the same truck, and be cross-docked to the correct end markets. The generator may save money on both sets of materials. A commercial company can routinely set up "milk run" pickups from multiple generators, building to that critical truckload volume and dividing transportation charges among multiple generators, with savings for all individual small generators.

The Universal Waste regulatory requirement is that all universal wastes must be handled by a licensed recycler. There are, however, only a few licensed recyclers in the United States available for services.

29.4 GENERAL REQUIREMENTS FOR COLLECTION, SEPARATION, AND DISPOSAL OF ELECTRICAL AND ELECTRONIC WASTES CONTAINING PARTICULARLY HAZARDOUS SUBSTANCES

All electrical and electronic wastes may be found to harbor components containing particularly hazardous substances. It is essential that these be removed (stripping of hazardous materials). Below are some examples of such components. Batteries and accumulators notably include the following:

1. Nickel–cadmium batteries accumulators
2. Batteries and accumulators containing mercury
3. Lithium batteries and accumulators
4. Condensers and ballasts (preswitches)
5. Mercury switches/mercury relays/mercury vapor lamps
6. Parts containing chlorofluorocarbons (CFCs) (refrigeration cycle in refrigerators/insulation materials)
7. Selenium drums in photocopying machines
8. Components that release asbestos fibers.

Stripping of electrical and electronic waste appliances must be carried out properly. During the processing of waste appliances (e.g., in shredders), it is essential to avoid that components highly contaminated with hazardous substances end up in fractions that are intended for recycling. It is furthermore necessary to ensure that the disposal of treatment residues (e.g., shredder residues) is not impeded by the presence of hazardous substances. As a rule, components containing particularly hazardous substances are to be removed manually. Future disposal processes, such as pyrolysis, may allow recycling of appliances without prior removal of hazardous substances, in which case it will be possible to do without the disassembly of hazardous components.[4,11]

It is the responsibility of the disposal company concerned to identify and separate novel components containing hazardous substances. However, the disposal company can do this only if the manufacturers or importers assume their responsibility as producers by making a corresponding declaration.

Fractions containing halogenated flame retardants (e.g., from printed circuit boards, cable insulation, and plastic housings) must be incinerated in suitable plants if recycling is not possible.

Besides the environmentally sound disposal of hazardous components, the recovery of ferrous, nonferrous, and noble metals is the main priority in the disposal of electrical and electronic appliances. Here, it is important to ensure that the requirements relating to scrap quality are met.

29.5 PRACTICAL EXAMPLES

29.5.1 General Management and Disposal of Electronic Waste Appliances

All appliances and modules consisting mainly of electronic components fall under the category of electronic waste appliances. This group comprises the following categories: entertainment electronics, office, information, and communication appliances, and electronic components of appliances.

Owing to the rapid pace of technical developments, the composition of appliances is subject to continual change. Particular attention must be paid to

1. Batteries and accumulators
2. Mercury switches/mercury relays
3. Condensers containing PCBs
4. Photoconductive drums of copying machines coated with selenium arsenate or cadmium sulfide
5. Cathode ray tubes (CRTs)
6. Printed circuit boards
7. Wood treated with paints, varnishes, and preservatives
8. Plastics containing halogenated flame retardants.

Furthermore, appliances also contain valuable constituents such as gold (from connectors), nickel, copper, iron, aluminum, and permanent magnets, which are worth recovering.

The objectives for disposal of electronic waste appliances are (a) stripping of hazardous substances; (b) reduction of pollutant and metal contents in the plastic fraction, thus permitting recycling or incineration in waste incineration plants or cement works; (c) recovery of nonferrous metals; and (d) attainment of commercially recyclable scrap quality.

The requirements for proper disposal of electronic waste appliances are as follows: (a) appliances may be broken up (shredded) only if the components containing particularly hazardous substances have previously been removed and (b) since in disposing of electronic appliances the main emphasis is on the recovery of nonferrous metals, nonstripped appliances must not be shredded together with scrap cars. As a rule, electronic appliances are dismantled manually to achieve effective separation of the components containing hazardous substances.

Typical examples of the disposal of electronic waste appliances include the following steps:

1. *Stripping of hazardous components*: In an initial step, the components containing particularly hazardous substances are for the most part removed manually.
2. *Shredding of appliances and separation of fractions*: The stripped appliances are, as a rule, ground in a fine shredder (e.g., rotary cutter). The material resulting from this can be further processed by several methods. Possible processes are air classification, riddle screening, cyclone, turborotor, sink–float, eddy current, or magnetic separation. The separated fractions are handed on to workable lots for further processing or recycling, or to resellers.
3. Recycling and disposal of waste fractions.
4. *Handling and processing of stripped components containing particularly hazardous substances*: Batteries and accumulators are classified as hazardous wastes even if they are recycled. Mercury is classified as a hazardous waste and can be recovered in special plants. Condensers containing PCBs must be incinerated in a hazardous waste incineration plant.
5. *Separation of ferrous and nonferrous metals, copper, and aluminum for separate recovery*: The scrap material and scrap metal dealers sort these metals (in part very finely) and send them to steelworks at home and abroad.
6. *Handling and processing of CRTs*: CRTs are handled for special processing.
7. *Processing of printed circuit boards*: Printed circuit boards are subjected to special treatment in order to recover their entire metal content.
8. *Recycling of plastic-sheathed cables*: Electrical cables are sent to cable recycling plants that separate the plastic and copper components.
9. *Disposal of residual fraction*: Depending on their quality and on the specific requirements applicable, residual fractions are disposed of in MSW incinerators, hazardous waste incinerators, cement works, or they are recycled.

29.5.2 GENERAL MANAGEMENT AND DISPOSAL OF LARGE ELECTRICAL WASTE APPLIANCES

Large electrically powered domestic waste appliances, such as cookers, ovens, washing machines and other cleaning appliances, mobile electrical heaters, and ventilators come under the category of large electrical waste appliances. The electricity for the large waste electrical appliances is supplied by the electrical mains.

These large electrical waste appliances consist mainly of iron, copper, aluminum, and insulation materials. The insulation materials are mostly inorganic. The electronic controllers contained in the appliances are classified as electronic scrap. They may contain particularly hazardous components (accumulators, batteries, condensers, mercury switches, etc.).

The objectives for management and disposal of large electrical waste appliances are (a) stripping of hazardous substances; (b) reduction of pollutant and metal content in the shredder residue; (c) recycling and recovery of ferrous metals; and (d) attainment of commercially recyclable scrap quality (e.g., low copper content in the scrap iron).

The requirements for management and disposal of large electrical waste appliances are that appliances may be shredded only if the particularly hazardous components have previously been removed.

Older appliances (such as ovens) still sometimes contain asbestos. A waste from which asbestos fibers may be released is classified as a hazardous waste and must be disposed of as specified in the appropriate environmental laws. The heat-transfer oils of older types of mobile convector heaters still sometimes contain PCBs. These fluids must be disposed of as hazardous waste.

Typical examples of the management and disposal of large electrical waste appliances include the following steps:

1. *Stripping of hazardous substances*: In an initial step, the components containing particularly hazardous substances are removed.
2. *Breaking up of appliances and separation of fractions*: After stripping, the large electrical appliances are, as a rule, ground in a shredder (hammer mill for scrap cars). The resulting fragments are separated by means of special equipment, such as air classifiers, magnetic separators, electrostatic separators, eddy current separators, and sink-float separators. The main fractions are fractions of ferrous or nonferrous metals, printed circuit boards (if applicable), and residual fraction (shredder residue).
3. Recycling and disposal of waste fractions.
4. *Handling and processing of stripped components containing particularly hazardous substances*: Batteries and accumulators are classified as hazardous waste even if they are to be recycled. Mercury is classified as hazardous waste and can be recovered in special plants. Condensers containing PCBs must be incinerated in a hazardous waste incineration plant.
5. *Separation of ferrous and nonferrous metals, copper, and aluminum for separate recovery*: The scrap material and scrap metal dealers sort these metals (in part very finely) and send them to steelworks at home and abroad.
6. *Processing of printed circuit boards*: Printed circuit boards are subjected to special treatment in order to recover their entire metal content.
7. *Recycling of plastic-sheathed cables*: Cables are sent to cable recycling plants that separate the plastics and copper components.
8. *Disposal of residual fraction*: Depending on their quality and on the specific requirements applicable, residual fractions are disposed of in MSW incinerators, hazardous waste incinerators or cement works, or are recycled.

29.5.3 GENERAL MANAGEMENT AND DISPOSAL OF SMALL ELECTRICAL WASTE APPLIANCES

The category of small electrical waste appliances comprises electrical appliances such as electric razors, music players, hair-removing appliances, hair dryers, egg boilers, immersion water heaters, coffee grinders, and so on. They are generally composed of plastics, ferrous, and nonferrous metals. A large proportion of these small appliances is powered by batteries or accumulators.

The objectives of disposal of small electrical waste appliances are simple: (a) stripping of hazardous substances; (b) recycling and recovery of ferrous and nonferrous metals; (c) reduction of pollutant and metal content in the plastic fraction; and (d) recovery of the copper fraction.

The only requirement for a disposal of small electrical waste appliances is that appliances may be shredded only if the components containing particularly hazardous substances have previously been removed. In the case of small cordless electrical appliances, the greater part of the hazardous substances can be eliminated by a prior removal of batteries and accumulators.

The following are typical operational steps for disposal of small waste appliances:

1. *Stripping of hazardous substances*: In an initial step, components containing particularly hazardous substances are for the most part removed manually.
2. *Breaking up of appliances and separation of fractions*: The stripped appliances are, for example, finely shredded (in a rotary cutter). Using an air classifier, plastics and nonmetallic components, and so on are removed. The ferrous metals are separated from nonferrous ones in a magnetic separator. An eddy current separator is used for fine separation of nonferrous metals. Copper and aluminum are separated in sink–float separators. The material resulting from the fine shredding can be processed by various means. Possible processes are air classification, riddle screening, cyclone, turborotor, sink–float, eddy current, or magnetic separation. The separated fractions are handed on to workable lots for further processing or recycling, or to resellers.
3. Recycling and disposal of waste fractions.
4. *Handling and processing of stripped components containing particularly hazardous substances*: Batteries and accumulators are classified as hazardous waste even if they are going to be recycled.
5. *Separation of ferrous and nonferrous metals, copper, and aluminum for separate recovery*: The scrap material and scrap metal dealers sort these metals (in part very finely) and send them to steelworks at home and abroad.
6. *Recycling of plastic-sheathed cables*: Cables are handed on to cable recycling plants that separate the plastic and copper components.
7. *Disposal of residual fraction*: Depending on their quality and on the specific requirements applicable, residual fractions are disposed of in MSW incinerators, hazardous waste incinerators or cement works, or are recycled.

29.5.4 General Management and Disposal of Refrigeration and Air Conditioning Waste Appliances

Refrigerators, deep freezers, ice machines equipped with a circulation system, mobile air conditioners, dehumidifiers, and so on are discussed in this section.

The cooling circuit of these appliances contains refrigerants. The most common are CFCs, ammonia, or pentane. In many types of refrigerators, the circulation system also contains oil. Other components are metals (steel, aluminum, and copper), plastics (housings, drawers, and shelves), polyurethane (PU) insulation, polystyrene (PS) insulation, glass, and so on. In older appliances, the insulation material also generally contains CFCs. The following components are removed prior to shredding: compressors, cooling coils, glass, cables, and switches.

The objectives sought to be achieved through disposal of refrigeration and air conditioning waste appliances are (a) separate disposal of the CFCs from the circulation system and the insulating material; (b) further stripping of hazardous substances (e.g., mercury switches); and (c) recovery of ferrous metals, the priority in metal recycling.

The requirements for proper disposal of refrigeration and air conditioning waste appliances are very stringent: (a) mercury switches and condensers containing PCBs must be removed in advance and disposed of; (b) 90% of the CFCs, both from the circulation system and the insulation, must be recovered and disposed of in an environmentally sound manner, as specified in the regulations; (c) the amount of residual CFCs in the pressed-out foam must not exceed 0.5% if it is to be reused; (d) the government emission standard for CFCs (20 mg/m^3 at a flow rate >100 g/h, for instance) must be complied with; therefore, the emission flow rate must be measured and recorded continuously; (e) recovered CFCs or recovered components containing CFCs (e.g., foam containing >0.5% CFCs) must be disposed of in suitable plants; (f) chrome-plated ferrous scrap (chromium VI) must not be mixed with unsorted scrap but must be delivered directly to the steelworks, in compliance with the relevant workplace protection and safety regulations.

Since pentane is a flammable gas that can form explosive mixtures in combination with air or oxygen, suitable safety precautions must be taken.

Typical operational steps for disposal of refrigerators and similar appliances are listed below:

1. *Stripping of hazardous substances*: Mercury switches and other components containing particularly hazardous substances must be removed; CFCs are recovered from the cooling circuit and PU foam with special equipment and appliances with varying degrees of automation; ammonia is dissolved in water; and separate disposal of waste oil (from compressors).
2. Breaking up of appliances and separation of fractions.
3. *Removal of special components*: Loose fittings are mostly removed. They include plastic accessories and trays, steel racks, glass shelves and doors made of plastic, metal, and insulation material.
4. *Handling of the main unit*: The first step is to extract the refrigerant. It must be recovered as completely as possible by means of suitable plants and equipment. The refrigerants and foaming agents are condensed by refrigeration and handed on to be destroyed.
5. Shredding and fractionation of the main unit takes place under partial vacuum in a special shredder. PU foamed with CFCs is pressed out as completely as possible. The vitiated air from the shredder and the press is cleaned through activated carbon and passed through a condensation cooling system. By this means, the foaming agent may be almost entirely recovered.
6. *Separation of the residual fractions is as follows*: separation of CFCs by condensation; separation of expanded PS and PU foam by air classification; separation of iron with a magnetic separator; and separation of nonferrous metals with an eddy-current separator.

Following stripping of hazardous substances, air conditioners and dehumidifiers can be further dismantled either manually or in a shredder. Figure 29.1 shows the flow diagram of management, separation, recycle, and disposal of used refrigeration appliances.[4]

29.5.5 GENERAL MANAGEMENT AND DISPOSAL OF UNIVERSAL WASTES

Universal waste is a legal environmental term used in the United States. The Universal Waste Regulations in the United States streamline the collection requirements for certain hazardous wastes in the specific categories decided by the Federal and the State governments. The Universal Waste Regulations ease regulatory burdens on businesses; promote proper recycling, treatment, or disposal; and provide for efficient, proper, and cost-effective collection opportunities.

The U.S. EPA Federal universal wastes are (a) batteries such as nickel–cadmium (Ni–Cd) and small sealed lead–acid batteries, which are found in many common items in the business and home setting, including electronic equipment, mobile telephones, portable computers, and emergency backup lighting; (b) agricultural pesticides that are recalled under certain conditions and unused, pesticides that are collected and managed as part of a waste pesticide collection program, and the pesticides that are unwanted for a number of reasons, such as being banned, obsolete, damaged, or no longer needed due to changes in cropping patterns or other factors; (c) thermostats that can contain

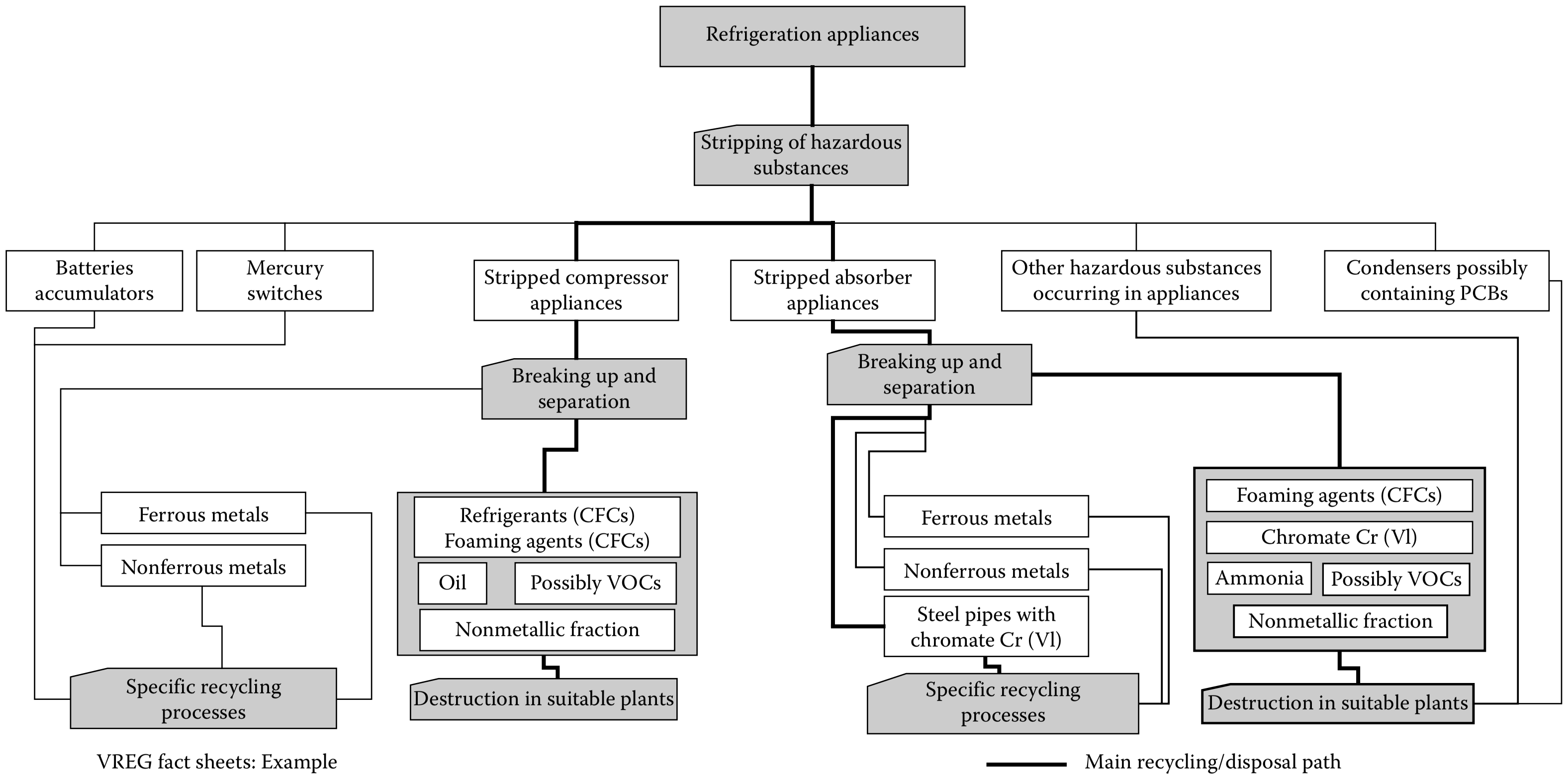

FIGURE 29.1 Flow diagram of the management, separation, recycling, and disposal of waste refrigeration appliances. [From SAEFL, *Waste Management Guidelines for the Ordinance on the Return, the Taking Back and the Disposal of Electrical and Electronic Appliances (ORDEA)*, Swiss Agency for the Environment, Forests and Landscape, p. 76, Bern, Switzerland, 2000. With permission.]

as much as 3 of liquid mercury and are located in almost any building, including commercial, industrial, agricultural, community, and household buildings; (d) lamps, which are the bulb or tube portion of electric lighting devices that have a hazardous component (Note that examples of common universal waste electric lamps include, but are not limited to, fluorescent lights, high-intensity discharge, neon, mercury vapor, high-pressure sodium, and metal halide lamps. Many used lamps are considered hazardous wastes under the Resource Conservation and Recovery Act (RCRA) because of the presence of mercury or occasionally lead.); and (e) mercury-containing equipment is proposed as a new universal waste category because mercury is used in several types of instruments that are common to electric utilities, municipalities, and households. Some of these devices include switches, barometers, meters, temperature gauges, pressure gauges, and sprinkler systems.

It is important to note that each State in the United States can add different wastes and does not have to include all the U.S. Federal universal wastes. In other words, the States can modify the Federal Universal Waste Rule and add additional universal waste in individual state regulations. A waste generator should check with the State for the exact regulations that apply to the generator.

For proper management and disposal of the aforementioned universal wastes, a waste generator, a waste handler, a transporter, or a destination facility must understand the legal definitions of wastes and their legal status. The following is an overview of legal definitions and related requirements.

1. *Universal waste*: A waste must be a hazardous waste before it can be considered a universal waste. A waste must also meet certain criteria to qualify as a universal waste. For instance, it must be widespread, commonly found in medium to large volumes, and exhibit only low-level hazards or be easily managed.
2. *Federal universal wastes*: In the United States, the universal wastes (such as batteries, pesticides, thermostats, lamps, and mercury-containing wastes) are decided and legally defined by the U.S. EPA.
3. *State universal wastes*: In the United States, the States do not have to include all of the Federal universal wastes when they use (adopt) the program and the States can make them more stringent and add their own universal wastes (antifreeze, for instance).
4. *Universal waste battery*: Battery means a device consisting of one or more electrically connected electrochemical cells, which is designed to receive, store, and deliver electric energy. An electrochemical cell is a system consisting of an anode, a cathode, and an electrolyte, plus such connections (electrical and mechanical) as may be needed to allow the cell to deliver or receive electrical energy. The term "battery" also includes an intact, unbroken battery from which the electrolyte has been removed.
5. *Universal waste pesticide*: Pesticide means any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest, or intended for use as a plant regulator, defoliant, or desiccant.
6. *Universal waste thermostat*: Thermostat means a temperature control device that contains metallic mercury in an ampule attached to a bimetal sensing element.
7. *Universal waste lamp: Lamp*, also referred to as "universal waste lamp" is defined as the bulb or tube portion of an electric lighting device. A lamp is specifically designed to produce radiant energy, most often in the ultraviolet, visible, and infrared regions of the electromagnetic spectrum. Examples of common universal waste electric lamps include, but are not limited to, fluorescent, high-intensity discharge, neon, mercury vapor, high-pressure sodium, and metal halide lamps.
8. *Universal waste handlers*: This could be (1) a business that generated (needs to dispose of) a universal waste (fluorescent lights, for instance); (2) a take-back program; and (3) a collection program.
9. *Small quantity handlers of universal waste (SQHUW)*: A handler that accumulates <5000 kg (11,000 lb) of universal waste at any one time.
10. *Large quantity handlers of universal waste (LQHUW)*: A handler that accumulates 5000 kg (11,000 lb) or more of universal waste at any one time.

11. *Universal waste transporter*: A transporter that transports universal waste from handlers to other handlers, destination facilities, or foreign destinations.
12. *Universal waste destination facilities*: The facilities that recycle, treat, or dispose of universal wastes as hazardous waste (no longer universal waste). Note that this does not include facilities that only store universal waste since those facilities qualify as a universal waste handler.

29.5.6 MANAGEMENT AND DISPOSAL OF A SPECIFIC ELECTRONIC WASTE: CRTs

CRTs, shown in Figure 29.2, are the display components of televisions and computer monitors. CRT glass typically contains enough lead to be classified as hazardous waste when it is being recycled or disposed of. Currently, businesses and other organizations that recycle or dispose of their CRTs are confused about the applicability of hazardous waste management requirements to their computer or television monitors. The Federal government is proposing to revise regulations to encourage opportunities to safely collect, reuse, and recycle CRTs.[4]

To encourage more reuse and recycling, intact CRTs being sent for possible reuse are considered to be products rather than wastes and therefore not regulated unless they are being disposed of. If CRT handlers disassemble the CRTs and send the glass for recycling, the U.S. EPA is also proposing to exclude them from being a waste, provided they comply with simplified storage, labeling, and transportation requirements. Furthermore, the U.S. EPA believes that if broken CRTs are properly containerized and labeled when stored or shipped before recycling, they resemble commodities more than waste.

Finally, processed glass being sent to a CRT glass manufacturer or a lead smelter is excluded from hazardous waste management under most conditions. If the glass is being sent to any other kind of recycler, it must be packaged and labeled the same as broken CRTs. The U.S. EPA believes that these proposed changes will encourage the recycling of these materials, while minimizing the possibility of releasing lead into the environment. Figure 29.3 shows a flow diagram of the management, separation, recycle, and disposal of CRTs.[4]

29.5.7 MANAGEMENT AND DISPOSAL OF MERCURY-CONTAINING EQUIPMENT INCLUDING LAMPS

Mercury is contained in several types of instruments that are commonly used by electrical utilities, municipalities, and households. Among others, these devices include barometers, meters, temperature

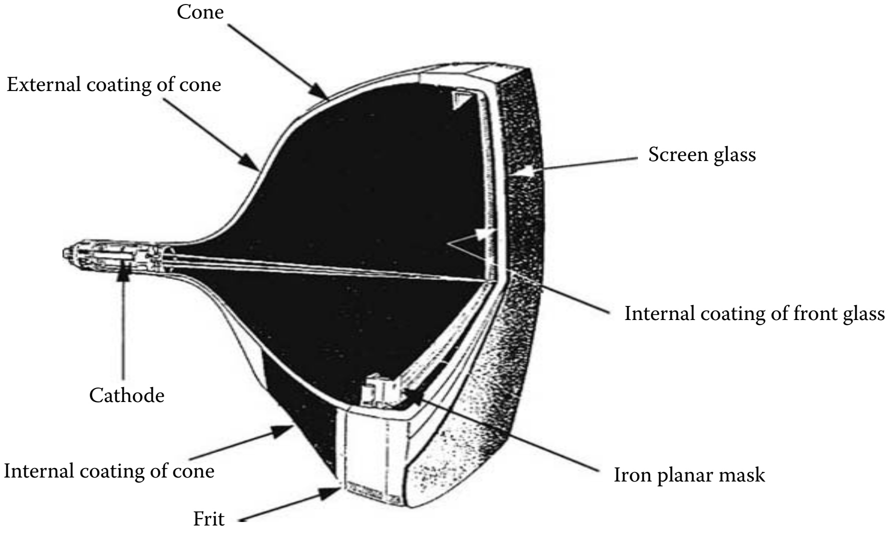

FIGURE 29.2 Schematic diagram of a CRT.

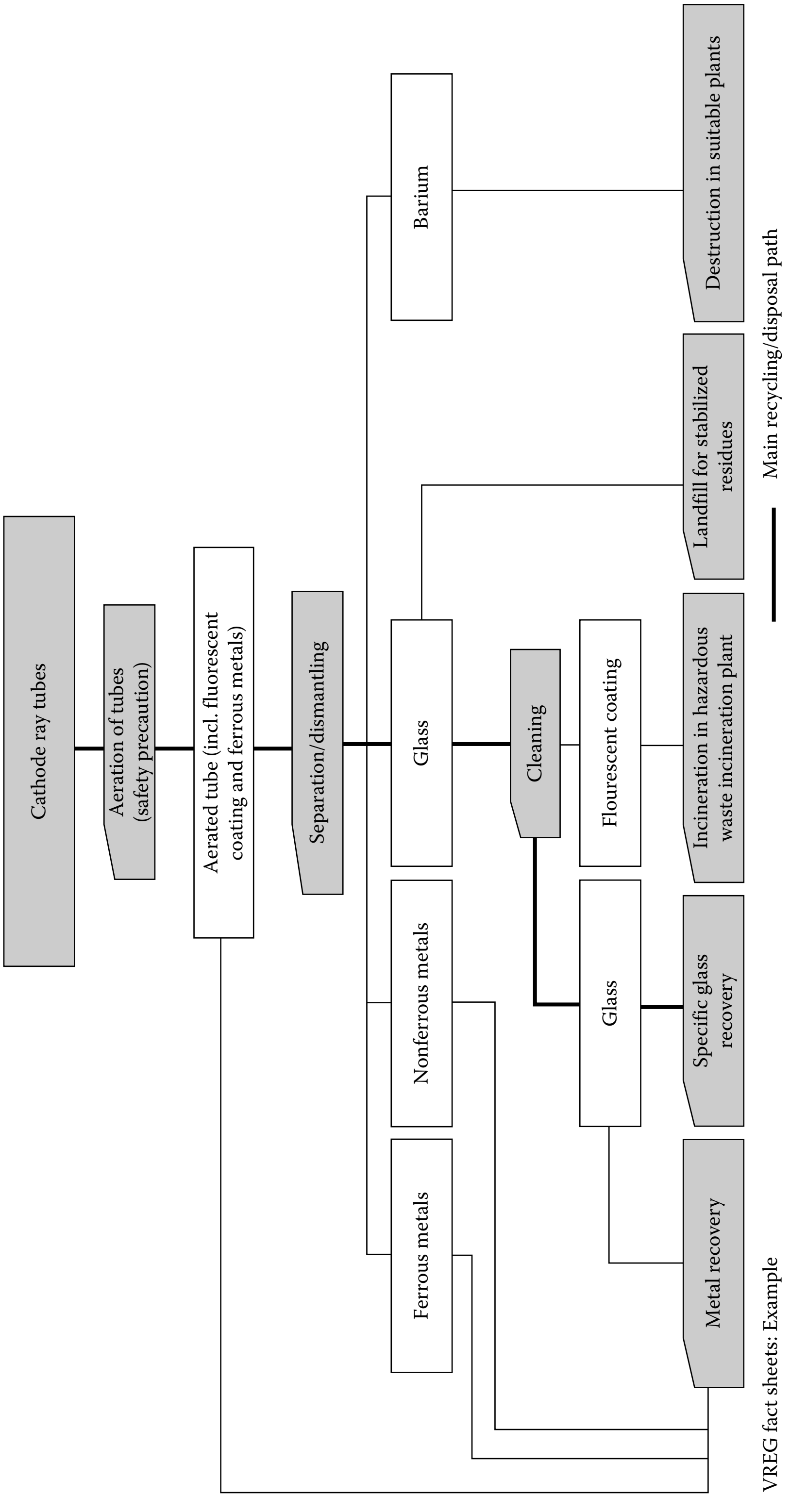

FIGURE 29.3 Flow diagram of the management, separation, recycling, and disposal of waste CRTs. [From SAEFL, *Waste Management Guidelines for the Ordinance on the Return, the Taking Back and the Disposal of Electrical and Electronic Appliances (ORDEA)*, Swiss Agency for the Environment, Forests and Landscape, p. 76, Bern, Switzerland, 2000. With permission.]

gauges, pressure gauges, sprinkler system contacts, and parts of coal conveyor systems. U.S. EPA has received data on mercury-containing equipment since 1995, when it issued the first Federal Universal Waste Rule. The Agency believes that adding mercury-containing devices to the universal waste stream will facilitate better management of this waste.[10]

The Universal Waste Rule tailors management requirements to the nature of the waste in order to encourage collection (including household collections) and proper management. Universal waste generators, collectors, and transporters must follow specific record keeping, storage, and transportation requirements. The U.S. EPA is proposing the same tailored requirements for all mercury-containing equipment.

U.S. EPA initiated a mercury-containing lamp recycling outreach program in 2002 to promote mercury lamp recycling by commercial and industrial users. The outreach program aims to increase awareness of the proper disposal methods of these lamps in compliance with Federal and State Universal Waste Rules. This outreach effort will be effective in increasing the amount of lamps recycled in the short term, as well as have a lasting impact over the long term. The U.S. EPA's goal is to raise the national recycling rate for mercury lamps from the current 20% to 40% by 2005, and to 80% by 2009.

U.S. EPA awarded funds in the form of 10 cooperative agreements for the development and implementation of a coordinated nationwide mercury-containing lamp recycling outreach program. This program is currently being implemented in two phases. Recipients of phase 1 cooperative agreements are developing outreach materials such as fact sheets, a recycling database, websites, public service announcements, and educational materials.

While phase 1 cooperative agreement recipients focused on developing outreach materials, the recently selected phase 2 recipients will focus on outreach program implementation. They will conduct outreach to segments of the lamp-disposing population by adapting outreach materials developed in phase 1 to target-specific audiences (i.e., industry-specific lamp users or lamp users within a certain geographic location).

29.5.8 MANAGEMENT, REUSE, RECYCLE, AND DISPOSAL OF VEHICLE BATTERIES

Every year in the United States, billions of batteries are bought, used, and thrown out. In 1998 alone, over 3 billion industrial and household batteries were sold. The demand for batteries can be traced largely to the rapid increase in automobiles, cordless, portable products such as cellular phones, video cameras, laptop computers, and battery-powered tools and toys.

Because many batteries contain toxic constituents such as mercury and cadmium, they pose a potential threat to human health and the environment when improperly disposed. Although batteries generally make up only a tiny portion of MSW, <1%, they account for a disproportionate amount of the toxic heavy metals in MSW. For example, the U.S. EPA has reported that, as of 1995, nickel–cadmium batteries accounted for 75% of the cadmium found in MSW. When MSW is incinerated or disposed of in landfills, under certain improper management scenarios, these toxics can be released into the environment.

Over the past decade, the battery industry, partly in response to public concerns and legislation, has played an active role in finding solutions to these problems. Industry efforts have touched on every stage of the product life cycle.

Seventy million vehicle batteries are produced each year in the United States. About 80% of discarded lead–acid batteries are being collected and recycled. Lead–acid batteries contain about 15–20 lb of lead per battery and about 1–2 gallons of sulfuric acid. Vehicle batteries are banned from disposal in Nebraska landfills as of September 1, 1994.

Environmental hazards of batteries can be briefly summarized as follows. A battery is an electrochemical device with the ability to convert chemical energy to electrical energy to provide power to electronic devices. Batteries may contain lead, cadmium, mercury, copper, zinc, lead, manganese, nickel, and lithium, which can be hazardous when incorrectly disposed. Batteries may produce the following potential problems or hazards: (a) they pollute the lakes and streams as the metals vaporize into the air when burned; (b) they contribute to heavy metals that leach from solid waste landfills; (c) they expose the environment and water to lead and sulfuric acid; (d) they contain strong acids that are corrosive; and (e) they may cause burns or danger to the eyes and skin.

Heavy metals have the potential to enter the water supply from the leachate or runoff from landfills. It is estimated that nonrecycled lead–acid batteries produce about 65% of the lead in the municipal waste stream. When burned, some heavy metals such as mercury may vaporize and escape into the air, and cadmium and lead may end up in the ash, making the ash a hazardous material for disposal.

Vehicle batteries may be recycled by trading in an old battery when replacing a battery. Most battery distribution centers, automotive garages, and repair centers have collection points. Batteries are also accepted at some scrap yards, automobile dismantlers, and some retail chain stores. Batteries should be stored in a secure area, locked, or kept away from children and sources of sparks. All old batteries should be recycled.

Prolonging battery life is another method of protecting the environment. To reduce waste, a consumer should buy longer-life batteries that may result in fewer batteries to recycle and follow recommended maintenance procedures to lengthen battery life.

Good maintenance of a vehicle battery can prolong a battery's life and for this the following procedures can be followed: (a) Check the battery for adequate water level if the battery is not a sealed one, and check the battery and the vehicle charge system to determine whether the battery is low on water. (b) Do not overfill a battery. (c) Make sure all the connections are clean. (d) If the vehicle has been seldom used, charge the battery at least every 2 months to maintain the battery charge, because in a discharge state, the battery might freeze. (e) If the battery must be stored outside of the vehicle, store it in a cool dry place. (f) Do not jump start a battery when the battery is extremely cold. (g) When jump starting, connect the jumper cables first to the power source, then connect the positive cable to the positive cable on the battery to be jumped and the negative to a solid ground on the vehicle (e.g., the bracket on the alternator). This avoids electricity going directly to the battery to be charged to prevent sparking.

Redesign, reuse, and recycling will be the best management practice (BMP) for waste vehicle-battery management. Some battery manufacturers are redesigning their products to reduce or eliminate the use of toxic constituents. For example, since the early 1980s, manufacturers have reduced their use of mercury by over 98%. Many manufacturers are also designing batteries with a longer life.

Most states have passed legislation prohibiting the disposal of lead–acid batteries (which are primarily vehicle batteries) in landfills and incinerators and requiring retailers to accept used batteries for recycling when consumers purchase new batteries. For example, Maine, USA, has adopted legislation that requires retailers to either (a) accept a used battery upon sale of a new battery or (b) collect a USD10 deposit upon sale of a new battery, with the provision that the deposit shall be returned to the customer if the buyer delivers a used lead–acid battery within 30 days of the date of sale. This legislation is based on a model developed by the lead–acid battery industry. Lead–acid batteries are collected for recycling through a reverse distribution system. Spent lead batteries are returned by consumers to retailers, picked up by wholesalers or battery manufacturers, and finally taken to secondary smelters for reclamation. These recycling programs have been highly successful: The nationwide recycling rate for lead–acid batteries stands at roughly 95%, making them one of the most widely recycled consumer products. Automotive and other industrial batteries are, more and more, being recycled and better designed now.

29.5.9 Management, Reuse, Recycle, and Disposal of Household Batteries

An increasing number of household batteries are being used today. On average, a person owns about two button batteries, 10 normal (A, AA, AAA, C, D, 9V, etc.) batteries, and throws out about eight household batteries per year. About 3 billion batteries are sold annually in the United States averaging about 32 per family or 10 per person.[5–9] Table 29.1 indicates the typical types of household batteries.

TABLE 29.1
Typical Types of Household Batteries

	Common Uses
Primary Cells (Nonrechargeable)	
Alkaline	Cassettes players, radios, appliances
Carbon–zinc	Flashlights, toys, etc.
Lithium	Cameras, calculators, watches, computers, etc.
Mercury	Hearing aids, pacemakers, cameras, calculators, watches, etc.
Silver	Hearing aids, watches, cameras, calculators
Zinc	Hearing aids, pagers
Secondary Cells (Rechargeable)	
Nickel–cadmium	Cameras, rechargeable appliances such as portable power tools, hand-held vacuums, etc.
Small sealed lead–acid	Camcorders, computers, portable radios, and tape players, cellular phones, lawn mower starters, etc.

Battery manufacturers are producing more rechargeable batteries each year. The National Electrical Manufacturers Association has estimated that the U.S. demand for rechargeable batteries is growing twice as fast as the demand for nonrechargeable batteries.

The Rechargeable Battery Recycling Corporation (RBRC) started a nationwide take-back program in 1994 for the collection and recycling of used nickel–cadmium batteries. The RBRC expanded in 2001 to include all portable rechargeable batteries in its take-back program. This is the first nationwide take-back program that involves an entire U.S. industry. Much of this progress has come in response to far-reaching legislation at the State and the Federal level in the United States. Starting in 1989, 13 States took the lead by adopting laws (including battery labeling requirements) to facilitate the collection and recycling of used rechargeable batteries. In 1996, the U.S. Congress passed the Mercury-Containing and Rechargeable Battery Management Act, which removed barriers to the rechargeable battery recycling and helped facilitate the RBRC's nationwide take-back program. In addition, many States have passed legislation prohibiting incineration and landfilling of mercury-containing and lead–acid batteries.

The following are important legal terminologies for this section. The term "mercuric-oxide battery" means a battery that uses a mercuric-oxide electrode.

The term "rechargeable battery" (a) means one or more voltaic or galvanic cells, electrically connected to produce electric energy, that are designed to be recharged for repeated uses and (b) includes any type of enclosed device or sealed container consisting of one or more such cells, including what is commonly called a battery pack (and in the case of a battery pack, for the purposes of the requirements of easy removability and labeling under law, means the battery pack as a whole rather than each component individually); but it does not include a lead–acid battery used to start an internal combustion engine, a lead–acid battery used for load leveling or for storage of electricity, and a battery used as a backup power source for the memory or program, nor a rechargeable alkaline battery.

The term "rechargeable consumer product" (a) means a product that, when sold retail, includes a regulated battery as a primary energy supply and which is primarily intended for 1 kW personal or household use, but (b) does not include a product that uses only a battery as a sole source of backup power for memory or program instruction storage, timekeeping, or any other similar purpose that requires uninterrupted electrical power, in order to function if the primary energy supply fails or fluctuates momentarily.

The term "regulated battery" means a rechargeable battery that (a) contains a cadmium or a lead electrode or any combination of cadmium and lead electrodes or (b) contains other electrode chemistries and is the subject of a determination by the Administrator of the U.S. EPA under environmental laws.

The term "remanufactured product" means a rechargeable consumer product that has been altered by the replacement of parts, repackaged, or repaired after initial sale by the original manufacturer.

As stated previously, a battery is an electrochemical device with the ability to convert chemical energy to electrical energy to provide power to electronic devices. Household batteries may also contain cadmium, mercury, copper, zinc, lead, manganese, nickel, and lithium, which may create a hazard when disposed incorrectly. The potential problems or hazards of household batteries are similar to that of vehicle batteries.

In landfills, heavy metals have the potential to leach slowly into soil, groundwater, or surface water. Dry cell batteries contribute about 88% of the total mercury and 50% of the cadmium in the MSW stream. In the past, household batteries accounted for nearly half of the mercury used in the United States and over half of the mercury and cadmium in the MSW stream. When burned, some heavy metals such as mercury may vaporize and escape into the air, and cadmium and lead may end up in the ash.

Controversy exists about reclaiming household batteries. Currently, most batteries collected through household battery collection programs are disposed of in hazardous waste landfills. There are no known recycling facilities in the United States that can practically and cost effectively reclaim all types of household batteries, although facilities exist that reclaim some button batteries. Currently, battery collection programs typically target button and nickel–cadmium batteries, but may collect all household batteries because of the consumers' difficulty in identifying battery types.

There are two major types of household batteries: (a) Primary batteries are those that cannot be reused. They include alkaline/manganese, carbon–zinc, mercuric oxide, zinc–air, silver oxide, and other types of button batteries. (b) Secondary batteries are those that can be reused; secondary batteries (rechargeable) include lead–acid, nickel–cadmium, and potentially nickel–hydrogen.

Mercury reduction in household batteries began in 1984 and continues today. During the last five years, the industry has reduced the total amount of mercury usage by about 86%. Some batteries such as the alkaline battery have had about a 97% mercury reduction in the product. Newer alkaline batteries may contain about one-tenth the amount of mercury previously contained in the typical alkaline battery. Some alkaline batteries have zero-added mercury, and several mercury-free, heavy-duty, carbon–zinc batteries are on the market.

Mercuric oxide batteries are being gradually replaced by new technologies such as silver oxide and zinc-air button batteries that contain less mercury.

Nickel–cadmium rechargeable batteries are being researched. Alternatives such as cadmium-free nickel and nickel hydride systems are also being researched, but nickel–cadmium batteries are unlikely to be totally replaced. Nickel–cadmium batteries can be reprocessed to reclaim the nickel. However, currently, approximately 80% of all nickel–cadmium batteries are permanently sealed in appliances. Changing regulations may result in easier access to these nickel–cadmium batteries for recycling.

To reduce the amount of waste, start with pollution prevention. Starting with pollution prevention leads to less or no leftover waste that could potentially become hazardous wastes. The use of rechargeable batteries results in a longer life span and use fewer batteries. However, rechargeable batteries still do contain heavy metals such as nickel–cadmium. When disposing of rechargeable batteries, recycle them if possible.

The use of rechargeable nickel–cadmium batteries can reduce the number of batteries entering the waste stream, but may increase the amount of heavy metals entering the waste stream unless they are more effectively recycled. As of 1992, the percentage of cadmium in nickel–cadmium batteries was higher than the percentage of mercury in alkaline batteries; so substitution might only replace one heavy metal for another, and rechargeable batteries do use energy resources during recharging. Rechargeable alkaline batteries are available along with rechargers.

Recycle waste batteries if possible. Batteries with high levels of mercury or silver can be recovered for the refining process. The mercuric oxide batteries can be targeted for recollection and mercury recovery. There are a few mercury-refining locations in the United States that accept mercury batteries, and they could be contacted about battery recycling.

Mercury oxide and silver oxide button batteries are sometimes collected by jewelers, pharmacies, hospitals, and electronic or hearing aid stores for shipping them to companies that reclaim mercury or silver. Some batteries cannot be recycled. If recycling is not possible, batteries should be saved for disposing of at a hazardous waste collection. Battery recycling and button battery collection may be good options at present, but may change as the mercury concentration in the majority of button batteries continues to decrease.

Batteries may be taken to a household-hazardous-waste collection or a local battery collection program. One can also contact the battery manufacturer for other disposal options or for information on collection programs. If disposal is the only option, and the household batteries are not banned from the permitted landfill in the area, one should protect the batteries for disposal by placing them in a sturdy plastic bag in a sturdy container to help guard against leakage. Waste batteries should not be burned because of the metals that could explode. When burned, some heavy metals such as mercury may vaporize and escape into the air, and cadmium and lead may end up in the ash.[12]

In the United States, Federal and State initiatives are assisting the businesses and consumers in managing, reusing, recycling, and disposal of household batteries. These include the Universal Waste Rule and the Mercury-Containing and Rechargeable Battery Management Act.

The Universal Waste Rule, promulgated in 1995, was designed to encourage recovery and recycling of certain hazardous wastes (including batteries, thermostats, and some pesticides) by removing some of the regulatory barriers. Under the rule, batteries recovered and properly managed are exempt from some RCRA provisions, no matter who generates the waste. Promulgation of the Universal Waste Rule facilitated the battery industry's take-back system for Ni–Cd batteries in states that adopted the rule through state rulemaking.

The Mercury-Containing and Rechargeable Battery Management Act (the "Battery Act"), which was turned into a law on May 13, 1996, removed previous barriers to Ni–Cd battery recycling programs resulting from varying individual state laws and regulatory restrictions governing the labeling, collection, recycling, and transportation of these batteries. The Act facilitated and encouraged voluntary industry programs for recycling Ni–Cd batteries, such as the national "Charge Up to Recycle" program. The Act also established national labeling requirements for rechargeable batteries, ordered that rechargeable batteries be easy to remove from consumer products, and restricted the sale of certain batteries that contain mercury.

The 1996 Battery Act eased the burden on battery recycling programs by mandating national, uniform labeling requirements for Ni–Cd and certain small sealed lead–acid batteries and by making the Universal Waste Rule effective in all 50 States. The Battery Act indicates (a) the State labeling requirements for these battery types and (b) the State legislative and regulatory authority for the collection, storage, and transportation of Ni–Cd and other covered batteries. States can, however, adopt standards for battery recycling and disposal that are more stringent than existing Federal standards. They can also adopt more stringent requirements concerning the allowable mercury content in batteries.

Several States have passed legislation mandating additional reductions in mercury beyond those in the Battery Act and prohibiting or restricting the disposal in MSW of batteries with the highest heavy metal content (i.e., Ni–Cd, small sealed lead–acid, and mercuric oxide batteries). A handful of States have gone further, placing collection and management requirements on battery manufacturers and retailers to ensure that certain types of batteries are recycled or disposed of properly.

Many States and regional organizations have developed far-reaching legislation for battery management, which is beyond the scope of the Federal law. Only the following two organizations are introduced here: (a) the Northeast Waste Management Officials' Association (NEWMOA) and (b) the New England Governors' Conference.

The NEWMOA, a coalition of state waste program directors from New England and New York, has developed a model legislation meant to reduce mercury in waste. The model legislation proposes a variety of approaches that states can use to manage mercury-containing products (such as batteries, thermometers, and certain electronic products) and wastes, with a goal of instituting consistent controls throughout the region. The proposed approaches focus on notification, product phaseouts and exemptions, product labeling, disposal bans, collection and recycling programs, and a mechanism for interstate cooperation. Bills based on the model legislation have been under consideration by legislators in New Hampshire and Maine. In April 2000, NEWMOA released a revised version of the model legislation following a series of public meetings and the collection of comments from stakeholders.

The New England Governors' Conference passed a resolution in September 2000 recommending, among other things, that each New England State work with its legislature to adopt mercury legislation based on the NEWMOA model (see above). The NEWMOA model legislation is meant to reduce the amount of mercury in waste through strategies such as product phaseouts, product labeling, disposal bans, and collection and recycling programs. Certain types of mercury-containing batteries are among the products targeted by the model legislation.

29.5.10 MANAGEMENT OF ELECTRONIC WASTES: WASTE COMPUTERS

In the early 1980s, the world witnessed the sale of the first personal computers. Its transition from the relatively bulky and slow first units to the sleek, speed demons has made the computer truly revolutionary. With each improvement in computers, however, comes the increasing problem of what to do with the ever increasing number of computer e-wastes. The U.S. EPA estimates that nearly 250 million computers will become obsolete in the next five years in the United States alone. Unfortunately, only approximately 10% of these old computers that are retired each year are being recycled. This presents a substantial concern because toxic elements such as lead, cadmium, mercury, barium, chromium, beryllium as well as flame retardant, and phosphor are contained in a typical computer and there would be potential harm if there was a release of these elements into the environment.[1]

The Town of Colonie, County of Albany, New York, USA, has a good management policy. The Town residents can bring their old computers to the Town Solid Waste Management Facility's "Residential Recyclables Drop Off Area" for recycling. The Town collects old computers from residents and packages them to be shipped out to a private recycling firm, SR Recycling, who separate the salvageable components for reuse, remove the special metals/materials that have recyclable value, and dispose of only the remaining waste materials. The Town charges the residents a fee, USD10 per computer system (monitor, CPU, printer, keyboard, mouse, etc. as a set or parts of set) to pay for the recycling of these units. When the Town collects sufficient units to make up a shipment, the vendor is called to collect the computers.[1]

Through the Town's recycling system, the residents are provided an environmentally and economically sound means of managing the e-wastes. This assures that the materials of concern within these e-wastes are effectively and appropriately managed.

29.5.11 NANOTECHNOLOGY FOR MERCURY REMOVAL

When the mercury-containing equipment is improperly disposed of on land, the mercury will eventually leachate out from the waste equipment. Once released into the environment, mercury remains there indefinitely, contaminating the soil, sediment, and groundwater. This contamination eventually enters the food chain, exposing local populations to mercury's harmful effects.[2]

Until now there has been no effective technology for reducing groundwater mercury to two parts per billion, as required by the maximum contamination limit for drinking water established by the U.S. Food and Drug Administration and the U.S. EPA.

According to the U.S. Department of Energy's Pacific Northwest National Laboratory (PNNL), a new nanotechnology has been developed by PNNL for mercury removal without producing harmful by-products or secondary waste. The technology is an advanced adsorption technology involving the use of a powder adsorbent, called SAMMS. SAMMS stands for "self-assembled monolayers on mesoporous supports" and is critically important in the constantly changing industries and environment. It has broad applications in environmental cleanup where mercury contamination is prevailing, or for the removal of mercury from radiological hazardous waste.

Technically speaking, SAMMS is a hybrid of two frontiers in materials science: molecular self-assembly techniques and nanoporous materials. SAMMS is created by attaching a monolayer of contaminant-specific molecules to nanoporous ceramic supports. The nanoporous materials arranged from 2 to 20 nm (nanometer), with large surface areas (about 600–1000 m^2/g), are functionalized with a self-assembled monolayer, resulting in the extremely high density of the binding sites. The functionalized material exhibits fast kinetics, high loading, and excellent selectivity for contaminants.

Both the monolayer and the nanoporous support can be tailored for a specific application. For example, the functional group at the free end of the monolayer can be designed to selectively bind targeted molecules, while the pore size, monolayer length, and density can be adjusted to give the material specific adsorptive properties. This monolayer will seek out and adsorb specific contaminants. When tested on 160 L of waste solution containing about 11 ppm of mercury, or a total of 1.76 g, mercury concentration in the solution was reduced by about 99.5%. Estimates indicate that it will cost about USD200 (October 2004 cost), including material, analysis, and labor, to treat similar volumes of this waste solution, resulting in a savings of USD3200 over the more traditional polymeric adsorbent (resin) or activated carbon disposal methods.

29.5.12 Solidification (Cementation) Technology for Hazardous E-Waste Disposal

Cementation technology is one of the solidification technologies and involves the use of a solidifying agent (i.e., cement, in this case) for solidifying as hazardous solid e-wastes (such as mercury-containing batteries or equipment). Conventional cementation technology has problems: (a) as the solidified cement or concrete is still porous, hazardous substances may leak out eventually, and (b) the solidified cement or concrete blocks are not strong enough and may break upon impact or earthquake.

An improved solidification (cementation) technology has been used by Dr. Lawrence K. Wang of the Lenox Institute of Water Technology, Massachusetts, USA, for successful solidification of mercury-containing batteries in concrete blocks. The concrete blocks, which are environment friendly, can then be properly buried in the government-approved hazardous waste landfill sites.[3]

Specifically, the improved solidification (cementation) technology involves the use of (a) a special dry powder admixture for the generation of a nonsoluble crystalline formation deep within the pores and capillary tracts of the concrete—a crystalline structure that permanently seals the concrete against the penetration or movement of water and other hazardous liquids from any direction; (b) special nonmetal reinforced bars for enhancing the concrete block's tensile and compressive strengths; and (c) a unique chemical crystallization treatment for the waterproofing and protection of the concrete block's surface.

To create its crystalline waterproofing effect, the special solidifying agent must become an integral part of the concrete mass. It does so by taking advantage of the natural and inherent characteristics of concrete; concrete is both porous (capillary tract system) and chemical in nature. By means of diffusion, the reactive chemicals in the agent use water as a migrating medium to enter and travel through the capillary tracts in the concrete. This process precipitates a chemical reaction between the agent, moisture, and the natural chemical by-products of cement hydration (calcium hydroxide, mineral salts, mineral oxides, and unhydrated and partially hydrated cement particles). The end results are crystallization and, ultimately, a nonsoluble crystalline structure that plugs the pores and capillary tracts of the concrete and is thereby rendered impenetrable by water and other liquids from any direction.

The chemical treatment is permanent. Its unique, crystalline growth will not deteriorate under a wide range of conditions. The treated concrete block is structurally strong, and is not affected by a wide range of aggressive chemicals including acids, solvents, chlorides, and caustic materials in the pH range of 3–11.

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30 Food Industry Wastewater Treatment

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Yu-Ming Zheng, and Jiaping Paul Chen

CONTENTS

30.1 INTRODUCTION

Food production and processing is one of the most essential industries in the world. It provides some 20% of employees ranging from farmers, herders, processors, transportation workers, wholesalers, and retailers. Agriculture production essentially starts with the photosynthesis reactions, which convert carbon dioxide and water into organic matters. The final products include grasses, hay, fruits, vegetables, and grains (e.g., wheat, barley, and corn). The products are then collected, processed, packaged, and distributed for consumption by human beings or as feed for animals that can produce food products such as milk, eggs, and meat. The food industry has a wide scope. According to the North American Industry Classification System (NAICS), it consists of nine industrial groups listed in Table 30.1.[1] In this chapter, we limit the food industry to food processing operations.

The food industry is also considered as one of the major traditional industries. The United States is the largest producer and consumer of "processed" food products in the world and renders approximately 26% of the world food processing output. The food industry accounts for around one-sixth of the whole manufacturing sector's activities in the United States. The industry is dominated by large-scale, capital-intensive, and highly diversified corporations. There were 26,401 establishments from 22,037 food firms in the United States in 2000, and these firms hired 1,468,254 employees with an annual payroll of more than 43 billion USD.[2] However, the market is mainly dominated by the top 20 manufacturers. Food products of more than 460 billion USD are produced every year.[3] Meat processing was the largest employer, leading to 30% of workers; fruit and vegetable processing and bakery production are the second and the third, accounting for 13% and 12%, respectively.[4]

Compared to the "new economy" such as the computer and software industry, the food industry is usually regarded as an "old economy" covering all the basic needs of human beings. Its slow growth has been seen in the last decade; as a result, the industry is under significant reorganization so as to improve its profitability through consolidation, overseas growth, and the introduction of new products. In addition, food manufacturing plants are more automated and integrated to achieve the goals.[3,5]

It is predicted that the global population will increase to 7.9 billion by 2025, over 80% of whom will live in developing countries and 58% in rapidly growing urban areas[6]; in response to the rapid population growth and economic development, the demand for food will significantly rise. However, the food industry has a strong relationship with water and wastewater treatment, since water is employed in food processing and is sometimes partially involved as food products while wastewater is produced during the process. Therefore, increasing requirements for food will contribute to a greater more consumption of water for food processing. There are many types of food processing units due to various food products, which can be cataloged into a few sections as illustrated in Figure 30.1. Each of them may become a pollution-creating source with different strengths and quantities.

As one of the top water consumers, the food industry is estimated to account for about 9% of water and wastewater treatment market sales. The wastewater discharged from food manufacturing facilities has become a major concern. In this chapter, we will be discussing a series of physical,

TABLE 30.1
Food Industry Market in the United States

Name	Percentage of Establishments (%)
Meats	14.7
Seafood	3.1
Grains	3.3
Sugars	6.2
Dairy	6.4
Fruits and vegetables	6.5
Bakery	38.8
Beverages	10.0
Other	10.9

Source: Web site of D&B Sales and Marketing Solutions (accessed 12/03/2003). Industry reports are available at http://www.zapdata.com upon registration.

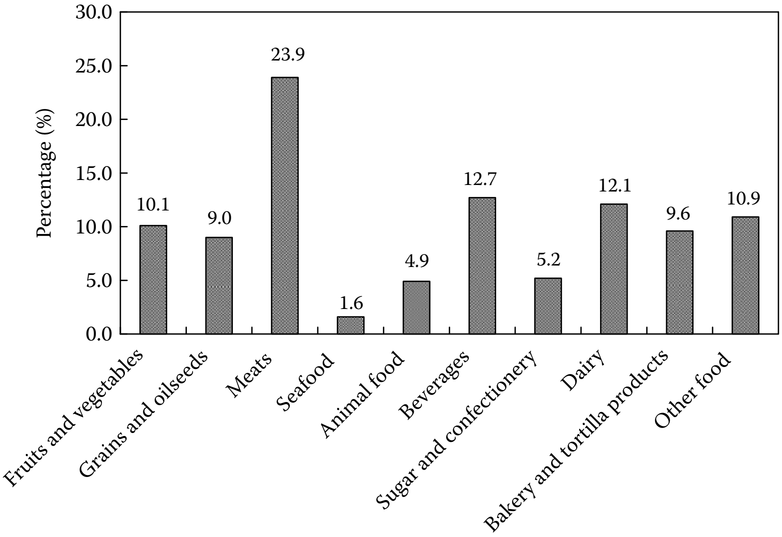

FIGURE 30.1 Components of U.S. food and beverage manufacturing.

chemical, and biological technologies for wastewater treatment. Pollution prevention and cleaning technology will also be addressed.

30.2 WATER USAGE IN FOOD PROCESSING

Out of the fresh water withdrawn annually, agricultural, industrial, and domestic consumptions lead to 69%, 23%, and 8% of water usage, respectively.[6] The food processing industry is one of the largest potable water users in the world. Some thousands to multimillions of gallons per day are used by individual facilities in the United States.[6] Water consumption varies significantly among the different sectors. It is reported that 3 L-water/kg-product is required for food in general; however, meat processing requires 33 L-water/kg-product.

Water can usually be used as an ingredient, a solvent, and a principal agent for cleaning and disinfection in plants or transportation systems for delivering raw materials. Since water consumption will always be a part of the food processing industry, it has become the key target for pollution prevention and source reduction practices.

Water conservation, reuse, and recycling are increasingly being implemented. Some common practices have been applied in water conservation; for example, installing shutoff valves and flow reduction devices, choosing dry cleaning instead of wet cleaning methods, and so on. As the wastewater from food processing mainly contains organics, it can be treated biologically and subsequently reclaimed by a combination of physico-chemical and biological approaches. Application of the reclaimed water into food processing can in turn save cost and decrease the consumption of fresh water. Many successful experiences have been witnessed in the food industry; for instance, the starch industry has reduced the use of fresh water by 20%. This substantial cost reduction is attributed to process integration and the internal recycling of process water. Cooling water systems have also been optimized to minimize the cooling water requirement and use of fresh water.[3] The concept and practice of "ecoefficiency measures" have been widely applied throughout business and notably in the food industry, which has been recognized to be helpful for both environment and business.[3]

In the food industry, water can be classified into several types: general purpose, process, cooling, and boiler feed. Its use starts with raw materials, such as soaking, cleaning, blanching, and chilling. Water use continues with cooling, sanitizing, steam generation for sterilization, power and process heating, and finally direct process usage. The water requirements for food products are different. Generally, a large amount of water is necessary for processing raw materials and converting them into products.[7]

General-purpose water: The application includes washing and sanitizing raw materials, processing equipment, plant facility, and ancillary equipment. The water must be free of contaminants since the water contacts food directly.

Process water: Water is used for cooking or is directly added into the product. It must be free of contaminants.

Cooling water: Water is used for cooling purposes, the requirement of which is not strict since it does not contact food products directly.

Boiler feed water: Water is used for boiling purposes, and is required to have low hardness in order to avoid scaling problems.

30.3 CHARACTERISTICS OF FOOD INDUSTRY WASTEWATER

Food processing wastewater has distinctive characteristics. It can be characterized as nontoxic due to the existence of few hazardous and persistent compounds such as those regulated under the U.S. Environmental Protection Agency's (EPA's) toxic release inventory (TRI) listing. However, the wastewater from food processing industries contains high levels of biochemical oxygen demand (BOD) or chemical oxygen demand (COD), large amounts of total suspended solids (TSS), and various inorganic substances such as nitrogen and phosphorus. Another contaminant of food processing wastewater, especially from meat, poultry, and seafood processing facilities, is the pathogenic organism. In general, the constituents of wastes generated are complicated and dependent on different factors such as BOD, COD, pH and temperature variation in effluents, nature of food processing, and so on.

Food processing can be divided into four major sectors: fruit and vegetables; meat, poultry, and seafood; beverage and bottling; and dairy operations.

30.3.1 Fruit and Vegetable Food Processing Sector

The major steps in processing fruits and vegetables include general cleaning and dirt removal, removal of leaves, skin, and seeds, blanching, washing and cooling, packaging, and cleanup. Wastewater is the primary area of pollution control. Such wastewater is normally high in suspended solids (SS), organic sugars, proteins, and starches, and may contain residual pesticides.

30.3.2 Meat, Poultry, and Seafood Sector

Meat, poultry, and seafood facilities produce a more difficult wastewater to treat. Meat and poultry processing wastewaters typically contain blood, hair, feathers, bones, fat, and manure. Such wastewaters have extremely high organic loads and high contents of oil and grease (O&G), salt, nitrogen, and phosphorus. BOD and SS of untreated streams can be as high as 8000 mg/L and 800 mg/L, respectively.[8] Pathogens can also exist, including *Salmonella* and *Shigella* bacteria, parasite eggs, and amebic cysts. A variety of antibiotics, hormones from animals/poultry, and pesticide residues also create specific problems for treating water. Chloride concentrations may be very large (up to 77,000 mg/L) from curing and pickling operations. Cooking activities also greatly increase the fat and grease content.[9]

Major sources for seafood processing wastewater include storage and transport; cleaning, freezing, and thawing; brines preparation; steam generation; cooling water; and so on. It can be very high in BOD, O&G, and nitrogen content. A literature study shows that the production of BOD in white fish filleting processes ranges from 25 to 75 lb BOD/ton of product.[3,8] BOD mainly originates from butchering and cleaning operations while nitrogen is primarily the result of blood in the wastewater (Environment Canada, 1994a). Half of the generated wastewater streams can be caused by thawing processes.[8]

30.3.3 BEVERAGE AND BOTTLING SECTOR

The primary units in processing beverages are raw material handling and processing, mixing, fermentation, cooking, cooling, bottling and packaging, pasteurization, and cleanup. Effluent discharged from the beverage industry is normally generated by wasted drinks and syrup, water in the fermentation process, water from bottle cleaning, which contains detergents and caustics, and lastly lubricants used in the machinery. Thus, the associated wastewater pollutants contain TSS, various organics, nitrates, phosphates, sodium and potassium, and so on. The wastewater of fermentation processes usually has higher organic loads and overall wastewater volume compared to other food processing sectors. Table 30.2 gives a list of parameters for soft drink wastewater.

30.3.4 DAIRY SECTOR

The waste milk in dairy wastewaters mostly comes from start-up and shut-down operations performed in the high-temperature, short-time pasteurization process. This waste is pure milk raw material mixed with water. Another wastewater of the dairy sector originates from equipment and tank-cleaning wastewaters. These waste streams contain waste milk and sanitary cleaners that are the principal waste constituents of dairy wastewater. Over time, milk waste degrades to form corrosive lactic and formic acids. Approximately 90% of a dairy's wastewater load is milk.

30.4 PRETREATMENT ALTERNATIVES

Pretreatment is a series of physical and chemical processes to precondition the wastewater and remove some wastes. The treatment is usually arranged in the following sequence: screening; flow equalization and neutralization; optional fat, oil, and grease (FOG) separator; optional acidification;

TABLE 30.2
Characteristics of Soft Drink Wastewater

Parameter	Concentration (mg/L)
COD	1200–1800
BOD_5	600–4500
Alkalinity	1000–3500
TSS	0–60
VSS	0–50
NH_3-N	150–300
PO_4-P	20–40
SO_4	7–20
K	20–70
Fe	10–20
Na	1500–2500
Ni	1.2–2.5
Mo	3–8
Zn	1–5
Co	3–8

Source: Chen, J.P., Seng, S.S., and Hung, Y.T., *Soft Drink Waste Treatment, Handbook of Industrial and Hazardous Waste Treatment*, 2nd ed., Marcel Dekker, New York, 2004, pp. 1077–1091.

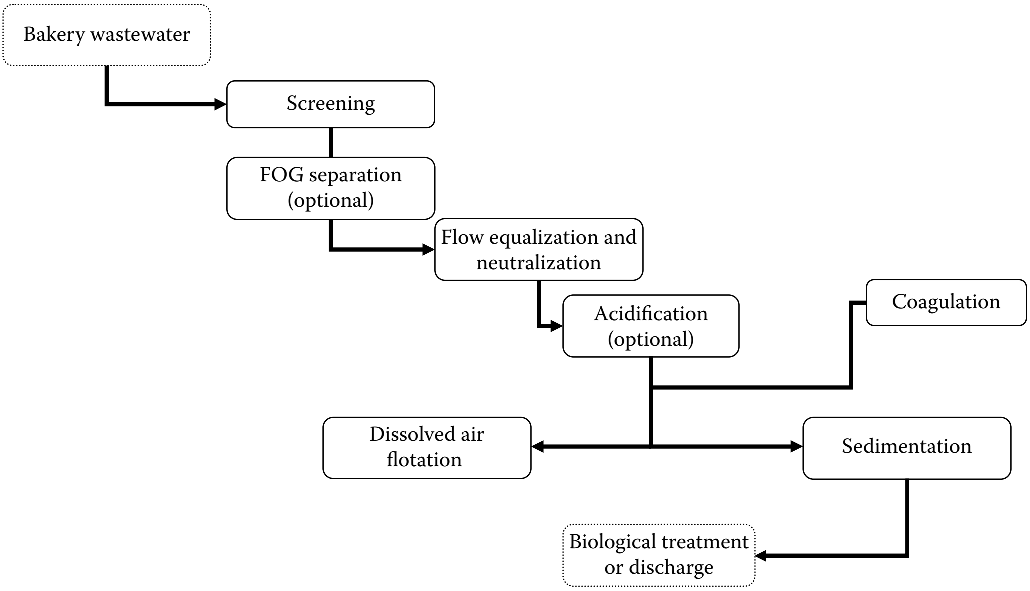

FIGURE 30.2 Bakery wastewater pretreatment system.

coagulation–sedimentation; and dissolved air flotation (DAF). The pretreatment of bakery wastewater is given in Figure 30.2.

Due to the high content of SS and FOG, pretreatment is always necessary for the food industry. It can decrease contaminant loading for subsequent biological and/or chemical treatment processes as well as protect process equipment. In addition, pretreatment is economical in the total process view as it is not as expensive as biological and chemical treatment.

30.4.1 Flow Equalization and Neutralization

Applying a flow equalization tank is usually considered to be an economic approach to meet the peak requirement. However, too long a retention time may result in an anaerobic environment. A decrease in pH and bad odors are common problems during the process.

30.4.2 Screening

Screening is generally used to remove coarse particles in the influent. There are different screening pores ranging from a few micrometers (termed as microscreen) to more than 100 mm (termed as coarse screen). Coarse screen openings are between 6 and 150 mm whereas fine screen openings are below 6 mm. Smaller openings can have better removal efficiencies; however, operational problems such as clogging and higher head loss are always observed.

Fine screens are often used, of which the medium is generally stainless steel material. Velocity, selection of screen openings, and head loss through the screens are the main parameters in the design. Clean operations and waste disposal must be considered. The design capacity of fine screens can be as high as 0.13 m^3/s; the head loss ranges from 0.8 to 1.4 m. Depending on the design and operation, the 5-day biological oxygen demand (BOD_5) and SS removal efficiencies are 5–50% and 5–45%, respectively.[9,10]

30.4.3 FOG Separation

It is recommended that FOG separation be installed because of the high amount of FOG in food wastewater. Generally, FOG can be separated and recovered for possible use or for easy biological treatment in the future. Figure 30.3 shows one FOG separation and recovery system.[11]

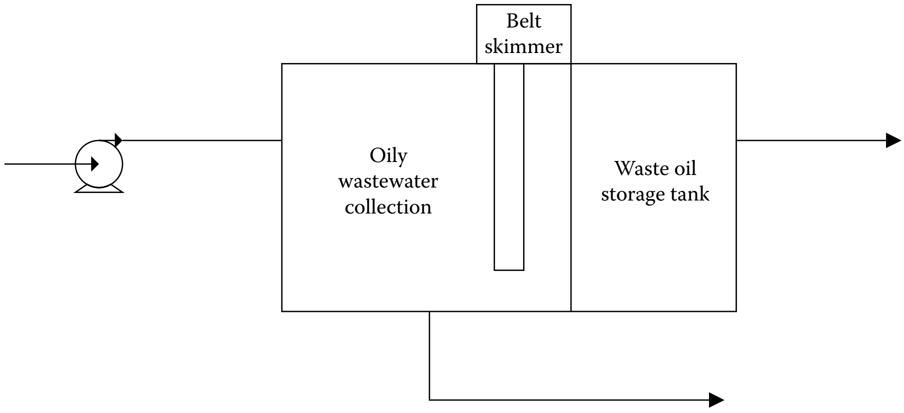

FIGURE 30.3 Fat, oil, and grease separation unit.

30.4.4 Acidification

Depending on the properties of wastewater, acidification is sometimes required in pretreatment. In the presence of FOG, when acid (e.g., concentrated H_2SO_4) is added into the acidification tank, organics will be hydrolyzed, which improves biotreatability. Grove et al.[12] designed a treatment system using nitric acid to break the grease emulsions followed by an activated sludge process. A BOD_5 reduction of 99% and an effluent of <12 mg/L were achieved at a loading of 40 lb $BOD_5/1000\,ft^3$ and a detention time of 87 h. The nitric acid also furnished nitrogen for proper nutrient balance for the biodegradation.

30.4.5 Coagulation–Flocculation

Coagulation is used to destabilize stable fine SS, whereas flocculation is used to grow destabilized SS; therefore, SS will become heavier and larger enough to settle down. The coagulation–flocculation process normally serves as a precondition operation for sedimentation and/or DAF. For the treatment of beverage industrial wastewater, coagulation and flocculation pretreatment processes were used by Amuda and Amoo[13] to remove COD, SS, and phosphorus using ferric chloride and organic polyelectrolyte and the removal efficiencies were 91%, 97%, and 95%, respectively. Such pretreatment units were demonstrated to be very useful prior to biological treatment.

30.4.6 Sedimentation

The mechanism for sedimentation (clarification) is based on the density difference between SS and liquid. In addition, SS with larger particle sizes can settle down more easily. Rectangular tanks, circular tanks, combination flocculator-clarifiers, and stacked multilevel clarifiers can be used.[14] Oliveira et al.[15] reported that flocculation and sedimentation were conducted in the cassava meal industry and reduced the effluent concentration of organics from 14,000 to 2000 mg/L in the bench-scale reactor, with a hydraulic retention time (HRT) of 37 min.

30.4.7 Dissolved Air Flotation

DAF is usually designed by pumping compressed air bubbles to remove fine SS and FOG. The wastewater is first stored in an air-pressured closed tank and then enters the flotation tank through pressure-reduction valves. Due to a sudden reduction in pressure, air bubbles form and rise to the surface in the tank. SS and FOG adhere to the fine air bubbles and are carried upward. Both dosages of coagulant and pH are important in the removal of BOD_5, COD, FOG, and SS. Other important impact factors include the solids content and air/solids ratio. Optimal operation conditions should be determined through pilot-scale experiments. Manjunath et al.[16] used a DAF process to decrease waste strength by about 50%, which provides both float and subnatant with higher degradability than raw waste in a slaughterhouse. Furthermore, a DAF unit was adopted by Liu and Lien[17] to treat wastewater from a large-scale bakery. The wastewater was preconditioned by alum and ferric chloride. 48.6% of COD and 69.8% of SS were removed in 10 min at a pressure of 4 kg/cm^2 and pH 6.0. de Nardi et al.[18] found that the removal efficiencies of SS and O&G achieved 74% and 99%, respectively, with 24 mg Al^{3+}/L polyaluminum chloride (PAC) and 1.5 mg/L anionic polymer as well as under a pressurization of 40% recycled DAF-effluent at 450 kPa.

30.5 BIOLOGICAL TREATMENT SYSTEMS

In biological treatment systems, microorganisms are used to degrade the biodegradable organics in wastewater.[19] Biological treatment systems can be "suspended growth systems" (e.g., activated sludge systems) or "attached growth systems" [e.g., rotating biological contactors (RBCs) and trickling filters] according to the growth type of the microorganisms.[19,20] Considering the type of oxygen utilization, biological treatment systems can be classified as aerobic, anaerobic, and facultative. In the aerobic system the organic is decomposed to carbon dioxide, water, and a series of simple compounds, whereas in the anaerobic system the final products are carbon dioxide and methane.

Typically, the aerobic biological process achieves better quality in treated effluent, easy operation, and shorter solid retention time. However, the cost of aeration is high in the aerobic system and excess sludge is produced. When it comes to the high-load influent treatment (COD > 4000 mg/L), aerobic biological treatment becomes less economical than anaerobic treatment. In most of the cases, the anaerobic biological process is used as a treatment process prior to the aerobic treatment. Selecting the appropriate treatment process largely depends on the wastewater characteristics and the required level of treatment.[19]

30.5.1 ANAEROBIC BIOLOGICAL TREATMENT SYSTEMS

The anaerobic biological wastewater treatment process is generally practiced if the organic strength of the wastewater is comparatively high (e.g., COD > 4000 mg/L). In this process, anaerobic and facultative microorganisms are utilized to convert the organic pollutants in wastewater to carbon dioxide and methane. Anaerobic treatment consists of two major steps: acid fermentation and methane formation. During the first step, complex organic matters are converted into soluble products such as fatty acids and amino acids, which further leads to the formation of volatile acids and alcohols. The second stage (methane formation) consists of acetogenesis (conversion of volatile fatty acids to acetate, hydrogen gas, and carbon dioxide) and methanogenesis (methane formation by the products of acetogenesis).[21]

The anaerobic treatment process is pH dependent, especially when it involves methane formation (optimal pH range 6.8–7.2).[21,22] Sodium bicarbonate and calcium bicarbonate can be added to provide sufficient buffer capacity to maintain pH in the above range.[21] Temperature is another important factor to be considered during the anaerobic treatment process. The acid fermentation stage can withstand a higher temperature range due to the presence of microorganisms that can tolerate different levels of temperature. However, in the methane formation step, the temperature changes should be controlled. Usually, the temperature of anaerobic digesters can be mesophilic (30–40°C) or thermophilic (50–60°C).[23] Other than the factors discussed above, maintaining the proper nutrient levels and organic loading rate is important to control the anaerobic treatment process.[22]

In this section, we will discuss selected anaerobic treatment systems that are in use for food industry wastewater treatment.

30.5.1.1 Anaerobic Filters

The anaerobic filter (AF) was developed by Yong and McCarty in the late 1960s.[21] It is typically operated like a fixed-bed reactor,[23] where growth-supporting media in the AF contact wastewater. The growth-supporting media can be rock, plastic, or an other synthetic material. Anaerobic microorganisms grow on the supporting media surfaces and void spaces in the media particles. Wastewater flow into the filter can be from the top of the filter (down-flow) or from the bottom of the filter (up-flow). A predetermined portion of the effluent is recycled through the reactor. The magnitude of the recycled portion determines whether the reactor flow pattern is plug flow or completely mixed.[21] Periodic backwashing prevents filter clogging and head loss.[22] Turbulent fluid motion that accompanies the rapid rise of gas bubbles through the reactor can be helpful to remove solids in the media.[24]

In a laboratory-scale study carried out by Mustapha et al.[25] for treating palm oil mill effluent using an up-flow AF, a 97% removal of BOD and a 94% removal of COD were obtained. COD loading to the reactor was 0.1–0.5 kg COD/m^3 d. In another study conducted by Siino et al.,[26] an AF was used to treat soluble carbohydrate waste (soft drink wastewater). It is reported that, at an HRT of 1.7 d, an organic loading of 44–210 lb COD/(1000 ft^3 d) and, at an SRT of 137 d, a removal of 85–90% of COD from 1200 to 6000 mg/L can be achieved. The percentage of methane ranged from 60% to 80%; its product was 0.13–0.68 ft^3/d.

30.5.1.2 Up-Flow Anaerobic Sludge Blanket Reactor

The up-flow anaerobic sludge blanket (UASB) reactor was developed by Lettinga, van Velsen, and Hobma in 1979.[27] It is simple in design and is a combination of physical and biological processes.[27,28] It can be categorized under suspended growth systems.[28] The wastewater flow to be treated is sent upward from the bottom of the reactor. At the bottom of the reactor, wastewater contacts with the active anaerobic sludge solids distributed over the sludge blanket. The sludge blanket contains granules of microorganisms (0.5–2 mm in diameter). If maintained under the proper conditions (e.g., proper mechanical agitation), the good flocculation/settling characteristics of these granules do not allow them to wash out from the reactor.[27,28] The sludge solids concentration in the sludge blanket can be as high as 100,000 mg/L. At the sludge blanket, organics convert into methane and carbon dioxide following the steps explained in Section 30.5.1.[21] The mixture of the above two gases is separated from the sludge at the "three-phase separator" located at the top of the reactor. The success of the UASB reactor is dependent on the ability of the three-phase separator to retain sludge solids in the system. Bad effluent quality occurs if the sludge flocs do not form granules or form granules that float.[21,28] A schematic diagram of the UASB reactor is shown in Figure 30.4.

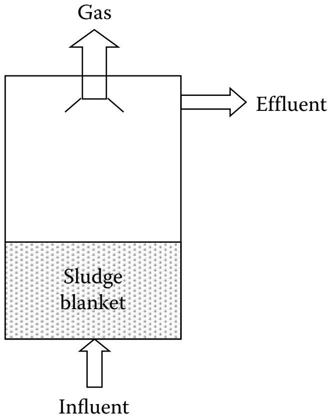

FIGURE 30.4 UASB reactor.

Miranda et al.[29] reported the performance of a full-scale UASB reactor. Target wastewaters for their work were effluents from a meat packing plant and a pig and cattle slaughterhouse. The volume of the UASB reactor was 800 m^3. The high O&G content was reduced using coagulation–flocculation pretreatment and subsequently the wastewater flow was sent through the UASB reactor. This kind of pretreatment reduced sludge washout and the performance of the UASB reactor improved. A COD removal of 70–92% and a maximum organic loading of 2.43 kg COD/(m^3 d) were achieved. In another study conducted by El-Gohary et al.,[30] the laboratory-scale UASB reactor was studied for the treatment of wastewater from a potato-chips factory. A BOD reduction of 86% and a COD reduction of 82% were reported. The corresponding HRT and organic loading rate were 18 h and 2.9 kg BOD/(m^3 d), respectively. Soft drink wastewater containing COD 1.1–30.7 g/L, TSS 0.8–23.1 g/L, alkalinity 1.25–1.93 g CaCO$_3$/L, nitrogen 0–0.05 g N/L, and phosphate 0.01–0.07 g P/L was treated by a 1.8 L UASB reactor.[31] The pH of wastewater was 4.3–13.0 and the temperature was between 20°C and 32°C. The highest organic loading reported was 16.5 kg COD/m^3 d. A treatment efficiency of 82% was achieved. Housley et al.[32] have reported on the industrial application of the "Biothane" reactor (a patented UASB system) in order to treat wastewater from a soft drink factory. The average flow rate, BOD, and COD of the wastewater were 900 m^3/d, 2340 kg/d, and 3510 kg/d, respectively. A supervisory control and data acquisition system (SCADA) was used for continuous monitoring of the process and on-site equipment. Under normal operation, a COD removal of 75–85% and 0.35 m^3 of biogas production per kilogram of COD were achieved.

30.5.1.3 Anaerobic Fluidized Bed Reactor

An anaerobic fluidized bed reactor (AFBR) utilizes small particles such as sand and activated carbon as the media for microorganism growth. Wastewater flow enters the reactor through the bottom of the reactor. Media are kept in the fluidized state by controlling the up-flow velocity of the wastewater stream in such a way that the weight of the media particles equals the drag force exerted by the wastewater.[21,22] The height of the fluidized bed is stabilized. On average, a packing size of 0.3–0.8 mm and up-flow wastewater velocities of 10–30 m/h can be used in order to provide 100% bed expansion. The depth of the fluidized bed ranges between 4 and 6 m (Figure 30.5).

However, in the AFBR process, due to the decrease in particle density of the media after the accumulation of biomass on the surface, particle density can drop. As a result, particles tend to wash

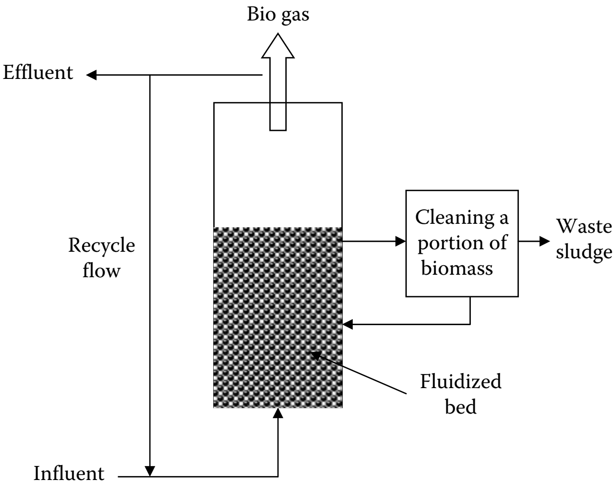

FIGURE 30.5 Anaerobic fluidized bed reactor (AFBR).

out from the reactor. Therefore, it is necessary to clean and remove the attached biomass from a portion of the media from time to time. After cleaning, the particles are returned to the reactor and the separated biomass is wasted as sludge.[21,33,34] Due to high turbulence and the thin biofilms developed in the AFBR, biomass capture is relatively weak; therefore, an AFBR is better suited for wastewater with mainly soluble COD.[21]

Borja and Banks[35] investigated an AFBR to treat ice-cream wastewater. The COD of the wastewater to be treated was 5.2 g/L. The operating temperature was 35°C and the duration for start-up was reported as 30 d. At steady state, COD removal efficiency was 94.4%. The HRT and organic loading rate, while achieving the above performance, were 8 h and 15.6 g COD/(L d), respectively. Moreover, temperature, pH, flow rate, and COD loading shocks deteriorated reactor performance. However, after restoring favorable conditions, the system regained its steady state after 6–16 h. The same authors reported the use of an AFBR for wastewater from the soft drink industry.[36] Three different media (bentonite, saponite, and polyurethane) were used for the growth of microorganisms. The composition and parameters of the soft drink wastewater were total solids (TS) 3.7 g/L, TSS of 2.9 g/L, volatile suspended solids (VSS) 2.0 g/L, COD of 4.95 g/L, volatile acidity (acetic acid) 0.12 g/L, alkalinity 0.14 g $CaCO_3$/L, ammonium 5 mg/L, phosphorus 12 mg/L, and pH 4.8. The average COD removal of reactors was 89.9%, 93.3%, and 91.9% when the media used in the reactor were bentonite, saponite, and polyurethane, respectively. The percentage of methane in biogas was 66%, 72%, and 69% for reactors with bentonite, saponite, and polyurethane, respectively. It has been reported that the production of biogas reduced with increasing HRT.

The design and performance of the anaerobic treatment processes that we have discussed are shown in Table 30.3. According to the table, the AFBR outperforms the UASB and the AF. An AFBR can achieve higher removal efficiency within a shorter HRT. The volumetric loading rate of the AFBR is comparatively higher than that of the UASB and AF. However, the choice of appropriate technology should consider factors such as the footprint, operational and maintenance cost, and the level of treatment required.

30.5.2 AEROBIC BIOLOGICAL TREATMENT SYSTEMS

In aerobic biological treatment systems, oxygen has to be supplied through aeration. The biodegradable portion of organics in the wastewater converted into carbon dioxide, water, and other simple compounds. Usually, aerobic treatment systems are employed if the wastewater is of low strength. Compared to the anaerobic biological treatment processes, the quality of effluents from aerobic processes is higher. In this section, selected aerobic biological treatment systems that can be used in the food processing industry are discussed.

TABLE 30.3
Design and Performance of Anaerobic Treatment Processes

Reactor	Influent COD (g/L)	HRT (d)	Volume Loading Rate (kg COD/m^3 d)	Removal (%)
AF	3–40	0.5–13	4–15	60–90
AFBR	1–20	0.5–2	8–20	80–99
UASB	5–15	2–3	4–14	85–92

Source: Chen, J.P., Yang, L., Bai, R., and Hung, Y.T., *Bakery Waste Treatment, Handbook of Industrial and Hazardous Waste Treatment*, 2nd ed., Marcel Dekker, New York, 2004, pp. 1093–1111.

AF: Anaerobic filter, AFBR: Anaerobic fluidized bed reactor, UASB: Up-flow anaerobic sludge blanket reactor, COD: Chemical oxygen demand, HRT: Hydraulic retention time.

30.5.2.1 Activated Sludge Process

The activated sludge process is a suspended growth treatment system where a mixture of microorganisms is utilized for the degradation of organic pollutants. It consists of a pretreatment system, an aeration tank where biological treatment occurs, sedimentation to separate water from the SS, and, finally, sludge treatment. A portion of sludge from the sedimentation is recycled back to the aeration tank and the rest is removed from the system as waste sludge for further treatment and disposal. A recommended complete activated sludge process is given in Figure 30.6.

According to the flow characteristics, the activated sludge process can be a plug-flow reactor (PFR), a completely stirred tank reactor (CSTR), or a sequencing batch reactor (SBR). In order to maintain the plug-flow behavior, the reactor length to width ratio should exceed 10:1. When it comes to the CSTR, the main benefit is the higher buffer capacity due to complete mixing. Therefore, the CSTR is capable of handling toxic wastewater compared to the PFR. However, it should be noted that the PFR requires a lower volume compared to the CSTR in order to achieve the same effluent quality. The SBR contains five steps: fill, react, settle, draw, and idle. All of the steps are conducted in the same reactor. Due to the complex nature of operation, the SBR is suitable if the wastewater flow is low.

Other than the configuration of the bioreactor, the performance of activated sludge processes is affected by influent characteristics and operational parameters. Influent characteristics are wastewater flow rate, COD and BOD, nutrient compositions (nitrogen and phosphorus), FOG, alkalinity, heavy metals, toxins, pH, and temperature. Operational parameters in the treatment are biomass concentration (mixed liquor volatile suspended solids (MLVSS) and VSS, organic load, food to biomass ratio (F/M), dissolved oxygen (DO), sludge retention time (SRT), HRT, sludge recycle ratio, and surface hydraulic flow load. Among these, SRT and DO are the most important control parameters and significantly affect the treatment results. A suitable SRT can be achieved by judicious sludge wasting from the final clarifier. DO in an aeration tank should be maintained at a level slightly above 2 mg/L.

The activated sludge process for meat processing wastewater treatment was reported by Annachhatre and Bhamidimarri.[37] When a model reactor was operated at an HRT of 5–15 h, a COD removal of more than 85% was achieved. The COD loading for the above performance was 3.2 kg COD/(m^3 d). An SRT of 13 d resulted in almost complete nitrification. El-Gohary et al.[30] reported that the activated sludge process reduced the BOD and COD of a potato-chips factory wastewater by 86% and 84%, respectively. The organic loading rate and HRT were reported as 8.9 kg BOD/(m^3 d) and 6 h, respectively.

30.5.2.2 Trickling Filter Process

Trickling filter systems are classified under the aerobic attached growth systems (Figure 30.7). Crushed rock and stone, slag, wood, or synthetic media with higher permeability are used to fill the filter bed. The size of the media is in the range of 25–100 mm diameter. The depth of the filter

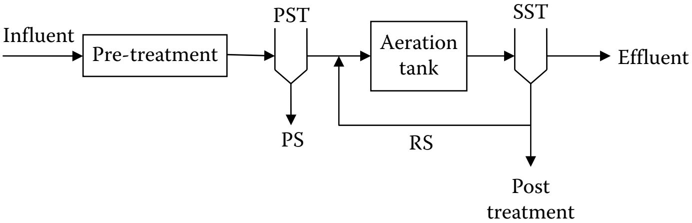

FIGURE 30.6 Schematic diagram of the activated sludge process.

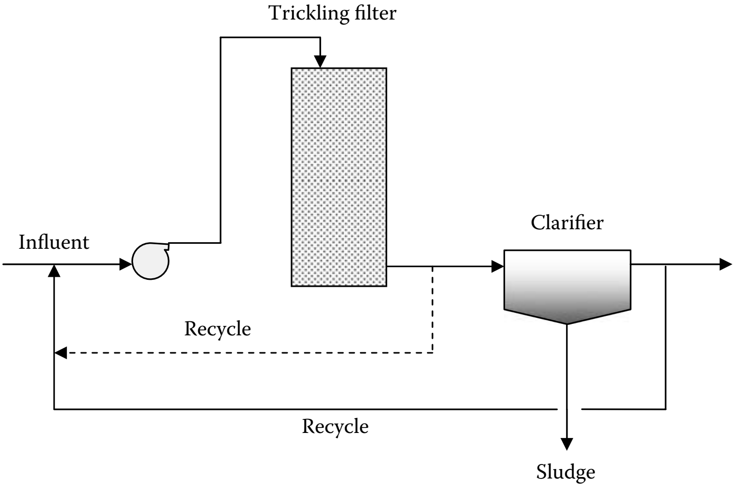

FIGURE 30.7 Flow diagram of the trickling filter.

bed is about 1.8 m on average.[38] The wastewater is spread over the bed from the top of the filter using a rotary distributor. During the process, microorganisms are attached and grow on the surface of the solid medium on the trickling filter bed. Organic pollutants in the incoming wastewater are degraded by the attached biofilms and complex organics are converted into a group of simple compounds such as water, carbon dioxide, and nitrate.[19] Once the biofilms that are grown on the solid medium increase in thickness, they undergo the process called “sloughing” and are detached from the medium. In order to collect the detached biofilms and treated wastewater, and provide air circulation, an under-drain system is constructed for the trickling filters.[36] The surface area and the void ratio of the filter bed are crucial for the performance of the reactor. Clogging of the reactor bed due to excess biofilm growth is one of the common problems in trickling filters.[19] Trickling filter treatment systems can be single stage or multiple stage, depending on the level of treatment required. The design parameters and the performance of the trickling filter are shown in Table 30.4.

Trickling filter technology can be used for the treatment of pretreated dairy industry wastewater.[39] A trickling filter packed with ceramic tiles was used to treat sugar wastewater. The influent BOD_5 and COD were 142–203 and 270–340 mg/L; the organic loading was from 5 to 120 g BOD_5/m^2 d.

TABLE 30.4
Design and Performance of the Trickling Filter

Type of Filter	BOD_5 Loading (kg/m^3 d)	Hydraulic Loading (m^3/m^2 d)	Depth (m)	BOD Removal (%)	Medium
Low rate	0.07–0.4	1–3	1.8–2.4	80–90	Rock, slag
Mid-range rate	0.2–0.45	3–7	1.8–2.4	50–70	Rock, slag
High rate	0.5–1	6–20	1–1.8	65–85	Rock

Source: Chen, J.P., Yang, L., Bai, R., and Hung, Y.T., *Bakery Waste Treatment, Handbook of Industrial and Hazardous Waste Treatment*, 2nd ed., Marcel Dekker, New York, 2004, pp. 1093–1111; Wastewater Treatment Fact Sheet—Trickling Filters, EPA 832-F-00-014, U.S. Environmental Protection Agency, 2000. Available at http://www.epa.gov/owm/trickling_filter.pdf.

Removal efficiencies of BOD_5 of 88.5–98% and COD of 67.8–73.6% were achieved. The process was able to cope effectively with organic shock loading up to 200 g COD/L.[40]

30.5.2.3 Rotating Biological Contactor

RBCs are classified under aerobic attached growth treatment systems. An RBC consists of a series of circular disks, which are closely connected to a rotating shaft. These circular disks can be made of polystyrene or polyvinyl chloride.[38] About 40% of the disk is submerged in the wastewater during the process.[41] During the operation, a biofilm is formed on the surface of the disks. As the disks are rotating and contact with wastewater is alternative, the organics contact with the biological growth and oxygen time to time. This is advantageous to maintain the aerobic condition in the biofilm as well.[38] The RBC has advantages and disadvantages. The large area of biofilms, good settling of detached biomass, and low sludge production are some of the advantages of the RBC system. Due to its rotating nature, frequent maintenance is required. Moreover, the protection of the unit from climate changes (e.g., freezing) is problematic.[41]

RBC technology has been studied for different types of food industry wastewaters. In a study carried out by Najafpour et al.,[42] a bench-scale RBC was studied for the treatment of wastewater from palm oil mill effluents. The COD of the wastewater was reported to be as high as 16,000 mg/L. COD removal with 55 h HRT was 88%. Surface loading to the RBC ranged from 38 to 210 g COD/(m^2 d). A total Kjeldahl nitrogen (TKN) removal of 80% and an SS removal of 89% were achieved as well. Meat processing industry wastewater was treated using a combination of an UASB a reactor and a RBC.[43] It should be noted that meat processing wastewater is of high organic strength and it is difficult to treat this using a single step. Wastewater was first treated using the UASB reactor and the removal of total COD, total BOD, TSS, and O&G were 56%, 56%, 85%, and 58%, respectively. This wastewater was then treated with the RBC. The overall removal percentages of COD, BOD, TSS, and O&G were 91.5%, 94%, 96%, and 91%, respectively.

30.6 EMERGING TECHNOLOGIES

Apart from the conventional biological treatment systems discussed above, there are several emerging technologies for the food industry wastewater. The use of different types of membrane bioreactors (MBRs) is one of them. The MBR process can be considered as a modification to the activated sludge process that we have discussed above. Usually, the membrane module is submerged in the bioreactor.[44,45] The incorporation of membrane modules is not limited with aerobic systems, but it is possible to combine them with anaerobic systems as well.[46] Use of the MBR for wastewater treatment, including the food industry wastewater, has several advantages compared to the conventional methods. The major advantage is the ability to retain higher concentrations of biomass in the reactor.[44,46] As a result, SS concentration in the effluent is lower.[46] Moreover, the SRT can be controlled without any effect on the HRT.[44] The footprint of the treatment plant is lower compared to the conventional biological treatment systems due to the reducted need for further filtration (tertiary treatment) and the low sludge volume to be treated.[45]

Sridang et al.[47] reported the treatment of seafood processing wastewater using a submerged MBR. Influent COD and BOD_5 values of the wastewater for the study were 943–1923 and 560–1127 mg/L. It was found that during 1000 h of filtration, the COD and BOD_5 removal values were 85% and 99%, respectively. Other than that, anaerobic MBRs are in use for the treatment of wastewater from field crop processing, the dairy industry, and the beverage industry.[48] It has been reported that a laboratory-scale anoxic/aerobic MBR is used for the simultaneous removal of C and N from food industry wastewater.[44] The maximum volumetric loading of COD and the total nitrogen (TN) were 3.4 kg COD/(m^3 d) and 1.26 kg N/(m^3 d), respectively. Removal percentages of COD, NH_4^+-N, and TN were reported as >94%, >91%, and >74%, respectively. A pilot and full-scale study has been reported for the treatment of food industry wastewater using a submerged vacuum ultrafiltration (UF) membrane technology combined with a biological treatment system. The capacity of the full scale is reported as 120,000 US gpd. BOD and COD removals of 95–96.5% and 96–99% were achieved, respectively. HRT is reported as 5–6 d.[46]

Membrane filtration is another treatment technology that is emerging in the field of food industry wastewater treatment. Nowadays, membrane separation technologies are been widely used in the field of water and wastewater treatment. A membrane essentially acts as a barrier to separate two phases, depending on the physico-chemical properties when a driving force, either a gradient of chemical potential or electrical potential, is applied across this filtration medium. Membrane processes contain four major categories for processing water and wastewater: microfiltration (MF), UF, nanofiltration (NF), and reverse osmosis (RO). Flux and rejection are two basic parameters for filtration processes. The major target is to improve the flux while maintaining the quality of treated water. Treated water is usually higher in quality compared to the other treatment systems. However, problems such as higher energy inputs and membrane fouling have to be considered when it comes to the actual operation.

Vourch et al.[49] studied the applicability of the RO process for the dairy industry wastewater. The treated wastewater total organic carbon (TOC) was <7 mg/L. It was found that in order to treat a flow of 100 m^3/d, 540 m^2 of the RO unit is required with 95% water recovery. Dead-end NF and RO were studied for the treatment of dairy wastewater.[50] Permeate COD, monovalent ion rejection, and multivalent ion rejection for the dead-end NF were reported as 173–1095 mg/L, 50–84%, and 92.4–99.9%, respectively. When it comes to the dead-end RO membranes, the values for permeate COD, monovalent ion removal, and multivalent ion removal were 45–120 mg/L, >93.8%, and 99.6%, respectively. Membrane filtration technology can be better utilized as a tertiary treatment technology and the resultant effluent quality will be high. There can be situations where the treated effluents can be reused (especially if RO is used for the treatment).

Electrocoagulation technology attracts the attention of food industry wastewater treatment. This technology can be considered as a combination of two concepts: electrolysis and chemical coagulation. In general, the anode and the cathode are charged with direct current while the electrolyte is the solution to be treated. For the purpose of electrocoagulation, the anode material is either aluminum or iron. These materials will produce cations of aluminum and iron that are capable of acting as “coagulants.” Meanwhile, at the anode, oxygen production occurs. Moreover, at the cathode, fine bubbles of hydrogen are generated. These two agents help in the formation of “flocs.” At a later stage, flocs can be removed using techniques such as flotation, settling, or filtration.[51–53] Electrocoagulation technology has advantages such as simplicity in operation, good settling characteristics of the resulting flocs, *in situ* chemical production, and, if needed, the system itself can be used for flotation of the flocs. Additional benefits such as disinfection can be achieved as well. Anode replacement, use of electricity, passivation of the cathode, and need for enough conductivity in wastewater are the disadvantages of electrocoagulation.[54]

Roa-Morales et al.[51] used electrocoagulation technology using aluminum electrodes to treat wastewater from a pasta and cookie processing industry. Further, it has been found that the addition of small a amount of hydrogen peroxide will enhance performances. Removal percentages of COD, BOD_5, total solids, and fecal coliforms were reported as 90%, 96%, 95%, and 99.9%, respectively. In another study for the electrocoagulation technology for the treatment of agro-industrial wastewater (meat processing, cereal processing, food beverage, and abattoir wastewater), the total cost of treatment was 0.95–4.93 USD/m^3.[55] Electrocoagulation has also been reported for the treatment of poultry slaughterhouse wastewater.[56] COD removal efficiency can be as high as 93% with aluminum electrodes while 98% of oil–grease removal can be achieved using iron electrodes. Furthermore, a combination of aluminum and iron materials can produce higher performances for removing both COD and O&G. Kobya and Delipinar[57] studied the treatment of baker’s yeast wastewater by electrocoagulation in a batch reactor. The maximum removal efficiencies of COD, TOC, and turbidity were found to be 71%, 53%, and 90% for aluminum and 69%, 52%, and 56% for iron electrodes; the operating costs for each were 1.54 and 0.51 USD/m^3 of COD, respectively. Use of electrocoagulation technology for the treatment of dairy wastewater was reported by Sengil and Ozacar.[58] COD, O&G, and conductivity of the wastewater were reported as 18,300 mg COD/L, 4570 mg O&G/L, and 1200 μS/cm, respectively. In order to treat the above-mentioned wastewater, an iron anode was used. The overall removals of COD and O&G were as high as 98% and 99%, respectively. Optimum current density was 0.6 mA/cm^2 while the optimum electrolysis time was 1 min. These two optimum parameters resulted in a mean energy consumption of 0.003 kWh/kg of COD. Electrode consumption during the process was 0.0204 g electrode/kg of COD removal.

30.7 SUMMARY

1. The food industry is one of the essential industries and almost all the processes produce wastewater that contains relatively higher amounts of organics.
2. Pretreatment is necessary for the treatment of the food industry wastewater. Pretreatment options such as flow equalization and neutralization, screening, FOG separation, acidification, coagulation–flocculation, sedimentation, and DAF are available. Selecting the appropriate technology depends on the wastewater characteristics.
3. Due to the higher amounts of organic pollutants in the food industry wastewater, conventional biological treatment systems can be used.
4. Anaerobic treatment systems such as AFs, UASBs, and AFBRs are available for the treatment. Factors such as the organic strength of the target wastewater stream, footprint, and cost of operation are important when it comes to the selection of suitable technology.
5. Aerobic treatment systems can be used for the food industry wastewater treatment as well. However, if the organic strength is very high, the use of aerobic systems may not be effective. A combination of anaerobic/aerobic treatment may be necessary.
6. Apart from the conventional technologies, there are several emerging technologies for the food industry wastewater treatment.
7. MBRs and membrane filtration provide great alternatives for wastewater treatment and reuse of water.
8. Electrocoagulation is one of the emerging technologies for the food industry wastewater treatment. If the wastewater contains higher concentrations of O&G and SS, this technology outperforms various conventional technologies. Disinfection can be an added advantage in the system.

NOMENCLATURE

AF	Anaerobic filter
AFBR	Anaerobic fluidized bed reactor
BOD	Biological oxygen demand
BOD_5	5-day biological oxygen demand (mg/L)
COD	Chemical oxygen demand (mg/L)
CSTR	Continuous stirred tank reactor
DAF	Dissolved air flotation
DO	Dissolved oxygen (mg/L)
EPA	Environmental Protection Agency
F/M	Food to microorganism ratio [kg-BOD_5/(kg-biomass·d)]
FOG	Fats, oils, and greases
HRT	Hydraulic retention time (d)
MBR	Membrane bioreactor
MF	Microfiltration
MLVSS	Mixed liquor volatile suspended solids (mg/L)
NAICS	North American Industry Classification System

NF	Nanofiltration
OG	Oils and greases
PFR	Plug-flow reactor
RBC	Rotating biological contactor
RO	Reverse osmosis
SBR	Sequencing batch reactor
SCADA	Supervisory control and data acquisition system
SRT	Sludge retention time (h)
SS	Suspended solids
TKN	Total kjeldahl nitrogen (mg/L)
TN	Total nitrogen
TOC	Total organic carbon
TRI	Toxic release inventory
TS	Total solids
TSS	Total suspended solids
UASB	Up-flow anaerobic sludge blanket
UF	Ultrafiltration
VLR	Volumetric loading rate
VSS	Volatile suspended solids (mg/L)

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31 Radon Mitigation in Buildings

Nazih K. Shammas and Lawrence K. Wang

CONTENTS

31.1 INTRODUCTION

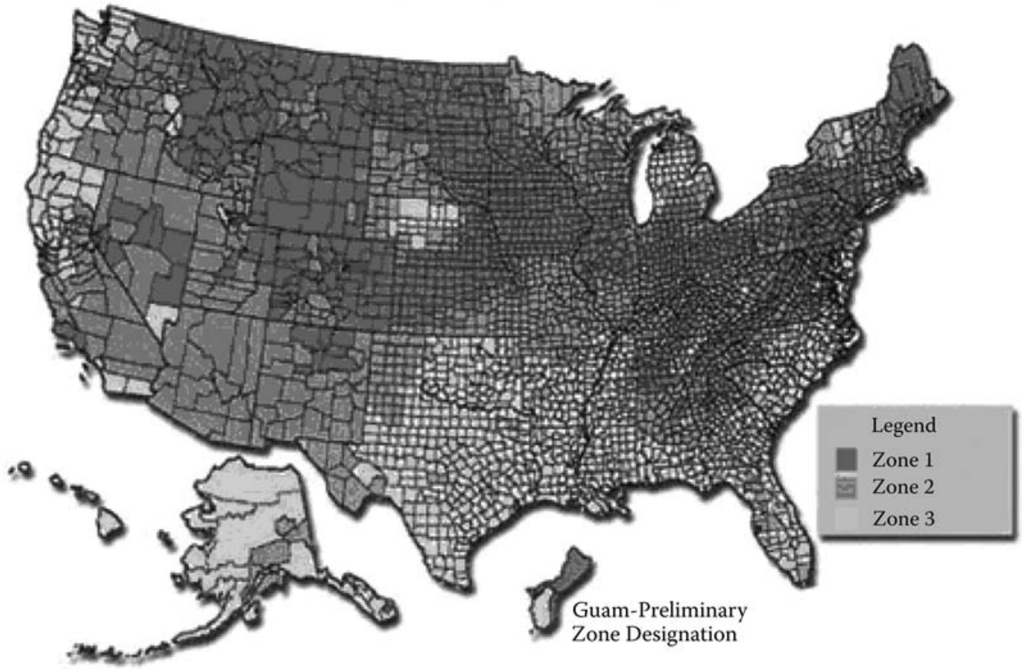
Radon is a naturally occurring, chemically inert, radioactive gas. It is colorless, odorless, and tasteless. It is part of the uranium-238 decay series, the direct decay product of radium-226. Radon moves to the earth's surface through tiny openings and cracks in soil and rocks. High concentrations of radon can be found in soils derived from uranium-bearing rocks, such as pitchblende and some phosphates, granites, shales, and limestones. It may be found also in soils contaminated with certain types of industrial wastes, such as the by-products of uranium or phosphate mining, or from industries using uranium or radium.

In outdoor air, radon is diluted to such low concentrations that it is usually nothing to worry about. However, radon can accumulate inside an enclosed space, such as a home, posing a threat to people. The extents of radon in the United States, Massachusetts State and New York State are shown in Maps 31.1 through 31.3 where[1]:

- *Zone 1:* Counties that have a predicted average indoor radon screening level greater than 4 pCi/L (picocuries per liter)—the highest potential.
- *Zone 2:* Counties that have a predicted average indoor radon screening level between 2 and 4 pCi/L—moderate potential.
- *Zone 3:* Counties that have a predicted average indoor radon screening level less than 2 pCi/L—low potential.

The known health effect associated with exposure to elevated levels of radon above the action or guidance level is an increased risk of developing lung cancer. The guideline levels for radon in existing homes are as follows:

- U.S. EPA (U.S. Environmental Protection Agency)[2] 4.0 pCi/L
- Canada[3] 21.6 pCi/L
- Sweden[4] 10.8 pCi/L
- ICRP (International Commission on Radiation Protection)[4] 16.2 pCi/L
- WHO (World Health Organization)[5] 10.8 pCi/L
- NCRP (National Council on Radiation Protection)[4] 8.0 pCi/L



MAP 31.1 United States map of radon zones. (Adapted from U.S. EPA, *EPA Map of Radon Zones*, EPA-402-F-93-013, U.S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/radon/zonemap.html, February 2009.)

MAP 31.2 Massachusetts state map of radon zones. (Adapted from U.S. EPA, *EPA Map of Radon Zones*, EPA-402-F-93-013, U.S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/radon/zonemap.html, February 2009.)

Scientists estimate that about 20,000 lung cancer deaths a year in the United States may be attributed to radon.[6] In general, the risk of developing lung cancer increases as the level of radon and the length of exposure increase. Radon can seep into the home in numerous ways—through dirt floors, cracks in concrete floors and walls, floor drains, sumps, joints, and tiny cracks or pores in some hollow-block walls. This seepage of gases into the house most often occurs when air pressure inside the house is lower than air pressure outside, or underneath, the house. In this case, cracks or other openings in the house allow radon-laden gas to be pulled inside.

Since radon is a colorless, odorless, and tasteless gas, the only way to detect its presence is to sample and analyze an area's air using a conventional radon measurement test. If the test reveals elevated radon levels, the homeowner will have to decide what steps to take to reduce the levels.[7] The higher the level of radon present in a home, the more likely an active radon reduction system such as subslab depressurization (SSD)[8] may be required. Lower radon levels may require only a passive reduction system, such as simple sealing.

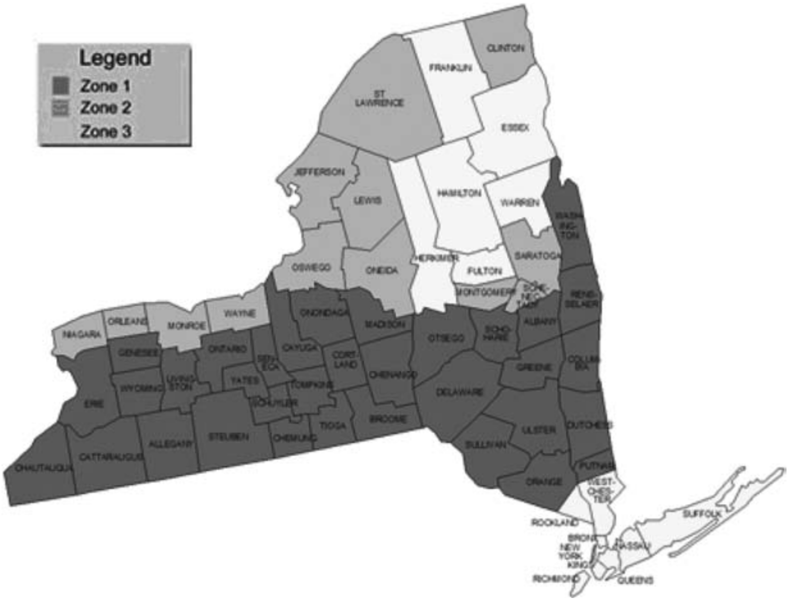
Growing concern about the risks posed by indoor radon has underscored the need for dependable radon-resistant residential construction techniques. In response to this public health exposure, the U.S. EPA has developed and demonstrated a variety of methods that have been used to reduce radon levels in existing homes.[2,8] Many of these methods could be applied during construction, involve less labor and financial investments, and provide greater homeowner satisfaction and safety than would a radon-reduction technique installed after the home is built and occupied.

This chapter is designed to provide homeowners and builders with an understanding of operating principles and installation details of the construction of a new radon-resistant home. This chapter should provide a basic understanding of the types of products and systems that are available and being used. In this way, the reader will be able to select the radon-resistant products and systems that will be best applicable to a particular situation.

31.2 SOURCE OF RADON AND ITS CONTROL

31.2.1 SOURCE OF RADON

Radon gas is the result of the radioactive decay of radium-226, an element that can be found in varying concentrations throughout many soils and bedrock. Figure 31.1 shows the series of elements that begins with uranium-238, and, after undergoing a series of radioactive decays, leads eventually to lead-210. At the time radium decays to become radon gas, energy is released.[9] Of all the elements



MAP 31.3 New York state map of radon zones. (Adapted from U.S. EPA, *EPA Map of Radon Zones*, EPA-402-F-93-013, U.S. Environmental Protection Agency, Washington, DC. Available at http://www.epa.gov/radon/zonemap.html, February 2009.)

and isotopes illustrated in Figure 31.1, radon is the only one that behaves like a gas and can easily slip through the small spaces between bits of soil. While many of the isotopes in the uranium-238 decay series exist for a long time before they decay, radon does not remain radon for very long. It has a half-life of 3.8 days. If 1 lb of radon were put in a jar, 3.8 days later, only 1/2 lb of radon would be left; the other 1/2 lb would have decayed into short-lived decay products, namely, polonium,

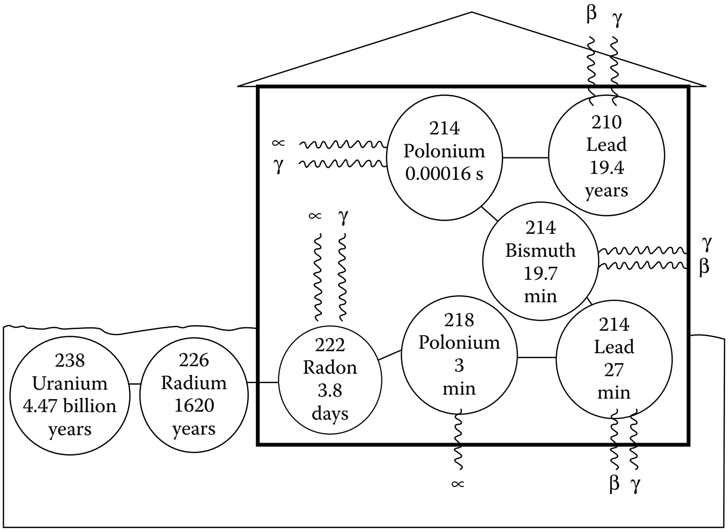


FIGURE 31.1 Radon decay showing half-lives of products. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

bismuth, and lead. After another 3.8 days, only 1/4 lb of radon would be left in the jar. The radon decay products shown inside the building have even shorter half-lives than radon, and decay within a few hours to the relatively stable isotope lead-210. It is this rapid release of energy that causes radon and radon decay products to pose such a significant health risk.

If radon and radon decay products are present in the air, they will be inhaled. Because the decay products are not gases, they will stick to lung tissue or larger airborne particles that later lodge in the lung. The energy given off as these isotopes decay can strike the cells in the lung, damage tissue, and may eventually develop into lung cancer. The amount of risk depends on how long a person is exposed to how high a concentration of radon and radon decay products. Estimates of the number of lung cancer deaths in the United States attributable to radon and radon decay products range from 5000 to 20,000 deaths per year.[9] In all, 1.2 million new homes have been built with radon-resistant features since 1990. U.S. EPA continues to focus its risk reduction on mitigating existing homes and building new radon-resistant homes. As a result of these actions through 2003, U.S. EPA estimates that as many as 650 future lung cancer deaths are prevented (lives saved) each year.[10]

31.2.2 RADON ENTRY INTO BUILDINGS

A house will contain radon if the following four conditions exist:

1. A source of radium exists to produce radon.
2. A pathway exists from the radium to the building.
3. A driving force exists to move the radon to the building.
4. An opening in the house exists to permit radon to enter.

If one of these conditions does not exist, then the building will not have a radon problem. An estimated 10–20% of the existing homes in the United States have annual average radon concentrations above 4 pCi/L. This may seem like a small percentage of problem homes until one considers that, of the million or so U.S. houses built each year, 100,000–200,000 homes will likely have radon concentrations higher than 4 pCi/L. Similar radon problems do exist in commercial and industrial buildings with basements.

The most common way radon enters a building is when lower indoor air pressure draws air from the soil, bedrock, or drainage system into the house. If there is radon in the soil gas, it will also be drawn in. Just as gravity will make water flow from a high elevation to a lower elevation, pressure differences will make radon-laden air move from an area of higher pressure to an area of lower pressure. For a variety of reasons, most buildings tend to maintain an indoor air pressure lower than outdoor air pressure. If cracks and holes in the foundation are open to the soil, radon will be drawn indoors. Radon movement by pressure differences is called pressure-driven transport.

Radon can also enter buildings when there are no pressure differences. Place a drop of food coloring in a glass of water; eventually, the coloring will spread out (diffuse) and color the water—even without stirring. Radon will do the same thing—spread from an area of higher concentration to an area of lower concentration until the concentrations are equal. Radon movement in this way is called diffusion-driven transport.

A less common entry mechanism is the outgassing of radon from well water. A well supplied by groundwater that is in contact with a radium-bearing formation can transport the dissolved radon into the home. It is estimated that the health risks associated with breathing radon gas released from the water are 10 times higher than the risks associated with ingesting water containing radon.[9]

Radon can also emanate from the building materials themselves. The extent of the use of radium-contaminated building materials is unknown but is generally believed to be small.

Figure 31.2 illustrates the percentages of contribution by each type of radon entry made to a specific group of study houses in the Pacific NW.[11] Any one house can vary significantly from these figures. However, on a national basis, this is an indication of the relative importance of each of the contributors.

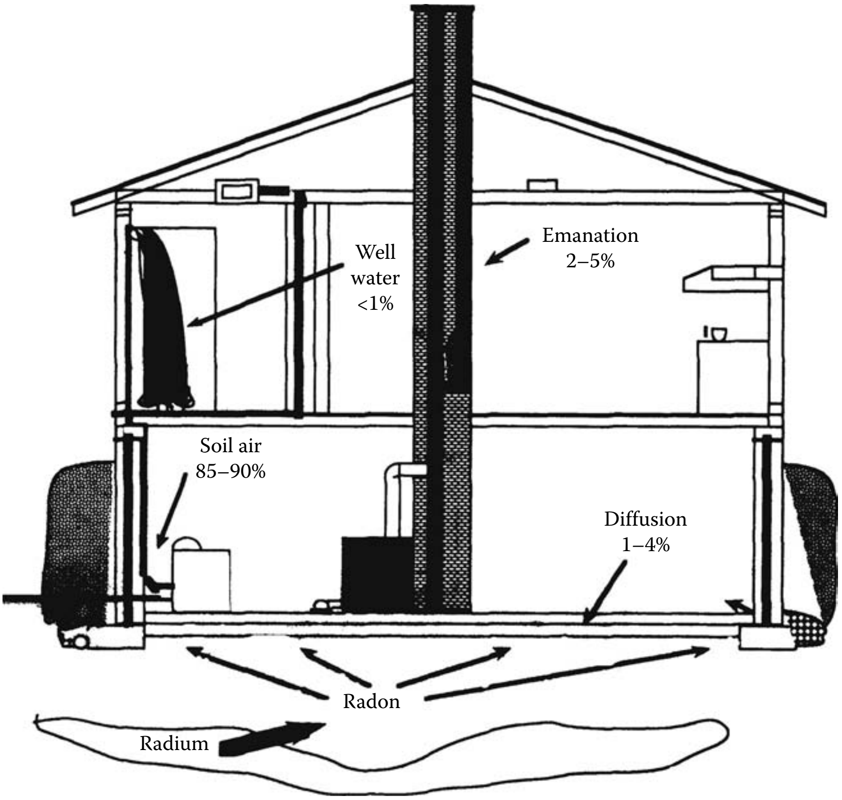


FIGURE 31.2 Percentage of radon contribution by source from 15 homes. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

Figures 31.3 through 31.5 illustrate typical radon entry routes found in basement, crawlspace, and slab-on-grade construction, respectively.

31.2.3 RADON CONTROL IN NEW CONSTRUCTION

Like most other indoor air contaminants, radon can be controlled by keeping it out of the house, or reducing the concentration by mixing it with fresh air after it has already entered. The following approaches have been tried or suggested[9]:

1. Prevent entry
   - Make provisions for an SSD or pressurization system during construction.
   - Install mechanical barriers to block soil gas entry.
   - Avoid risky sites.
2. Planned mechanical systems
   - Supply fresh air to reduce radon by dilution.
   - Control pressure relationships to reduce soil gas entry.

Figure 31.6 illustrates the following four major topics to be considered in this chapter:

1. Site evaluation
2. Mechanical barriers

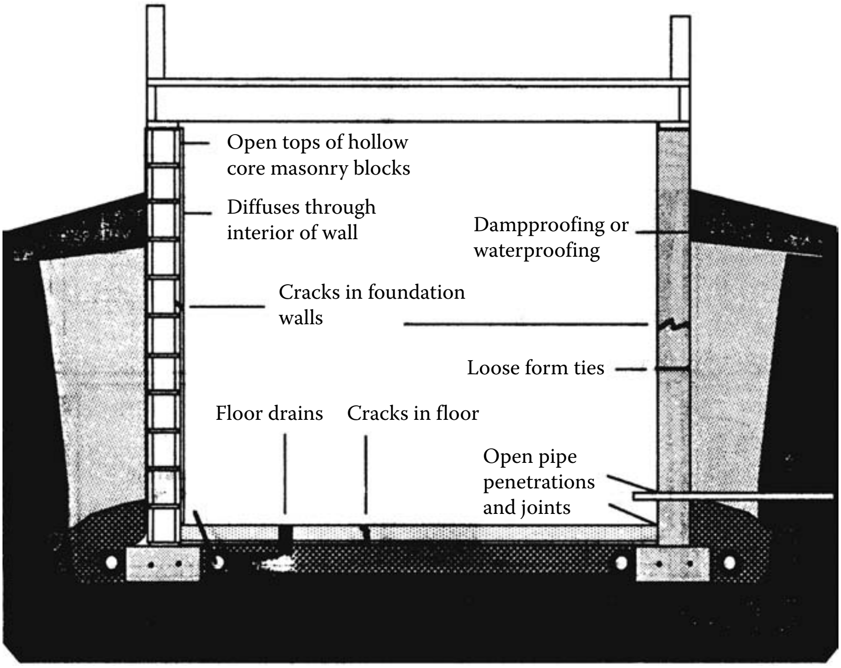


FIGURE 31.3 Typical radon entry routes in basement foundations. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

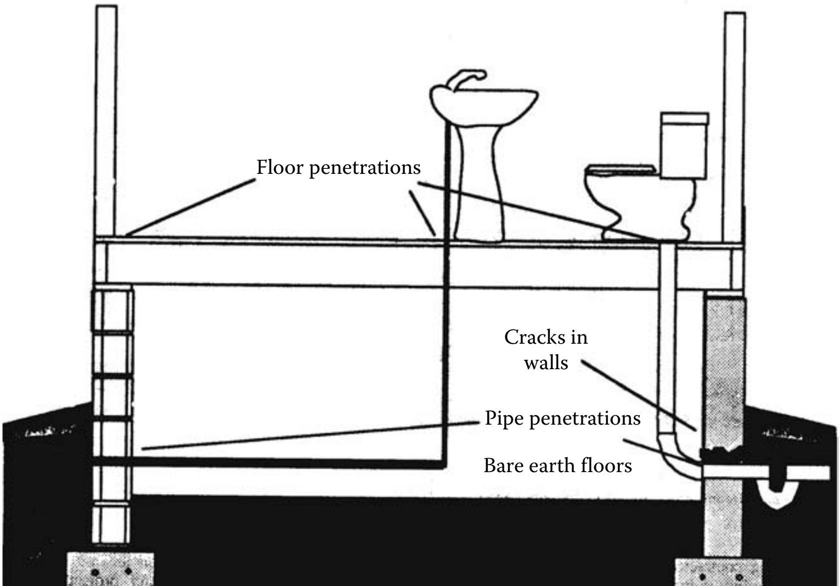


FIGURE 31.4 Typical crawlspace foundation entry route. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

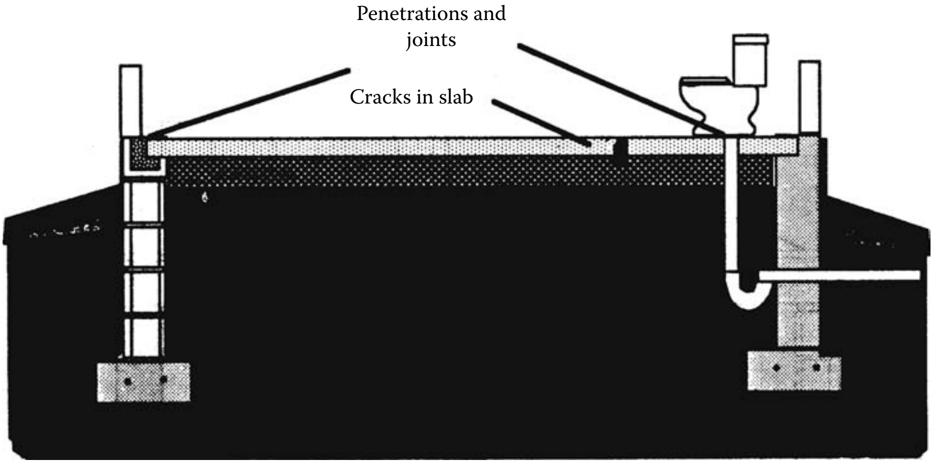


FIGURE 31.5 Typical radon entry routes in slab-on-grade construction. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

3. SSD
4. Planned mechanical systems.

31.2.3.1 SSD/Pressurization Systems

One of the most frequently used radon reduction techniques in existing homes is an SSD system. Typical installation costs for a system in existing homes currently range from USD1500 to USD2500.[9,12] If the same system is installed or at least planned for, and roughed in during construction, the cost is much lower; so a prudent builder who is erecting a radon-resistant home should include features that will allow for the easy installation of such a system.

Radon mitigation by SSD has been proven to be very effective, often decreasing indoor radon concentrations by 90% or more following mitigation.

The theory of operation for the SSD system is that by penetrating the concrete floor slab with an exhaust pipe one gains access to the area beneath the slab. The area, often a gravel bed, serves as a

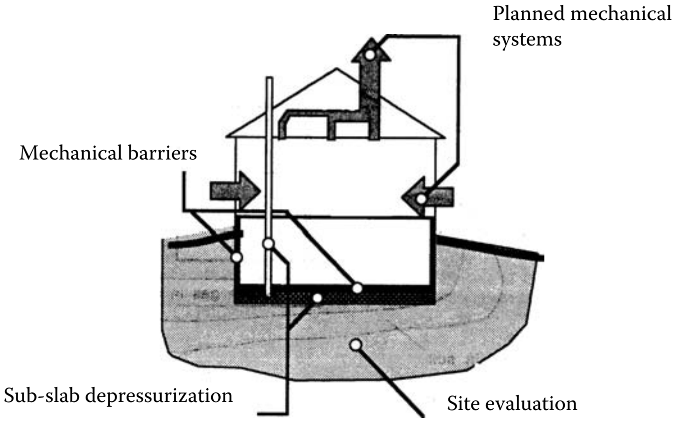


FIGURE 31.6 Major radon-resistant new construction topics. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

collection site for the soil gas-containing radon. The exhaust pipe is then routed to the outside of the building, typically through the roof. The negative pressure provided by the exhaust pipe reduces the convective flow of soil gas into the building and causes the soil gas to be removed from the subslab area. If communication exists between the subslab volume and the walls of the building, soil gas will simultaneously be exhausted from the walls. The exhaust mechanism can be passive, which implies that suction pressures beneath the slab will vary seasonally, with the greatest suction occurring during the coldest weather due to increased buoyancy of the air in the vertical exhaust stack (if it is routed through the inside of the building). Active systems, where exhaust fans are used, were shown to maintain near constant suction pressures under the slabs during the entire year.

The key point to remember, in the merits of year-round radon removal, is that there is no guarantee that radon problems will not be present even in the summer months. The radon levels found in individual houses are a complex result of radon source strength, soil transport, the number, size, and location of entry points, weather, and the way the house is operated.[2] To be certain of maintaining low radon levels in the house normally requires that an SSD mitigation system works properly 24 h per day, 365 days per year. It is for this reason that durability and system performance are very important considerations. The performance level goal for the system is 100% on-time operation for the life of the building. This requires excellent durability of system components and a reliable means for determining whether the system is fully operational at all times.

The question of durability of the mitigation system arises not only from the need for lifetime operation in the house, but also from concerns about the environment to which the SSD system is subjected.[13–15] Soil gas is often very humid, causing condensation problems in the piping and the fan of the mitigation system. Also, particles can be drawn from the gravel bed or soil; they in turn may line the pipes and deposit on the fan or possibly interfere with the fan bearings.

The moisture removal from the subslab can be very substantial, and could amount to many gallons of water per day.[13–15] Unless the piping design allows for that water to drain back into the soil, the water could block flow of air in the piping or interfere with the fan operation. Evidence of moisture and other debris has also been found in the staining of roofs near the exhaust pipes of the SSD systems.

The amount of sand and other particles sucked from the soil must be viewed as a possible cause for bearing failure or for the generation of bearing noise (such effects can also be caused by the moisture). Noise can directly influence the occupant to shut down the SSD system. Sandblasting of the fan blades or plateout on the fan blades by particles sucked into the mitigation system could lead to degradation of fan performance over the long term.

Another environmental effect that should not be overlooked is the amount of airflow through the fan. To remain at an appropriate operating temperature the fan requires sufficient airflow to remove fan motor heat. Fan motor capacitor failure will cause the motor to operate at a lower speed and efficiency, especially after the motor has been shut off by the occupant or electrical power interruption. Operating the fan in either of these modes will lead to higher radon levels in the living space and invites early fan failure.

For a simple view of the SSD system and its operating principle, refer to Figures 31.7 through 31.9.

A subslab pressurization system creates a high-pressure zone beneath the slab. Although this does not reverse the direction of the airflow (the air from the system will still flow into the home through cracks and holes), it does dilute the radon concentrations beneath the slab and may keep the radon that is being produced in the site from reaching the foundation. In a number of existing houses, it has been found that this technique performed better than SSD. In buildings where pressurization works best, there are a few common factors. One is the presence of soil or bedrock that allows air to move very easily through it—so easily, in fact, that it is difficult to establish a low-pressure field by exhausting 100 cfm or so of air from beneath the slab. It is this feature that limits the performance of soil depressurization systems. The other factors that seem important are a relatively low concentration of radon in the soil gas and a remote location for the source radium, with radon transported some distance from the house through the very permeable soil. It is thought that a positive pressure created by blowing low-radon-concentration air under the slab dilutes the

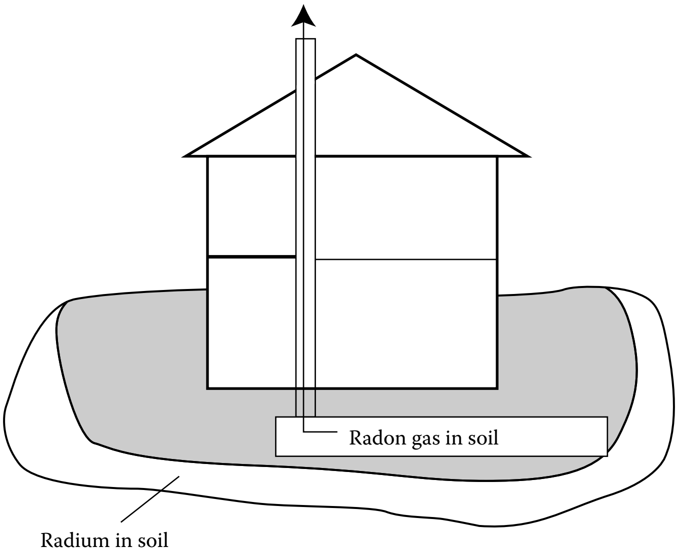


FIGURE 31.7 SSD theory. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

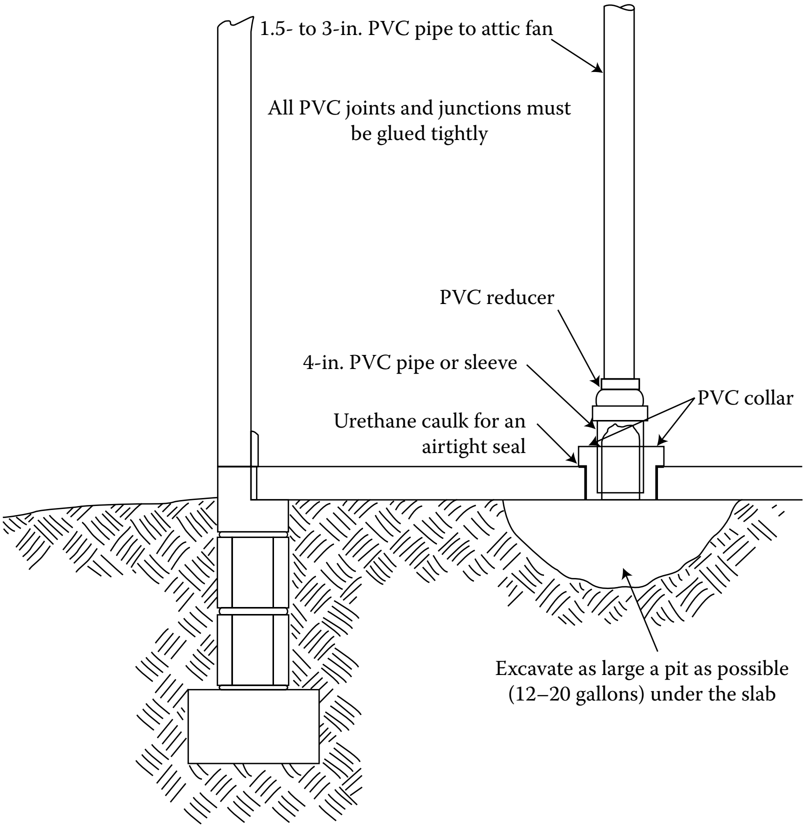


FIGURE 31.8 Typical interior suction point. (Adapted from U.S. EPA, *Sub-Slab Depressurization for Low-Permeability Fill Material—Design and Installation of a Home Radon Reduction System*, EPA/625/6-91/029, U.S. Environmental Protection Agency, Washington, DC, July 1991.)

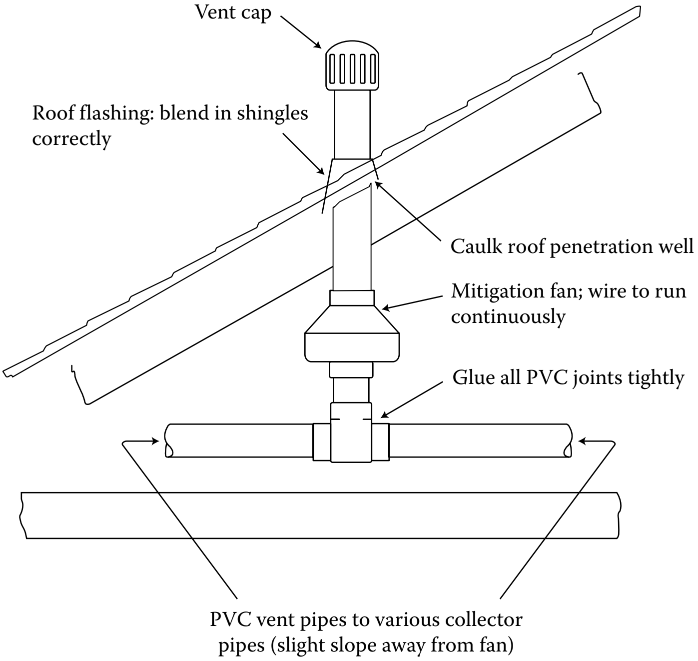


FIGURE 31.9 Schematic of the fan placement and roof penetration of a typical installation. (Adapted from U.S. EPA, *Sub-Slab Depressurization for Low-Permeability Fill Material—Design and Installation of a Home Radon Reduction System*, EPA/625/6-91/029, U.S. Environmental Protection Agency, Washington, DC, July 1991.)

soil gas near the foundation, and diverts soil gas originating farther away. Pressurization has been successfully used in buildings built in coarse gravel, shattered shales, and limestones. This technique has been used in existing homes to reduce radon concentrations; however, there has been no major research effort to verify the actual effectiveness of pressurization. Other factors to consider when installing a pressurization system are the effect the introduction of, in some climates, below-freezing or high-humidity air will have on the concrete floor slab and the effort that must be made to ensure that the air intake does not become blocked by foreign matter.

31.2.3.2 Mechanical Barriers

Knowing that the greatest contributor to indoor radon concentrations is the air from the soil entering the building through the foundation, it was thought that a good place to begin building a radon-resistant home is to make the foundation as radon resistant as possible. Figure 31.10 illustrates the principle of a radon barrier. Many materials (concrete, polymeric coatings, and plastic films) are outstanding air barriers and retard the transfer of radon gas by a large factor. In practice, the difficulties that arise when using barrier techniques are numerous. Failure to seal a single opening may negate the entire effort. Barriers may degrade with time or may be damaged during installation. The use of barrier techniques as a stand-alone system is not recommended, but it is recommended that some amount of effort be made to limit the entry of radon through the foundation. This can be done by using[9]

1. Foundation materials themselves, sealing cracks, joints, and penetrations.
2. Foundation coatings, normally used for dampproofing.
3. Membranes surrounding the foundation.

It should be pointed out that attempts to control radon by making a gastight barrier around the foundation have not been completely effective. It is likely that they have done some good, but many

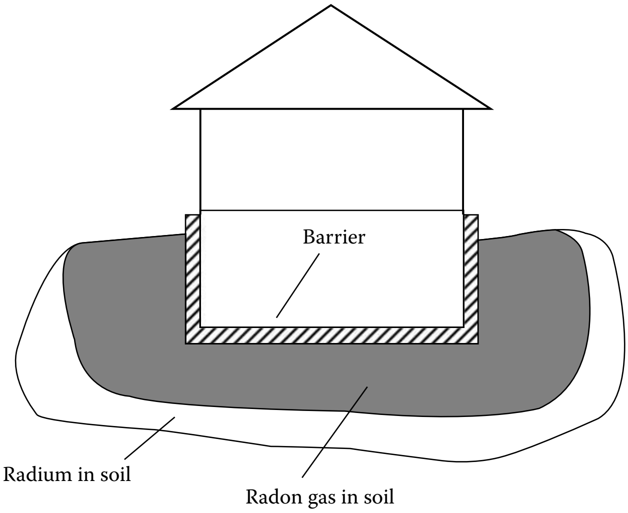


FIGURE 31.10 Radon-resistant barrier theory. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

newly constructed buildings that relied on barriers as the only radon reduction technique have elevated levels of indoor radon. It is not known, however, what the indoor radon concentrations would have been if the barriers had not been installed.

31.2.3.3 The Site

The question most often asked by homebuilders is: Can one determine whether radon-resistant construction techniques should be applied to a given site?

A simple test that could identify problem sites would be very helpful. At present, there are no simple, reliable methods for performing this. In the absence of a simple site screening test, guidance can be sought in the growing body of information developed at regional, state, and local levels. Many researchers, public agencies, and private homeowners are making soil, bedrock, and indoor radon measurements. From these data, a picture of the extent of the problem is emerging. Although it is not yet possible to be certain about a given site, some idea of where the problem areas are has been developed. At a recent meeting of several leading mitigation contractors, the general consensus was to install radon-resistant techniques rather than spend extra time and money performing the number of preconstruction tests it would take to confidently evaluate the site. However, a group of testing contractors may decide just the opposite. Although no definitive methods for predicting possible indoor radon concentrations based on preconstriction soil measurements exist, it is clear that a building being erected on a site that is known to contain high concentrations of radon should have radon-resistant construction techniques applied.[16] Another concern when evaluating the site potential for supplying radon to the soon-to-be-constructed home is the permeability of the soil. A highly permeable soil allows easy movement of soil gases; therefore, radon can move a greater distance from the source to the building than in a tighter, less permeable soil. This can also allow soil gases that contain lower concentrations of radon to enter the home in greater quantities, which can produce elevated indoor concentrations. The Swedish Authorities suggest that a building site with soil radon concentrations greater than 1350 pCi/L or with a highly permeable soil should use radon-resistant construction techniques.[17]

U.S. EPA does not recommend the avoidance of building sites that are suspected to contain strong radon; it does, however, strongly recommend that the homes built on those sites be designed and built with radon-resistant construction techniques.[9]

Water from wells has been found to be a major source of radon in some homes in the United States. Radon will outgas from the rocks into the groundwater. When the water is exposed to the atmosphere, some of the radon is released.

Builders should be aware that wells can be a potential problem. The only way to ensure that a well is not a potential radon source is to have the water tested after the well is drilled. It is not adequate to make a decision based on tests made in wells in the same area or even on adjoining building sites. A recent research project disclosed two homes with water radon concentrations of over 400,000 pCi/L, while the well used at a house between the two had waterborne radon concentrations of less than 1000 pCi/L.[18] It should be understood that, when considering waterborne radon, the concentrations that concern us are much higher than when we are considering radon in the air. As a rule of thumb, between 8000 and 10,000 pCi/L of radon in the water will contribute 1 pCi/L of radon to the air.

If radon is present in water, the current state of technology offers two possible solutions. Water that is aerated will release the radon it carries. Several manufacturers have systems designed to aerate the water and vent the redone outdoors. An alternative system filters the water through granular activated carbon, which removes the radon from the water. There are several manufacturers of granular activated carbon water filters. It should be noted here that at high radon levels (>5000 pCi/L) the buildup of radon decay products in the charcoal can produce a significant level of gamma radiation. Although this can be alleviated by proper shielding, disposal of the charcoal filter media can be a problem.

A site suspected to contain a waterborne source of radon should not be avoided solely on the basis of the existence of radon. Methods can be utilized to alleviate any problem that may arise from waterborne radon.

31.2.3.4 Planned Mechanical Systems

The entry of soil gas into buildings is the result of a complex interaction between the building shell, the mechanical system, and the climate. Important climatic variables are the wind velocity, indoor/outdoor temperature differences, rainfall, and atmospheric pressure changes. Indoor radon concentrations can be reduced by planning the mechanical system so that fresh air dilutes the radon that has entered the building, and by controlling interior air pressures to reduce soil gas entry. This approach requires a great deal of insight into the dynamics of building operation for a given climate. If this method is considered, the following guidance can be used:

1. Be sure that combustion appliance performance is not impacted.
2. Supply fresh air in accordance with ASHRAE requirements.

Consult American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE)[19] ventilation requirements and the National Fire Protection Association (NFPA).[20] As a system is designed, consider the use of

1. Power-vented combustion devices or combustion devices that use outside air.
2. Fresh air supply ventilation systems (heat recovery or nonheat recovery).

31.2.4 RECOMMENDATIONS

The following sections contain recommended radon-resistant construction techniques that a builder may wish to incorporate into the home. It should be understood that these are recommendations only and should not be construed as guidelines or regulations. The recommendations are based on the best available information gathered from numerous research projects.[9]

31.2.4.1 SSD Systems

To facilitate the use of soil depressurization, it is suggested that a permeable layer of material be placed beneath the slab, all major foundation penetrations be sealed, and a passive stack be run from the permeable layer up through the roof like a plumbing vent. Appropriate materials for the permeable layer are 3/8–1-1/2 in. diameter stone pebbles or manufactured drainage products (perforated plastic pipe or drain boards). A passive stack is much easier to add while building the house, and is easily power vented later if required. There is evidence that, while not foolproof, a properly designed passive venting system can sometimes have some impact on indoor radon levels.

31.2.4.2 Mechanical Barriers

Below-grade walls may be constructed of poured concrete, masonry blocks, or other materials such as all-weather wood or stone. This chapter discusses details for use of poured concrete and masonry foundation because these are the materials most commonly used for new construction. Recently, trade associations such as American Plywood Association (APA) and the National Forest Products Association (NFoPA) have issued publications on designing radon resistance permanent wood foundations. Information on these types of foundations can be found by contacting the appropriate trade association.[21]

The following is a list of recommendations that builders can use to utilize the foundation as a mechanical barrier to radon entry. Foundation walls and floor slabs are often constructed of poured concrete. Plastic shrinkage, and therefore cracking, is a natural function of the drying process of concrete. Many factors, such as the water/cement/aggregate ratio, humidity, and temperature, influence the amount of cracking that occurs in a poured concrete foundation. Cracking may be minimized by

1. Proper preparation, mixture, and curing of concrete.[22,23]
2. Ferrous reinforcing (rebar rods and woven wire meshes).
3. Use of concrete additives to change the characteristics of concrete.
4. Water-reducing plasticizers, fiber-reinforced cements.[24]

To help prevent cracking in masonry walls or minimize the effects of cracks that develop,

1. Use correct thickness of unit for depth of soil.[25]
2. Use ferrous reinforcing (corners, joints, and top course).[26]
3. Coat the interior and exterior of the wall with dampproofing.

Cracks and joints in concrete and concrete blocks can be sealed using caulks. Polyurethane caulks have many of the properties required for durable closure of cracks in concrete. These features are

1. Durability
2. Abrasion resistance
3. Flexibility
4. Adhesion
5. Simple surface preparation
6. Acceptable health and safety impacts.

Typical points that should be sealed with caulks are

1. Plumbing penetrations (soil pipes and water lines as minimum).
2. Perimeter slab/wall crack and expansion joints (tool crack or use “zip”-off expansion joint material.

The open tops of concrete block walls are openings that should be sealed. This can be carried out by installing a row of solid blocks, lintel blocks, or termite cap blocks at the top of the wall.

Drainage details that leave openings through the foundation should be avoided or modified. Sump holes and French drains are widely used examples of this type of detailing. It is best to avoid them if possible, by using alternate drainage systems. When these design details are unavoidable, a little thought can allow the use of these details and still keep radon from entering the home. In many areas of the country, some type of dampproofing or waterproofing treatment is required by codes.

The application of dampproofing and waterproofing materials on the exterior, interior, or both sides of the foundation that can serve as a radon-resistant barrier is recommended to help control radon entry. It must be understood that a coating applied to a foundation intended to resist the flow of radon into the building is in addition to the normal waterproofing/dampproofing requirements.

Coatings are applied to the outside or inside of the foundation, creating a radon-resistant barrier between the source and the inside of the home. They come in a wide variety of materials including paint-like products that can be brushed on the interior of the foundation, tar-like materials that are applied to the outside, and cementitious materials that can be brushed or troweled on. They cannot be applied to the underside of the concrete floor slab for obvious reasons, so they must be applied to the inside surface of the slab. The effective life of an interior coating can be greatly diminished by damage; therefore, care must be taken to provide protection to the material used.

Membrane banners are applied to the exterior of the foundation and also beneath the floor slab during construction. Materials used for the membrane barriers range from coextruded poly olefin to polyvinyl chloride to foil sheets with many other materials in between. All membrane barriers must have the edges sealed to prevent radon from migrating around the edges and back into the building.

It is recommended that, as a minimum, a membrane be placed beneath the slab, and all foundation penetrations to the soil be scaled or otherwise dealt with in a manner that will prevent the entry of radon into the home.

31.3 SOIL DEPRESSURIZATION

The next four sections contain details for a deeper understanding of radon-resistant construction issues. The four major topics are

1. SSD
2. Mechanical barriers
3. Site evaluation
4. Planned mechanical systems.

In theory, the application of radon barriers should be adequate to avoid elevated radon levels in houses. In practice, however, a backup radon mitigation system has been found essential for maintaining indoor radon concentrations below 4 pCi/L in most homes studied. In the recent radon-resistant residential construction projects conducted by U.S. EPA and/or private builders, several of the homes designed to be radon resistant have contained radon concentrations above 4 pCi/L. In each of those houses, a backup system consisting of an active (fan-assisted), or passive (wind-and-stack-effect-assisted), SSD system was installed at the time of construction. When mechanical barriers failed to adequately control radon, the soil depressurization methods were made operational.

31.3.1 SSD OVERVIEW

Of the study homes mentioned in the previous section, some passive systems seemed sufficient to lower the radon concentrations, while in all cases, active systems resulted in significantly lower concentrations. Table 31.1 summarizes the findings of these particular projects.[9]

The most common way radon enters a home is when air pressure differences move soil gases containing radon through the spaces between soil particles to the foundation of the home. Just as gravity will make water flow from a higher area to a lower area, pressure differences will make

TABLE 31.1
Summary of Radon Concentrations in U.S. EPA New Construction Projects

Project	No. of Houses	Barrier Only pCi/L	Soil Depressurization Passive pCi/L	Soil Depressurization Active pCi/L
EPA-VA1	10	14.5	6.0	<1
EPA-NY1	15	15.8	13.9	2.8
EPA-VA2	2	1.3	<1	<1
EPA-PA1	1	13.4	7.0	1.1

Source: Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.

radon-laden soil gases move from an area of higher pressure to an area of lower pressure. Most buildings tend to maintain themselves at an air pressure lower than the surrounding soil. This characteristic is due to weather-driven parameters such as indoor/outdoor temperature differences and wind. The use of exhaust fans and combustion devices in a home will also create a negative pressure in the home. If cracks and holes in the foundation are open to the surrounding soil, radon will be drawn into the building. Figure 31.11 illustrates the principle of pressure-transported radon and also shows some of the things that produce the differences in pressure.

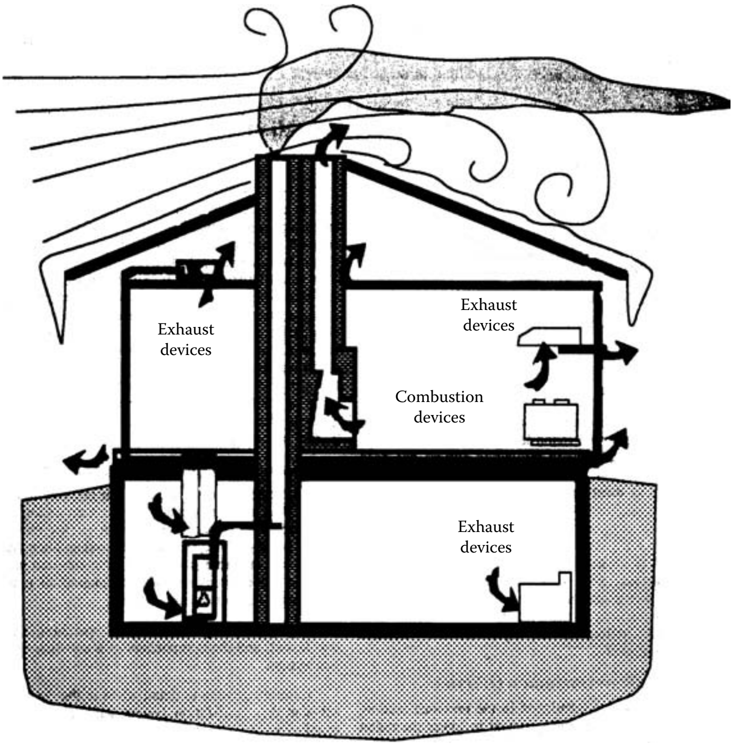


FIGURE 31.11 Negative pressure sources in a typical building. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

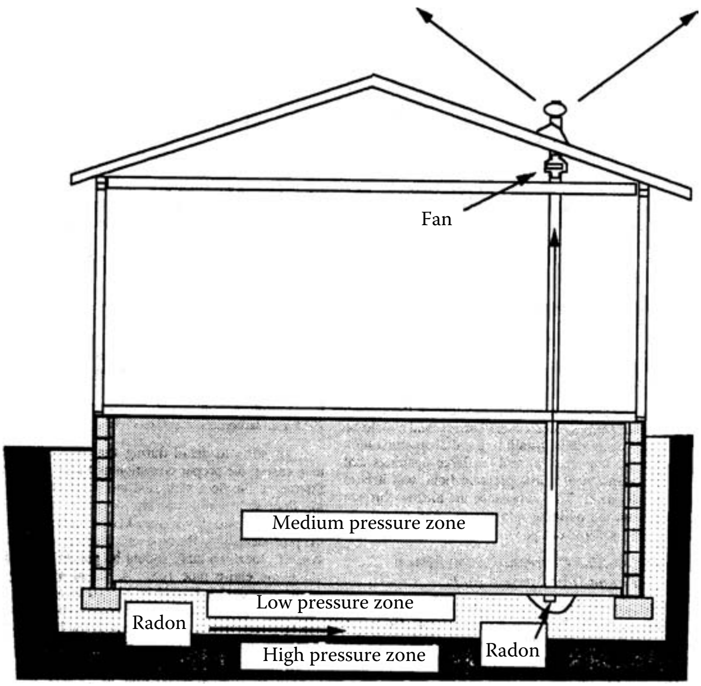


FIGURE 31.12 Theory of operation of a SSD system. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

31.3.2 SSD SYSTEMS

As previously mentioned, the air pressure in most homes is less than the air pressure in the surrounding soil. The difference in air pressure is what draws radon into the home. An SSD system alters the pressure beneath the concrete slab, making the subslab pressure less than the indoor pressure. It is the altered air pressures that keep radon from entering the home.

Figure 31.12 shows the theory of operation, a simple system layout, and the components of an SSD system.

Careful attention to details when in the design stage of an SSD system will help ensure the easy installation of a system if it is found to be required. The proper details are given in the following subsections, beginning at the subslab area and progressing upward to the exhaust.

31.3.2.1 Overall Design Considerations: Active and Passive Systems

When designing an active or passive system, many design considerations are common to the two systems. For example, some provision for removal of condensation that forms in the exhaust pipe will be required. Routing of the pipes from the basement to the roof must be considered when the house is being designed. Placement of the exhaust is extremely important.

Removal of condensation is an important consideration. Water collecting in an elbow or other low point of the system can effectively block the pipe, and reduce or disable the system. Builders should strive to design a pipe system that will allow condensation to run back through the pipe to the subslab aggregate. This can be accomplished by ensuring that the pipe run is vertical to the entire distance from the basement to the exhaust. A completely vertical pipe run with no bends or elbows will also provide a pipe system with lower static pressure losses that will enhance the effectiveness of both active and passive systems. If elbows or a low point is incorporated into the design, a condensate pump can be used to drain the water away. The use of condensate pumps will increase the cost of the system in both materials and labor; hence the ideal situation is to design a system that does not require pumps.

Pipe routing should be considered when the home is being designed. This will ensure that there is an area reserved for the exhaust pipe and preclude any possibility of having to build the system with numerous elbows and long horizontal pipe runs. Ideally, the pipes should be run through an interior wall of the home or up through closets.

The exhaust should be located above the highest ridge line. Some builders prefer to exhaust their systems out through an attached garage roof, rather than through the main roof. This type of design does require at least one short horizontal run, and will not seriously impact the effectiveness of an active system. When choosing the exhaust point, avoid the reentry of radon-laden soil gas into the home through open windows and doors. Do not exhaust the soil gas in an outdoor occupied area such as a porch or patio. Locating the exhaust close to a chimney that could back-draft and draw the exhausted soil gas back into the home should also be avoided. For a good discussion on the theory of exhaust design, see the ASHRAE Fundamentals Handbook.[19]

31.3.2.2 Subslab Preparation

Figure 31.12 illustrates that a low-pressure area being developed beneath the slab will draw the radon out of the soil, up the pipe, and exhaust the gas outdoors. If the subslab material consists of tightly packed soil or contains large rocks, the pressure field may not extend to all areas of the soil surrounding the foundation, and allow radon to enter the home where the pressure field does not exist. One way of ensuring the proper extension of the pressure field is to install media beneath the slab prior to the pour that will allow the easy movement of the air, thus helping to extend the pressure field.

In areas where it is available, crushed gravel is an inexpensive material to use. Subslab gravel provides a drainage bed for moisture and a stable, level surface for pouring the slab. The material preferred for radon reduction is crushed aggregate with a minimum of 80% of the aggregate being at least 3/4 in. in diameter. This stone should have a free void space above 40%. One standard specification of this type of gravel is D.O.T.No.2 gravel. A minimum of 4 in. of aggregate should be placed under the entire slab. Care must be taken to avoid introducing fine dirt particles during and after placement of the aggregate.

In areas where gravel is not readily available, drainage mats designed for soil stabilization may be used. The use of these drainage mats may not be cost-effective in areas where gravel is available, but where gravel must be shipped in from long distances, drainage mats can be cost-effective.

Some builders prefer laying perforated PVC piping in the gravel before the slab is poured and connecting the perforated pipe to the exhaust pipe of the system. The use of perforated pipe may not be necessary in active systems but probably will assist a passive system. Membranes beneath the slab help us to keep a continuous radon barrier in the event of slab cracking.

The use of footing drains for water control can affect the distribution of the pressure field. Interior footing drains sometimes terminate in a sump hole. If this is the case and the sump hole is not sealed airtight, the possibility exists for air to be drawn into the sump by the subslab system and weaken the pressure field. Make sure that all sumps are sealed air tight. Sometimes interior footing drains extend out beneath the footing and run to daylight, as shown in the section on mechanical barriers. If this is the case, provision must be made to make the ends of the drain airtight while still allowing water to drain. Reverse-flow valves are ideal for this application.

To summarize, any opening or connection that allows the depressurization system to draw air from anywhere but beneath the slab is detrimental to its effectiveness and must be avoided.

31.3.2.3 Preparation of the Slab

A thorough discussion of slabs is included in the section on foundation materials as mechanical barriers and should be referred to. However, when installing a soil depressurization system, it is more important to seal the large openings that would defeat extension of a low-pressure field than it is to seal every small crack. This is because the airflow through small cracks from the building into the soil will effectively seal them against soil gas entry.

31.3.2.4 Active SSD System: Materials and Installation Details

As can be seen in Figure 31.13, active SSD systems consist chiefly of a pipe system and a fan. There are several other components that should be included in a good system, but are not necessary to make the system reduce radon concentrations.

Most builders use 4 in. schedule 20 PVC pipes. Other sizes can be used but 4-in. PVC is readily available and is commonly used by builders for other purposes. Fans made for use in subslab systems are available in a variety of sizes from many vendors. The fans normally used are rated in a range of 90–150 cfm at no static pressure. Manufacturers of fans used for radon reduction are fairly quick to improve their products on advice from the people who are using their products. When the radon industry first started, many of the fans leaked at seams and joints, and required disassembly of the fan to seal those openings. Most manufacturers now supply fans that do not leak, but builders should be aware that this problem did exist and may still exist in some fans.

Additional materials and components that are normally included in a system satisfy safety needs, system performance indications, and common sense. Service switches should be placed within view of the fan to ensure that the system will not be activated while maintenance is in progress. Systems should be clearly marked as a radon reduction device to ensure that future owners of the building do not remove or destroy the system. An operation manual describing the system and its purpose should be made available.

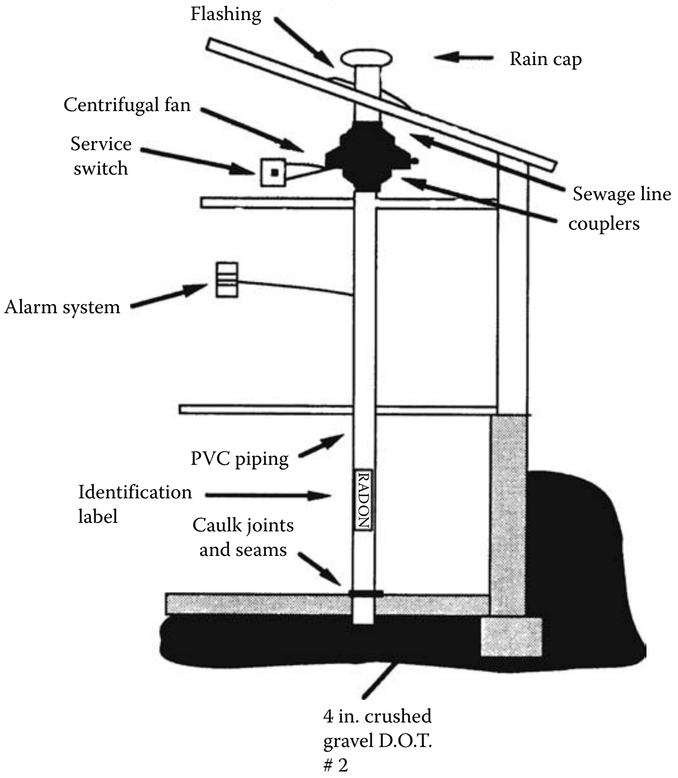


FIGURE 31.13 Typical SSD system. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

Some types of devices should be included in the system to advise the owners on system performance. These devices may be simple pressure gauges that tap into the pipe and measure and display the pressure in the exhaust pipe. A visual check of the gauge will alert the homeowner to possible system malfunctions. Electronic pressure-sensing devices that illuminate a warning light or sound an audible alarm when a pressure drop occurs are also used but they cost more than a simple gauge indicator. It is advisable to use a device that warns of a pressure change rather than something that warns that the fan is not running, because there are several things that can stop a system from operating effectively but that do not affect the fan.

Rain caps at the end of the pipe are intended to keep rain from entering the system. Builders use various cap designs for this purpose. The use of rain caps can cause a loss of airflow in a system, which may lessen the effectiveness of the system. It is advisable to use a rain cap that is designed in such a way as to not seriously impede airflow. For more information on rain caps and stack design, see the ASHRAE Fundamentals Handbook.[19]

Attention to detail during the installation process will help ensure the proper operation and long life of the system. Starting at the floor slab, seal the void between the pipe and the floor slab with a nonshrink grout or a flexible, highly adhesive sealant. Place a sticker or other labeling device on the pipe identifying the pipe as belonging to a radon reduction system. Ideally, a label should be placed at regular intervals along the entire pipe run. A visual system performance monitoring device should be placed in an area that is often visited and in plain view of the homeowner. Audible alarms can be placed in any area, as long as the homeowner can hear them. It is a good idea to place alarm sensors in easily accessible areas because they sometimes need adjusting. Run the pipe as straight as possible to the attic to ensure proper draining of condensation. The fan should always be located in a nonliving area as close to the exhaust as possible. This is extremely important because a leak in the fan or in the piping above the fan will blow the radon back out of the pipe. If the fan is placed in the basement, and a pipe leak occurs above the fan, radon-laden air will be introduced into the living area, and can cause radon levels to build to very high concentrations. Most builders connect the fans to the pipe system with rubber sewage pipe connectors. This allows for the easy removal and replacement of the fan if that should become necessary. Always install a service switch in sight of the fan. Run the pipe through the roof and flash well. If desired, cap the pipe with a rain cap.

31.3.2.5 Passive SSD System: Components and Installation Details

A passive system is much the same as an active system with the exception of the fan. A passive system relies only on stack and wind effects to produce the pressure field. As can be seen in Table 31.1, passive systems do not always reduce radon concentrations to acceptable levels, but careful design and installation may improve the effectiveness of a passive system.

It is probably beneficial to a passive system to lay a network of perforated drainage pipes in the gravel bed beneath the slab prior to the pour. The use of horizontal pipe runs and elbows in a passive system may greatly lessen the effectiveness the system and should be a voided. Some builders use a 6-in. PVC pipe in a passive system to help lessen the pressure drop.

31.3.3 Crawlspace Postconstruction Alternative

Due to difficulties often encountered in sealing subfloors and insulating pipes in crawlspace houses, which rarely have a poured floor slab, another radon-resistant alternative that can be applied after construction should be considered. This mitigation technique is a variation of the successful SSD methods used in basements. Polyethylene sheeting is often used as a moisture barrier applied directly over the soil in crawlspaces. The polyethylene sheeting can be used as a gastight barrier that forms a small-volume plenum above the soil where radon collects. A fan can be installed to pull the collected soil gas from under the sheeting and exhaust it outside the house.

The wide-width polyethylene sheets should be set directly on the earth in a way that produces at least 1-ft overlaps. Some field applications have included a bead of caulking to seal between sheets of polyethylene. A better seal has been achieved by using an aerosol spray. A good seal is obtained by spraying both surfaces of the polyethylene, allowing time for them to get tacky, and pushing the two pieces of polyethylene together. In locations where the soil surface is exceptionally hard and smooth or the crawlspace is very large, a drainage material can be placed under the sheeting to improve airflow. If a large number of support piers exist or if the suction point is located close to support piers, the polyethylene sheeting should be sealed to the piers with caulking and wood strips. The plastic sheeting may also be sealed to the foundation walls to reduce air leaks. Some retrofit applications of this crawlspace radon mitigation technique have worked well without attempting to seal the sheets of polyethylene together or sealing the polyethylene to piers or walls. Many others have not been successful without sealing. When this technique is used, a complete sealing job is recommended for greatest protection. Application of this technique may not be appropriate in crawlspaces that receive heavy traffic.

Some builders prefer to concrete the floor of crawlspaces when site and design conditions permit getting the mix into the crawlspace. If a crawlspace has a concrete slab, for radon-resistant construction, the crawlspace should be treated similar to a basement with the advantage of greater ventilation potential.

31.4 MECHANICAL BARRIERS

Theoretically, a gastight barrier could be placed between the soil and foundation to eliminate radon entry from the soil. Like many other building details, it is much easier to draw such a detail than to actually install it. Many materials form effective retarders to gas transport. The problem is effectively sealing cracks, joints, and penetrations. As anyone who has tried to build an airtight house can tell you, it is not as easy as it seems.

The types of mechanical barriers that have been tried or suggested for radon control fit into one of the following categories[9,27]:

1. Foundation materials themselves
2. Coatings
3. Membranes
4. Possibility of a "site" barrier.

Ongoing U.S. EPA research on radon-resistant new construction has encountered numerous difficulties in making a gastight mechanical barrier effective enough to confidently keep indoor radon levels below 4 pCi/L. The types of problems encountered included

1. Quality control on the job.
2. Incomplete communication between researchers, contractors, and subcontractors.
3. Reluctance of builders to change drainage detailing.
4. The smallness of radon atoms.

The first problems on the list are not specific to radon control but are encountered on nearly every construction job. In spite of quality control and communication problems and the understandable wariness builders show when asked to build something in a different way, the residential construction industry has responded to new techniques, materials, and public demands. The average house being built today is very different from a home built 20 years ago. If a product or a method can be demonstrated to reliably keep radon out without presenting significant problems with cost, scheduling, or installation, many builders would learn to use it. The major difficulty faced by mechanical barrier approaches is the thoroughness that seems to be required to ensure that no radon problem will occur.

In 1988 and 1989, U.S. EPA projects studied newly constructed houses, which incorporated mechanical barriers and provisions for active and passive SSD to determine the effectiveness of each approach. Preliminary results from these five studies found that, when there was a source of radon beneath the houses, the mechanical barriers were not adequate to ensure basement levels below 4 pCi/L. However, there is no way to judge how high the radon concentrations in these buildings would have been had the mechanical barriers not been employed. These data should not be used as evidence that the barriers used (or that mechanical barriers in general) do not reduce radon levels indoors. In fact there are good reasons to employ barriers to enhance the performance and reduce the energy penalty of soil depressurization techniques.

When trying to make a barrier to soil gas entry, the routes of concern in new construction are the same as those that have previously been identified for existing houses. Houses that are combinations of the above substructures often provide additional entry routes at the interface between the two substructures. The following subsections address the types of mechanical barriers (foundation materials, coatings, and membranes), the potential radon entry routes associated with common foundation detailing, and suggestions for details that reduce the risk of elevated indoor radon. When possible, these alternatives include barriers that can be used to block radon entry while continuing to use traditional construction methods. Depending on current local or regional building practices, some of the suggestions may require significantly different construction methods.

31.4.1 FOUNDATION MATERIALS

The materials used to construct a foundation can often be used as an effective barrier to the entry of radon-laden soil gas. Below-grade walls may be constructed of poured concrete, masonry, or other materials such as pressure-treated wood or stone. The materials covered in this section, poured concrete and masonry block, are the materials most commonly used for new construction. Details of radon protection in permanent wood foundations can be found in an NFoPA publication.[21]

In residential buildings, foundation walls made of poured concrete are generally constructed to a compressive strength of 2500–3000 psi. The forms are held together with metal ties that penetrate the wall. A poured concrete wall is a good barrier to radon transport. The major weaknesses in this regard are cracks, joints, and penetrations. It is these openings in the walls that allow soil gas to enter the building without actually having to diffuse through the concrete. It is recommended that concrete walls be built in compliance with guidelines established by the American Concrete Institute (ACI).[22] Such concepts as cover mix, reinforcing, slump, temperature, vibration, and a variety of other factors help keep the foundation from cracking.

Residential foundation walls built of concrete masonry units may have open cores, filled cores, or cores closed at the top course. Masonry walls are frequently coated with an exterior layer of cementitious material, referred to as "parging," for water control. This coating is usually covered at the bottom of the wal1 to make a good exterior seal at the joint between the footing and the block wall. Uncoated block walls can range in porosity depending on the type of aggregate used. Uncoated blocks are neither an effective water nor a radon barrier. It is recommended that concrete block walls be bulk according to guidelines issued by the National Concrete Masonry Association (NCMA).[28] Their publications cover thickness of blocks, reinforcing, pilaster location, control joints, sequencing, and other issues that prevent cracking or foundation failure.

There are geographic areas throughout the United States in which the majority of foundation walls are poured concrete and other areas where masonry walls predominate. Poured concrete walls are generally available only in areas where contractors have the in-house expertise to build them and either rent or have invested in reusable forms. In areas where both types of construction are found, the costs of each seem competitive.

There are building codes that dictate dampproofing or waterproofing treatment for both types of foundations. The treatments can also inhibit gas movement through the wall. Concrete blocks are much more porous than poured concrete, although the parge or waterproofing coats moderate the difference. Recent laboratory tests have confirmed that uncoated concrete masonry walls allow substantial airflow, but that there is a great deal of variation in the porosity of blocks, due mainly to the use of different aggregates by the block manufacturer. Block walls can allow substantial soil gas circulation in the cores of unfilled blocks, providing an area source of radon. Various measures are available to alleviate this problem, including exterior (or interior) gas barrier membranes and solid or filled block tops.

Although it is clear that concrete blocks are more porous than poured concrete, some studies reveal no strong correlations concluding that a home built with a concrete block foundation is more likely to have a radon problem than one built with a poured concrete foundation. A New Jersey study[29] found that the mean radon concentration in 581 basements with poured concrete walls was 6.3 pCi/L ± 14.1% and that the mean concentration in 3408 basements built with concrete block walls was 5.7 pCi/L ± 11.1%. There is no statistical difference between the two means. A survey conducted in Connecticut[30] in a smaller sample population revealed a geometric mean radon concentration of ~1.7 pCi/L in 755 homes with poured concrete foundations. The same study revealed a mean concentration of ~2.0 pCi/L in 129 homes with block foundations. This is another example of a variable that would seem to have an effect on indoor radon concentrations not meeting those expectations. The expected effect is lost in the complex interaction of the far more important factors that affect radon source strength and transport. It is interesting to note that the 639 stone foundations tested had mean basement radon concentrations of 6.2 pCi/L ± 10.1%, virtually identical to the other two types of foundation walls.

31.4.2 COMMON MASONRY WALL DETAILS AND THEIR IMPACT ON RADON RESISTANCE

31.4.2.1 Masonry Walls with Termite Caps, Solid Blocks, and Filled Block Tops

Builders may construct a foundation wall with solid, filled, or sealed block tops for several reasons, including termite-proofing, energy conservation, distribution of weight of the structure, and radon resistance. The NCMA[28] recommends that a solid or grouted top course be installed to distribute the loads of joists and beams. Some building codes require solid tops to block hidden termite entry. In spite of this, the block tops in many residences are left open except at anchor points. Houses have been observed in which block tops were generally sealed, but cores were left unsealed at access doors to crawlspaces, around ash pit doors, and other openings. Sealing hollow cores at or near their tops can prevent soil gas from entering the basement, but more importantly might make the building easier to mitigate in the event that it has elevated radon. Sealing the bottom course might prevent air beneath the slab from entering the block wall, but if the wall cores are used as part of a water control method this may not be possible.

It is recommended, for potential radon control, to seal open blocks at the time of construction. Block tops have been successfully sealed using

1. Mortar mixed with plastic binder to fill the top cores (quality control and shrinkage can be problems).
2. "Termite caps"—cored blocks with a 2-in.-thick solid cap as the top course.
3. Solid or lintel blocks to seal one of the top courses.

When solid blocks or termite caps are used, anchor bolts must be placed in the joints between the blocks. Lintel blocks and grouted top courses allow for more flexible placement.

31.4.2.2 Masonry Walls with Weep Holes

Weep holes are used to drain water from the block cores into the subslab area when surface waterproofing barriers fail. Such a connection between the exterior and interior subslab areas is an obvious channel for radon entry, allowing soil gas to pass from the subslab to the interior of the block wall. Openings from the subslab into the block wall would also make it difficult to apply active SSD at a later date. If the block tops are sealed and the interior of the block wall is sealed, then weep holes would be much less of a problem as radon entry points or as barriers to SSD.

The NCMA issues technical notes to provide contractors with guidance in construction practice. The NCMA-TEK 43, Concrete Masonry Foundation Walls[28] provides illustrated cross-sections of foundation walls showing weep holes through the footing. These run from the exterior of the wall to the subslab areas, connecting an exterior drainage system to an interior drainage system. This system does not directly drain the block wall, but the combination of dampproofing and exterior drainage should make it unnecessary.

Contractors often create weep holes in the bottom course of block rather than buying prefabricated weep block. Some masons open holes in both shells of the block; others open the block cores to the interior but leave the exterior shell intact. Some builders prefer weep holes as an alternative to exterior drainage, while other builders reportedly use weep blocks in lieu of backfilling with granular material, although such backfilling is recommended or required in most areas. The actual need for weep holes in properly designed and constructed masonry walls is questionable. Moreover, a solid block installed as the bottom course of a foundation wall is recommended to keep radon from seeping into block cores around the footing. The NCMA-TEK 160A, Radon Safe Basement Construction,[31] shows no weep holes in walls or footings but offers no prediction of the consequences of eliminating them. A potential concern is that even properly applied waterproofing materials may fail.

It has been suggested that it might be possible to retain the weep hole while venting the upper blocks above grade to allow soil gas to escape. This idea would need to be combined with an interior barrier such as paint. In general, weep holes should be avoided and if drainage problems are expected, an exterior drainage should be installed.

It is recommended that, if weep holes are used, care should be taken that they do not present a radon entry path or a barrier to later SSD. The best approaches appear to be either avoiding weep holes by carefully planning and installing a drainage system that would prevent water from entering the block walls or sealing the block tops and interior of the block wall.

31.4.2.3 Stemwalls in Slab-on-Grade Houses

Stemwalls, also called frost walls, are below-grade foundations that support the load of the above-grade walls and thereby the roof. There is usually a footing beneath them at some depth below the frost line. The major radon-related issue for these walls is the geometry of the slab/stemwall joint. This will be covered in the section on floors. If stemwalls are constructed of concrete blocks, then the block tops should be sealed.

31.4.2.4 Foundation Walls in Crawlspace Houses

Foundation walls in ventilated crawlspaces are substantially different from walls in basements and unventilated crawlspaces. In basements and slab-on-grade buildings, it is clear that barriers should be applied between the soil and the foundation or be the foundation itself. With ventilated crawlspaces, there are two locations that present themselves for the application of barriers. First, as in the other, barriers can be placed between the soil and the foundation. Second, a barrier effort can be made between the crawlspace and the upstairs living area at the floor deck. The second option will be treated in a following section. If the first option, making a barrier between the soil and the crawlspace, is selected, then the basement wall details that apply to sealing open blocktops and preventing the foundation from cracking also apply to the crawlspace walls.

31.4.3 FLOORS IN BASEMENTS, SLABS ON GRADE, AND CRAWLSPACES

As already pointed out, poured concrete is a good retarder for radon gas and soil gas. The major problems will be cracks, joints, and penetrations. The focus of this subsection will be on crack prevention and sealing joints and penetrations. A good deal of this material applies to both poured concrete and masonry walls.

31.4.3.1 Crack Prevention

Plastic shrinkage cracking of concrete is a natural function of the drying process. Many factors come into play as concrete cures, including water content, cement content, atmospheric humidity, temperature, humidity, air movement over the slab surface, and aggregate content. The preparation of the subslab area is also important. Reinforcement can be used to reduce shrinkage cracking. It has not been traditionally mandatory in residential floor slab. Residential builders typically become concerned about shrinkage cracking and/or slab reinforcement when they are working in areas with unstable soils or when they need to ensure slab integrity under specific finished floor systems (e.g., ceramic tile).

There are many ways to minimize slab cracking, although it probably cannot be eliminated entirely. The ACI publishes a number of documents outlining standard practice for building concrete and concrete masonry structures. A number of these apply to crack prevention. Specifically, the reader is referred to the Guide for Concrete Floor and Slab Construction[23] and the Guide to Residential Cast in Place Concrete.[22] The following discussion describes a number of treatments, some of which are familiar to the commercial institutional/industrial construction area but uncommon to the residential marketplace.

31.4.3.1.1 Reinforcement with Ferrous Metals

The use of metal reinforcement embedded in the slab increases its strength. Woven wire mesh is the most common material for residential applications. For slabs on grade the Council of American Building Officials,[32] One and Two Family Dwelling Code recommends 6 × 6 in.–W2.9 × W2.9 woven wire mesh. To help control cracking, it has been suggested that this is appropriate for a basement slab as well.

Rebar (also called rerod) is most commonly used for footings or garage slabs and would not generally be used throughout a basement slab. A no. 4 rebar (1/2 in. bar) runs 0.668 lb/ft. It would probably be installed in a garage slab of 12 in., on center leaving 3 in. at each end and running in both the directions.

31.4.3.1.2 Concrete Additives

A number of additives can be used to change the characteristics of concrete. The ACI discusses these additives in its technical guides. A discussion of the various fibers used to reinforce concrete is titled State of the Art Report on Fiber Reinforced Concrete.[33]

31.4.3.1.3 Water-Reducing Admixtures

Also known as plasticizers, these admixtures reduce the amount of water used in the concrete. This reduces shrinkage and cracking while increasing the workability of the concrete. One example of a plasticizer is WRDA-19, by Grace Construction Products, which is labeled “an aqueous solution of a modified naphthalene sulfonate, containing no added chloride.” Chlorides are frequently added to concrete as antifreezes, but various codes limit the chloride content of concrete because of its corrosive effect on ferrous metals and its reducing effects on concrete strength. American ATCON’s report to the Florida Phosphate Institute[34] recommends the use of a plasticizer to reduce the likelihood of water being added on-site to produce more workable concrete.

31.4.3.1.4 Fiber-Reinforced Concrete

Various fiber additives are available that can reinforce poured concrete and reduce plastic shrinkage cracking. Fiber reinforcing has the advantage over woven wire mesh in that the fibers are homogeneously distributed throughout the slab thickness. The type of fiber used is important because studies have shown that the alkaline environment of Portland cement destroys some of the fibers that are sold for this purpose. Polyester fibers and glass fibers have been noted by ACI as being vulnerable in an alkaline environment. Some companies apply a surface treatment to fibers to protect them from damage by alkalinity (glass fibers so treated are known in the trade as “AR fibers”), but the ends of the fibers are exposed when they are chopped up during the manufacturing process, and they can decay from the ends inward. The polypropylene material used in some fiber products is chemically stable in an alkaline environment. The much higher modulus of elasticity of glass fibers compared to organic fibers may be an advantage for the glass since it more nearly matches the modulus of elasticity of concrete. The comments above apply to fiber additives used in surface-bonding mortars as well as those used in poured concrete slabs.

31.4.3.1.5 Curing

Proper curing is critical to the strength and durability of poured concrete. Many avenues are available to ensure a good cure, ranging from watering the slab to covering it with wet sand, wet sawdust, or a waterproof film (e.g., waterproof paper, Burlene™ (burlap/polyethylene)) or coating it with a curing compound. Penetrating epoxy sealer applied to the slab while it is still wet can act as a curing agent and slab strengthener. Polyurethane sealants are applied after the slab is dry, because moisture would lift them off the slab. There are a number of other liquid membranes and emulsions, including a number of solvents that require substantial ventilation as they dry.

31.4.3.1.6 Use of Higher-Strength Concrete

Typical residential concrete slab construction requires a 28-day compressive strength of only 2500–3000 psi. Concrete can be made stronger by reducing the water/cement ratio. If the water/cement ratio is kept at 0.5 or less, the minimum 28-day compressive strength will increase to 3800 psi. Moreover, if the ratio is reduced to 0.45, the compressive strength increases to 4300 psi. To achieve compressive strengths above 3500 psi, the slump cannot exceed 3 in. The compressive strength and the slump of the concrete are no more important, however, than the placability of the concrete or the finishability of the surface. Unfortunately, placability and finishability are not easily measured quantities like slump and compressive strength, and often do not receive sufficient emphasis.

31.4.3.2 Joints

31.4.3.2.1 French Drains and Floor/Wall Cracks

The French drain (also called a channel drain or floating slab) is a construction feature that appears to provoke strong reaction from its defenders and detractors alike. French drains are only a concern in basement foundations. This slab detail is a standard feature in new houses in parts of the country as varied as New York and Colorado, but in other places it is virtually unknown. French drains are used in areas with expansive soils, such as parts of Colorado, to protect the slab from damage if the wall moves. In central New York State, the main function of the French drain is to drain away water that may seep down the walls. One national builder has discontinued and now prohibits the use of French drains in houses because of the potential for radon problems. This builder states that French drains also have been found to significantly increase indoor moisture levels.

Various treatments can be used to seal French drains against gas entry. Some of those treatments have crack-spanning capability in the case of structural movement. French drains can be sealed airtight and still preserve their water drainage function by caulking the channel to a level below the top of the slab and sloping the trough toward the sump. This assumes that the sump lid is inset below the surface of the slab and that a water-trapped drain in the sump lid drains water into the sump. Figure 31.14 shows a French drain treatment.

It is recommended that French drains be avoided if possible because of the difficulty in sealing them at the time of construction and the expense and difficulty of sealing them after construction.

31.4.3.2.2 Perimeter Crack

The perimeter crack is located between the edge of the floor slab and the foundation wall. This applies to slabs in basements, crawlspaces, and slab-on-grade foundations. As a cold joint, this perimeter crack is always a potential radon entry point. Contractors building radon-resistant houses

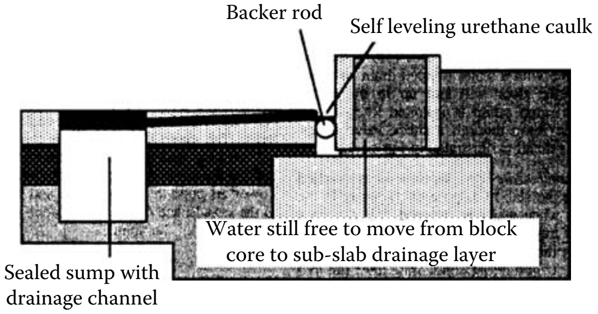


FIGURE 31.14 Sealing a French drain. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

may deliberately create a significant floor/wall crack so that it will be easy to work with and seal. A perimeter expansion joint is made of a closed-cell, flexible foam strip. The expansion joint is presliced so that the top 1/2 in. can be pulled off to leave room for caulk. Another approach is to tool the floor/wall joint with an edging tool and seal it with caulk. Particular attention should be paid to sealing this crack in slab-on-grade houses because the joint is often inaccessible after the house walls are raised.

31.4.3.2.3 Control of Joints

When large areas of slab are poured, some cracks are unavoidable. There will be cold joints because the slab was poured in small sections to avoid cracks, or the slab will crack because the pours were too large. To direct the inevitable cracking that will occur in either case, a control joint can be made by grooving the surface of the slab. The groove should be large enough to seal with caulk. Cold joints can make use of the same expansion joint materials that have a zip-off top that was described for the slab edge crack.

31.4.3.3 Penetrations

Every house has some minimum penetration through the slab or foundation walls. The ones always present are water pipe entry and sewer pipe exit. Common additional penetrations are floor drains, sump holes, and air conditioner condensate drains.

31.4.3.3.1 Openings around Water Pipe Entries and Sewer Exits

Openings around water pipe entries and sewer exits that pass through concrete can be easily sealed using caulks. Many builders use plastic sleeves to protect metal pipes from corrosion when they pass through concrete. In this case, an effort can be made to leave a space around the pipe that can be sealed with caulk or backer rod and caulk. The same techniques can be used for pipes passing through block walls.

Depending on the details of a floor drain, a great deal of soil gas can enter through large openings to the drainage matrix. This is true not only of slop drains that are simply holes through slabs into the subslab area, but also of other types of drains. Even water-trapped drains with water in the traps can allow radon an entry passage where the dish-shaped bottom of the drain seats into the drain pipe. It is recommended that floor drains connect to pipe that drains to daylight using solid PVC pipe glued at the joints, or that water-trapped drains or mechanical traps be installed that do not have unsealed joints on the room side of the water trap.

31.4.3.3.2 Sump Holes

Sump holes are usually a collection point for the drainage system. Almost by definition, this is a terrifically good radon collection system. It must have access to large areas of soil beneath the

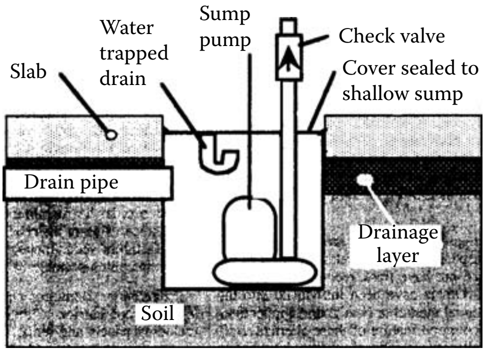


FIGURE 31.15 Sealing a slump hole to a shallow yet operable sump. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

foundation, so it is easier for water to run into the sump than to penetrate the foundation. It is better if there is no open sump at all. A subslab drainage system that can drain by gravity to a daylight opening serves the same purpose as a sump hole but offers no fewer radon entry routes. If this is not possible then the sump hole must be sealed (a code item in some places to keep children from playing in them). Sumps can be sealed airtight and still function as a water collection and removal system by routing the interior and/or exterior drainage pipes or layer into the sump. The sump hole is then sealed with a corrosion-resistant lid that is recessed a few inches to create a shallow sump. The lid is fitted with a water-trapped drain, so water that flows across the floor will end up in the sump. Lastly, a low-profile sump pump is installed to eject water collected in the sump through a check valve to approved disposal. This detail is illustrated in Figure 31.15.

31.4.3.3.3 Air Conditioner Condensate

Air conditioner condensate lines are sometimes installed so that they penetrate the slab to dispose of the water in the subslab area. Even when water is trapped, this can be a problem because the traps often dry up during the heating season. At this point they become radon entry routes. It is recommended that air conditioning condensate lines run to a drain that will not dry out or that a condensate pump is installed that collects the condensate and disposes of it through a water trap. Often a washing machine drain is located in a basement near enough to use it.

31.4.3.3.4 Sealants for Cracks, Joints, and Penetrations

Masonry sealants for radon-resistant applications must have good adhesion and be durable and elastic. Polyurethane comes in gunnable grades, and one- and two-part self-leveling types. Self-leveling urethanes can be used only on level surfaces as they are very mobile. In fact, if there is even a small crack at the bottom of a joint being sealed, the self-leveling caulk may drain out. The popularity of polyurethane is based on a combination of good adhesion even under difficult conditions, long service life, good elasticity, and easy availability. Copolymer caulks have very similar properties as the polyurethanes. Recently, some copolymer caulks have been packaged as sealants specific to radon control. Silicone caulks have also been used in radon control but require more extensive surface preparation for good adhesion. Many radon mitigators have adopted the use of silicone caulks for sealing sump lids and access ports because they make a tight-fitting gasket that can be removed more easily than polyurethane at a future date. Butyl caulk is susceptible to attack by groundwater acids. Polysulfides have been largely supplanted by polyurethanes because the former are more chemically reactive with asphalts.

Surfaces should be clean and dry when caulk is applied. Bear in mind that the idea is to get a flexible membrane to bridge between the two surfaces that the crack divides. It is a poor practice to simply fill every crack. Manufacturers usually specify appropriate dimensions for their caulks.

Often this is a minimum of 1/4 × 1/4 in. For small cracks, it may be necessary to grind them larger to meet the caulk manufacturers' specifications. For cracks much larger than 1/4 in., a backer rod should be used to support the caulk so that it can be applied correctly.

Caulks give off organic compounds. Some of these are carcinogenic. Users are reminded here that they should have the Manufacturers Data Sheets for any chemicals they use. These sheets identify hazardous aspects in the use of the products. OSHA requires that contractors have these sheets available for employees and that a safety training program be in effect for these products.

31.4.4 CRAWLSPACES

Crawlspaces are being treated here as a special case of using the foundation materials to make a mechanical barrier. In this subsection, isolating the living space from the crawlspace by sealing the floor between the two spaces will be discussed. A sheet of plywood is a relatively good barrier to radon-laden crawlspace air and, as with the other material barriers, it is the joints and penetrations that are the problems. The major entry points are through numerous electrical, heating, and plumbing penetrations in the house floor and via the return air duct often located in the crawlspace. Lower air pressure in the house and the return air duct than in the crawlspace draws radon-laden crawlspace air into the living space of the house.

During construction, all possible penetrations between the crawlspace and the house should be sealed to simply prevent the passage of radon up into the living areas. Attempts to seal penetrations can be made by using expandable closed-cell foam sealants and urethane caulk. Sealing these areas can be difficult because of limited access even during construction. Areas of particular concern include[9]

1. Openings in the subfloor for waste pipes including openings for tubs, toilets, and showers
2. Openings for water supply lines
3. Openings for electrical wiring
4. Openings for air ducting for the heating, ventilating, and air conditioning (HVAC) system
5. Openings around hot water heating pipes. Check on code requirements for clearance between hot water pipes and wood floors. These may require a special sealant
6. Joints between sheets of plywood.

Any sealing around plumbing traps must be done so that the trap can still be reached and serviced.

Return air for the HVAC system should not be supplied from the crawlspace. It is best to avoid routing return air ductwork through the crawlspace, but if it must be, then it should be thoroughly sealed with duct tape at a minimum. It should be understood, however, that duct tape may dry out and fall off. A better approach would be to use seamless ductwork in these areas. The use of floor joists and subflooring as three sides of a return air plenum should be avoided because of the difficulties encountered in sealing. If the space between the joists must be used, an alternative to ducts is to use a rectangular duct to fit the space.

If isolation of the crawlspace is the primary method of radon-resistant construction being used, the number and size of crawlspace vents should be maximized. The Florida's guideline for radon-resistant construction[35] suggests vents of not less than 1 ft^2 of vent for each 150 ft^2 of crawlspace. The guideline also requires that vents be located to provide good circulation of air across the crawlspace and should not include registers or other provisions for closure. This requirement would be impractical in cold climates with water pipes in the crawlspace. If there were no water pipes to worry about, then the floor would need to be well insulated in order to ensure that a large energy and comfort penalty was not incurred.

Other radon-resistant alternatives besides simple isolation of the crawlspace should be considered because of the difficulties encountered in getting an adequate seal between the house and the crawlspace. These alternatives will be discussed in the next section.

TABLE 31.2
Results Using Vented Crawlspace Technique

House No.	Fan Operation	Buried Crawlspace Level (pCi/L)	Basement Level (pCi/L)
1	Off	9.9	1.9
1	On 2 weeks	9.9	1.4
1	On 2 weeks	8.4	1.4
2	Off	27.8	1.8
2	On 1 week	18.6	1.2
2	On 1 week	16.7	0.9
3	On 1 day	26.4	1.3
3	On 1 day	15.5	0.9

Source: Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.

A NEWHEP builder in Denver uses an innovative foundation technique to simultaneously deal with problems of expansive soil and high soil radium and radon content. The foundation excavation is overdug to a depth of 10 ft. Caisson pilings are driven to support the 10-ft-tall reinforced poured concrete walls. Band joists are bolted to the walls 2 ft above the dirt floor, and a carefully sealed wood subfloor, supported by steel “I” beams and standard size floor joists, is installed. The 2-ft-high “buried crawlspace” is actively ventilated by installing a sheet metal inlet duct at one corner of the basement, drawing in outdoor air through an aboveground vent. A similar duct with an in-line fan is located at the opposite corner to exhaust air through an above-grade vent. Soil gas radon at levels from 3163 to 4647 pCi/L was measured at three of these building sites. Soil radium-226 content was measured at 1.05–1.62 pCi/g. Indoor radon measurements were then taken in the buried crawlspaces and in the basements. Measurements were made during summer with the exhaust fan off, and after 1 day, 1 week, and 2 weeks of operation. The results are shown in Table 31.2.[36]

31.4.5 COATINGS

If waterproofing or dampproofing treatments that are effective gas barriers and that can be sealed at joints and penetrations could be identified, then walls could be made radon resistant. Acceptable dampproofing or waterproofing treatments are specifically listed in building codes in many areas of the United States; these lists are periodically amended as new materials come into use. These coatings apply primarily to basement walls.

The terms “waterproofing” and “dampproofing” are often used interchangeably. Briefly, any waterproofing material can also be used for dampproofing; the converse is not true. Waterproofing materials must resist the penetration of water under a hydrostatic load. Dampproofing materials are not expected to keep out water under pressure, but do impede water entry and block diffusive movement of water through pores.

Any material that provides adequate protection against water should at least limit convective soil gas movement. Properly applied waterproofing materials should help block pressure-driven entry of soil gas.

The most common dampproofing treatment for residential foundation walls is a parge coat covered with bituminous asphalt. The parge coat is used for concrete masonry walls but is not necessary for poured concrete walls. This two-stage treatment has been replaced by surface bonding cement in some areas.

Oak Ridge National Laboratory indicates that bituminous asphalt may be attacked by soil and groundwater chemicals, specifically acids.[37] Bituminous materials may also lose their elasticity at below-freezing temperatures. These features render bituminous asphalt an undependable waterproofing treatment; in fact, it is listed by code organizations such as Building Officials and Code Administrators International (BOCA), Council of American Building Officials (CABO), and Southern Building Code Congress International (SBCCI) only for dampproofing.

A number of dampproofing systems are better gas barriers than bituminous asphalt. Some are relatively new to the residential marketplace but have track records in industrial/commercial settings. Others have been introduced into the most expensive residential market or have found applications at problem sites. A common feature of these alternatives is that they are generally more expensive than bituminous dampproofing. However, a survey of 31,456 properties by Owens-Corning Corporation[38] found that 59% of property owners with basements reported water leaks. As the supply of trouble-free building lots dwindles, home buyers may decide that investment is justified, and improved dampproofing systems may be developed to address radon and water problems simultaneously.

The following is a sampling of alternative waterproofing systems that are readily available to builders.

31.4.5.1 Coal Tar-Modified Polyurethane

Coal tar-modified polyurethane is a cold-applied liquid waterproofing system. The system by Sonneborn is an example of this approach to waterproofing. It is applied as a liquid at the rate of 10–15 mils/coat. The coating dries hard, but has some elasticity. This material may be attacked by acids in groundwater but can be defended by a protection board. The performance of any liquid-applied waterproofing systems is limited by the capabilities of the applicator (it is difficult to achieve even coats on vertical surfaces).

31.4.5.2 Polymer-Modified Asphalt

Polymer-modified asphalt is a cold-applied liquid waterproofing system. As with the Sonneborn system mentioned above, the quality of the installation depends on the applicator (it is difficult to achieve an even coating on a vertical surface). High-grade polymer-modified asphalt is superior to coal tar-modified polyurethane in elasticity, crack-spanning ability, and resealability, but inferior in its resistance to chemicals.

31.4.5.3 Membrane Waterproofing Systems

Waterproofing applied as a membrane has an advantage over liquid-applied systems in that quality control over thickness is ensured by the manufacturing process. Most membrane systems are also chemically stable and have good crack-spanning ability. On the other hand, effective waterproofing demands that seams be smooth so that the membrane is not punctured. Some masons apply parging to a half-height level and then return to finish the upper half of the wall. This tends to leave a rough section where the two applications overlap and means that the waterproofing crew has to grind the wall smooth before applying the waterproofing membrane. Thermoplastic membranes may be applied in various ways—affixed to walls or laid beneath slabs. Thermoplastic membranes are highly rated for resistance to chemicals and longevity. Rubberized asphalt polyethylene membranes have superior crack-bridging ability compared with fully adhered thermoplastic membranes. (Loosely hung thermoplastic membranes, by their nature, have obvious crack-bridging ability in that they are bonded to the walls.)

Seams and overlaps must be carefully and completely sealed in order for membranes to function as radon barriers. The choice of seam material varies with the type of sealant. Manufacturers' recommendations for sealant, procedure, and safety precautions should be followed.

31.4.5.4 Bentonite

Bentonite clay expands when moist to create a waterproof barrier. Bentonite is sold in various forms, including panels and mats. Bentonite is not as resistant to chemicals as the thermoplastic membranes, nor is it puncture resistant. The major flaw of bentonite as a radon barrier, however, is that it is only tightly expanded when wet. This is acceptable for a waterproofing material, but not for a gas barrier.

31.4.5.5 Surface Bonding Cement

Surface bonding mortar or cement is mentioned in some building codes as an approved dampproofing treatment, but not as a waterproofing treatment. A number of manufacturers produce cements and mortars impregnated with fibrous glass or other fibers. Some of these may be chemically unstable in the alkaline environment of Portland cement.

One technique of assembly using surface bonding cement is to dry stack blocks and apply the cement on both sides. As an alternative, the block wall is conventionally assembled with only an outside coating as a positive-side waterproofing.

31.4.5.6 Cementitious Waterproofing

A number of additives can be incorporated into concrete to create cementitious "waterproofing." This type of waterproofing is appropriate only for interior applications because it is inelastic, does not have good crack-spanning ability, and cannot resist hydrostatic pressure.

31.4.5.7 Interior Paint as a Barrier

A variety of interior applied masonry paints are available. Some of these have been tested by the AEERL laboratory at the U.S. EPA. Results of these tests are given in a paper presented at a Symposium on Radon Reduction Technology.[39]

31.4.6 MEMBRANES

Membranes of plastics and rubbers that are used to control liquid water penetration and water vapor diffusion are effective in controlling air movement as well. If they can be adequately sealed at the joints and penetrations and installed intact, then they could also provide a mechanical barrier to radon entry.

Construction film is already in common use as a subslab vapor barrier in many areas of the country. The current prevalence and low cost of this material mean that it may be worthwhile to continue its use even though it is an imperfect barrier. It is possible to seal polyethylene vapor barriers at the overlapped edges, at penetrations, and at the footing; but it may be that the extra effort will not be rewarded with improved radon resistance.

In Sweden, subslab membranes are not required in high-radon areas and a tightly sealed slab is considered to be a more effective radon barrier. The difficulty of achieving a completely sealed, intact subslab membrane is widely acknowledged; however, a subslab barrier may be worthwhile even if it is imperfectly installed. Polyethylene construction film (6-mil) can serve as a backup radon barrier to the concrete slab, even though it is not a complete radon barrier by itself. The barrier may continue to function, even with punctures, if incidental cracks and holes in the slab are aligned with intact areas of polyethylene.

In summary, it is worthwhile to continue the installation of a vapor barrier that serves as the added valid function of moisture barrier. More comprehensive installation measures and more expensive materials may be merited in areas where the radon source is strong because of either high radon concentrations or high soil gas flow rates.

31.4.6.1 Polyethylene Film

A vapor barrier of polyethylene film is a typical subslab feature in many areas of the country. The intent of the vapor barrier is to prevent moisture entry from beneath the slab.

Installation of any subslab membrane is problematic because an effective barrier should be both well sealed and intact. Builders who use polyethylene under the slab indicate that achieving a complete seal at all laps and edges and around pipe penetrations is difficult. It is difficult to seal the polyethylene to the footing because the weight of the concrete tends to pull it away from the walls during the pour. There is also a high probability that the vapor barrier will be punctured during installation. It has been observed that even a 10-mil polyethylene in a heavy felt membrane is likely to be punctured during installation.

Another issue is the stability of polyethylene vapor barriers. Polyethylene is known to be harmed by ultraviolet (UV) exposure. One radon mitigator has found polyethylene under slabs in Florida that deteriorated in less than 15 years; more frequently, polyethylene of comparable age is in mint condition.

Polyethylene films are manufactured with an array of additives selected to support specific applications. Durability varies according to the additives employed, film thickness, length of UV exposure, temperature swings, and other factors. Resins used in polyethylene manufacturing have improved over time, so that the life expectancy of polyethylene film is longer than that of films used in the 1960s and 1970s. The durability of polyethylene films in current use depends on the contractor's selection and proper storage of appropriate film for the job.

On the other hand, there is no evidence to support the assertion that polyethylene vapor berries deteriorate with exposure to soil chemicals. Construction film is a low-density polyethylene. High-density polyethylenes are used for the storage and transportation of an array of chemicals. Polyethylene is chemically stable, but may be adversely affected by aliphatic hydrocarbons (such as hexane, octane. and butane) and chlorinated solvents. It does not appear to be reactive with the acids and salts likely to be encountered in soil and concrete.

Polyethylene-coated kraft paper vapor barrier is available in 8 × 125 ft rolls. Overlaps of 6 in. are marked on the paper with a printed line. They can be sealed with polyethylene tape. This material is attractive to contractors because it is more puncture resistant than a 6-mil polyethylene construction film, but less expensive than many alternative products.

Polyethylene-based membranes are manufactured for use in hazardous waste landfills, lagoons, and similar applications. Two of these products have been tested to determine their effectiveness as barriers against radon diffusion. (In most cases, diffusive flow is considered of little or no significance as a mechanism of radon entry compared with convective flow). A 20-mil high-density polyethylene tested 99.9% effective in blocking radon diffusion under neutral pressure conditions. A 30-mil low-density polyethylene tested 98% effective in blocking radon diffusion under neutral pressure conditions.

31.4.6.2 Double-Layered High-Strength Bubble-Pack with Aluminum Foil

A material composed of a double layer of high-strength bubble-pack with aluminum foil bonded on both sides is available. It has high compression strength and doubles as an insulator. Concern exists over its fragility and susceptibility to pinhole punctures. Both foil-faced membranes can be punctured, but the double bubble-pack offers some defense against complete penetration. Punctures are easily repaired with aluminum tape, which is also used at seams. A well-made seal is diffusion resistant; however, gas can migrate through wrinkles in the tape. The fragility of the material is believed to be a significant limiting factor in using it under the slab or as perimeter insulation.

31.4.6.3 Two-Faced Aluminum Foil over a Core of Glass Scrim Webbing

Another available product has two faces of aluminum foil over a core of glass scrim webbing; it is coated with asphalt. The membrane is 0.012 in. thick. This material has not been tested as a barrier against diffusive flow of radon, but its performance should be similar to that of other foil-faced products. Seams are sealed with aluminum tape.

31.4.6.4 PVC Membranes

PVC membranes have been used as a subslab membrane during radon mitigation work in existing houses. They are usually sealed with solvents and were developed as roofing membranes.

31.4.6.5 Rubber-Like EPDM™

Another product EPDM™ is a rubber-like material. It comes in 60-mil thickness in 100 ft by 61-1/2 in. rolls. EPDM also comes in 45-mil thickness in 25 ft by 60 ft rolls. This product has gained popularity as a ground cover in crawlspaces because of its durability qualities.

31.4.7 MECHANICAL BARRIERS APPLIED TO THE SOIL

It has been suggested that mechanical barriers could be applied to the soil beneath the foundation that would prevent the migration of radon into the building. This has the benefit of being less susceptible to occupant behavior, future remodeling activities, and mechanical failure of fans. Two approaches have been brought forward. One would use an injection of slurry composed of clay to dramatically reduce the permeability of the soil. This technique is used in the construction of lagoons, landfills, and dams. The second idea is to spray the soil surface with polymer-modified asphalt. This technique has been used to cap landfills to control the release of methane and other organic compounds.

31.4.8 DRAINAGE BOARDS FOR SOIL GAS AND RADON CONTROL

Soil that has been excavated from the basement is commonly used as backfill against foundation walls. This should not be the case where the site material contains clays and silts, particularly organic clays and silts. If local soils are not appropriate, the builder may use gravel to backfill.

Drainage boards are a substitute to backfilling with gravel. Drainage boards have been used for a number of years, particularly in commercial projects and underground houses. Depending on the cost of hauling sand and gravel, a drainage board may be a cost-effective alternative.

It has been hypothesized that a drainage board that is laid up against a house wall might provide an air buffer that can break the pressure connection between the soil and the house interior. This is rather like having a hole in your straw when drinking through it.

31.4.9 SUMMARY OF RECOMMENDATIONS FOR MECHANICAL BARRIERS

31.4.9.1 Rules of Thumb for Foundation Walls

1. Use reinforcing to limit cracking.
2. Seal pipe penetrations.
3. Cap masonry walls with bond beam or solid blocks.
4. Dampproof walls (interior as well as exterior on masonry walls).

31.4.9.2 Rules of Thumb for Slab and Subslab Barriers:

1. Make a slab edge joint that is easy to seal (tooled joint or zip-off expansion joint material).
2. Caulk perimeter crack and control joints with polyurethane.
3. Reinforce slabs with wire mesh to help prevent large cracks and use control joints; caulk the control joint.
4. Drain to daylight if possible, or to a drywell or sewer. If you must use an interior sump pump, seal it.

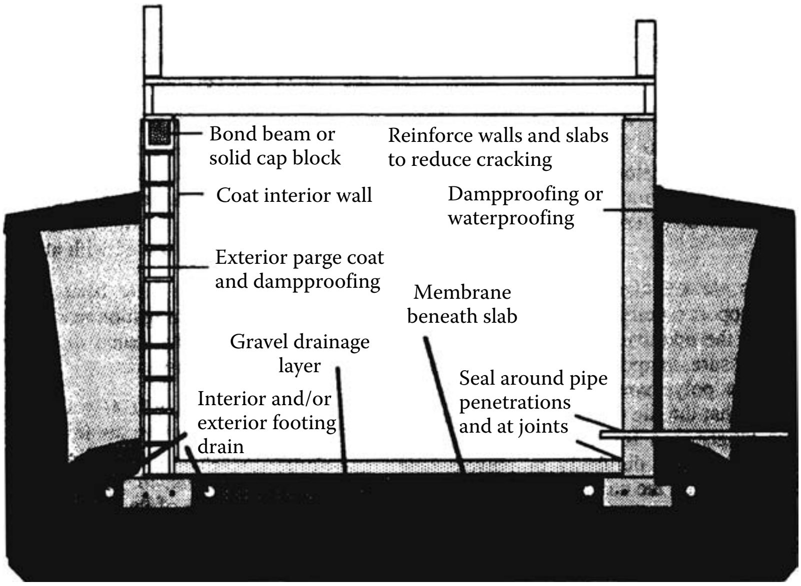


FIGURE 31.16 Summary of mechanical barrier approach for basement foundations. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

5. As a precaution, use interior footing drains (in addition to exterior drains) and 4 in. of No. 2 stone below the slab that drains to the building exterior. In this way, subslab ventilation can be added easily in case a problem is discovered later.[40]

These suggestions are illustrated in Figures 31.16 through 31.18.

31.5 SITE EVALUATION

When siting new residential construction, builders would like to determine the potential for radon problems associated with each building site. Unfortunately, at present there are no reliable, easily

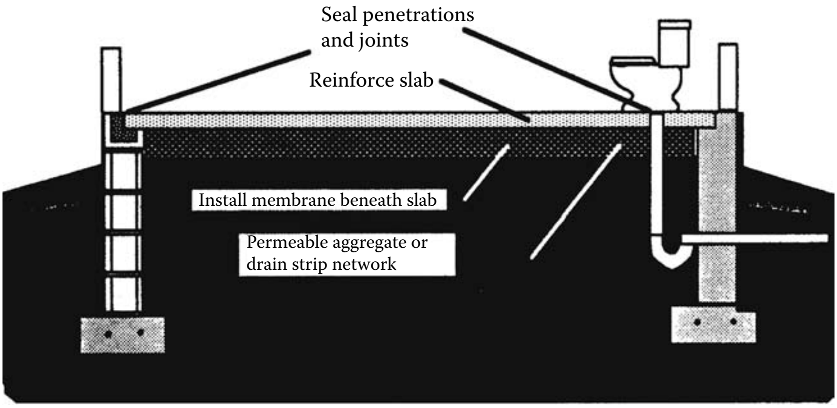


FIGURE 31.17 Summary of mechanical barrier approach for slab-on-grade foundations. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

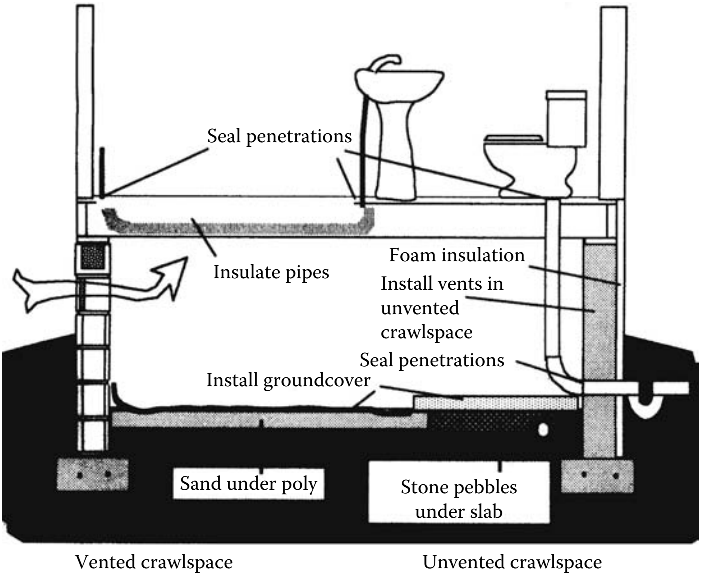


FIGURE 31.18 Summary of-mechanical barrier approach for crawlspace foundations. (Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.)

applied methods for correlating the results of tests made at a building site with subsequent indoor radon levels contained in a house built on that site. Houses vary significantly in their ability to resist radon entry. Bedrock and soils interact in complex ways with dynamic house behavior and environmental factors. There are too many combinations of factors that cause elevated indoor radon concentrations for simple correlations to exist.

In an effort to evaluate the risk of an indoor radon problem occurring in a home built on a particular site, researchers have made many types of measurements. The measurements commonly made include[9]

1. Soil and bedrock radium concentrations.
2. Radon measurements in the interstitial soil and bedrock pores.
3. Permeability of the soil or bedrock.
4. Airborne radiation measurements.

In addition to the above measurements, indexes using soil concentrations in combination with permeability measurements have been suggested by some researchers.[41,42] As elaborated on later in this section, these methods have been successful in establishing relationships between some of the site measurements and indexes, and indoor radon concentrations for specific areas and regions.

Although substantial progress has been made by investigators using geologic, radiation, and other site data to predict areas of high radon risk, it still requires many site measurements to adequately assess a particular site. The judgment that needs to be made is whether or not it is more cost-effective to make the building radon resistant to begin with, or to put the money into site evaluation and possibly avoid the need for radon-resistant construction techniques.

31.5.1 RADON IN THE SOIL

In buildings with indoor radon concentrations greater than 4 pCi/L, the majority of the radon is produced in the soil and enters the building through foundation openings. The radon gas found in soils is a product of the decay of radium-226, a radioactive chemical element present in trace levels in many types of soils and rocks. Radium and radon are elements that are part of the uranium-238 (U-238) decay series. See Figure 31.1 for details. Uranium-238 decays through a chain of radioactive elements. Radiation is released as each element decays. Radon will move through the porous soil or shattered bedrock by convection and diffusion because it is a gas. The other elements in the U-238 series will not easily move through the soil because they are particles and not gases. The amount of radon that enters the house depends on the amount of radon gas or radon parent compounds found in the soil beneath the house. The permeability of the soil, the presence of faults and fissures in underlying and nearby rock, openings between the house and soil, and the driving forces that move soil gas along pathways into the house also contribute to the total radon levels. To have a radon problem requires[9]

1. Radium nearby.
2. A pathway for the gas to move through the soil or rock.
3. A driving force.
4. Openings in the foundation.

31.5.1.1 Attempted Correlations between Indoor Radon and Measurement Made at Sites

Several studies have been attempted to make simple correlations between radon or radium concentrations in the soil and indoor radon concentrations.[43,44] No significant correlations were made between these variables.

The Florida Statewide Radiation Study performed by Geomet[44] illustrates the variability of radon-resistant construction and the resulting problem of trying to correlate soil radon levels with indoor radon levels. The study reports over 3000 paired soil radon and indoor radon samples. A total of 77 soil radon readings were greater than 1000 pCi/L. The two highest soil radon values were 6587.0 and 6367.2 pCi/L. Interestingly, corresponding indoor radon levels for the two highest sites were 6.8 and 0.2 pCi/L, respectively. In addition, almost half of the houses with soil radon levels in excess of 1000 pCi/L had indoor radon levels of less than 4 pCi/L.

The Florida data reported by Geomet have been evaluated and the houses are listed in order of highest measured indoor radon levels. This analysis is shown in Table 31.3.[44,45]

TABLE 31.3
Florida Survey Soil Radon and Corresponding Indoor Radon Concentrations

Indoor Radon Concentration (pCi/L)	Soil Radon Concentration (pCi/L)
32.4	1591.1
29.5	1846.9
28.0	786.9
25.3	555.9
25.3	200.1
25.0	353.9
24.1	439.7
22.9	3561.3
22.9	2144.5

Source: Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.

TABLE 31.4
Swedish Soil Risk Classification Scheme and Building Restrictions

Soil Radon Concentration (pCi/L)	Permeability of Soil	Risk Classification	Building Restrictions
<270	Very low permeability (e.g., clay and silt)	Low	Use conventional construction
270–1350	Average permeability	Normal	Use radon-protective construction
>1350	High permeability (e.g. gravel and coarse sand)	High	Use radon-safe construction

Source: Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.

It is clear from Table 31.3 that soil radon measurements that varied over an order of magnitude produced significantly less than a factor of 2 difference in the indoor radon levels. Predictions of radon potential based on soil radon measurements would be highly suspect based on these data.

In Sweden, soils have been classified as having high, normal, or low radon risk potential based on soil radon concentration and soil permeability. The soil radon values and permeability characteristics used to establish the soil classifications and the corresponding construction requirements are given in Table 31.4. Factors other than soil radon that are considered before classification in Sweden are permeability, ground humidity, and soil thickness. Clearly, Sweden has decided that a number of factors must be addressed to evaluate the radon problem potential of a site. Using the suggested soil radon concentrations but not the permeability guidelines included in the Swedish soil classification scheme, no building restrictions would have been required for many of the houses surveyed in Florida with indoor radon measurements greater than or equal to 4 pCi/L.

Fifteen of the houses in the Florida study with measurements greater than or equal to 4 pCi/L had soil radon concentrations less than or equal to 200 pCi/L. This corresponds to 13.5% of the houses with soil gas less than 270 pCi/L being above the U.S. EPA action level of 4 pCi/L. Nineteen of the 48 houses (39.6%) that had radon in the soil over 1350 pCi/L had radon levels in the house less than 4 pCi/L. This means that almost 40% of the houses that would have been required to be built "radon-safe" under the Swedish guidelines were already below 4 pCi/L using standard construction practices.

The Florida survey was an ideal opportunity to compare soil radon and corresponding indoor radon levels in slab-on-grade construction. By looking exclusively at slab-on-grade houses, additional variables, including depth below grade of basements, and height and ventilation rates of crawlspaces, are eliminated. These variables, which are inherent in common construction techniques used throughout much of the rest of the country, exaggerate the difficulty in correlating indoor air radon and soil radon levels.

The major drawback to using the Florida study to support the correlation between indoor and soil measurements was that the indoor measurements were obtained from 3-day closed-house charcoal measurements, and soil radon was obtained from 1-month alpha track measurements buried 1 ft beneath the soil surface. Comparisons of charcoal and alpha track data are generally not recommended since they are quite different measurement techniques, and represent radon levels over different time periods. However, the study was subjected to numerous quality control checks including deployment of alpha track detectors in 10% of the houses to obtain a check on indoor air measurements made by charcoal canisters. In spite of the measurement drawbacks, the study indicates that soil radon measurements taken alone are not a dependable predictor of potential indoor radon concentration.

TABLE 31.5
Geometric Means for Soil Gas Radon-222, Soil Radium-226, Permeability, RIN, and Indoor Radon-222

Study Area (Soil Type)	Soil Gas Rn-222 (pCi/L)	Soil Ra-226 (pCi/g)	Permeability ($cm^2 \times 10^{-6}$)	RIN[a]	Basement Rn-222 (pCi/L)
Cortland Co. (Gravel)	551	NA	12.0	19.0	17.2
Albany Co. (Gravel)	675	1.0	6.7	18.0	20.2
Rensselaer Co. (Gravel)	1003	1.0	1.1	11.0	9.4
State Wide (Gravel)	602	1.2	4.1	12.0	NA
Long Island (Sand)	164	0.4	0.22	0.8	1.0
Onondaga Co.	1671	2.8	0.12	9.0	6.1

Source: Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.

[a] RIN = 10[soil gas radon (pCi/L)] (permeability) 0.5.

31.5.1.2 Indexes Using Permeability and Soil Radon Concentrations

By making an index from the product of soil radon concentrations and soil permeabilities, a better assessment can be made of the risk of a problem on a given site. A radon index number (RIN) has been applied to three areas in New York State that have sandy, gravelly soils, and it predicted with some confidence the geometric mean of indoor radon concentrations using the geometric mean of the soil radon concentrations and the geometric mean of the square root of the soil permeability.[41] The results of this effort are summarized in Table 31.5. This research also points out the barriers to applying this technique more widely without a substantial amount of additional work. First, the index must be modified by a depth factor when the soil depth to an impermeable layer (water table, some bedrock, and clay) is less than 10 ft. Second, the soil radon concentrations in all three areas were typical of most soils in New York State only. They ranged from slightly below to slightly above the statewide average for radon levels in gravel.

Using the permeability and soil radon measurements for the gravel soils in New York State to compare with the Swedish guidelines would result in a recommendation for radon-resistant techniques to be used in a large fraction of new houses in all the areas listed, except Long Island.

In U.S. EPA Office of Radiation Program's New House Evaluation Program (NEWHEP), two builders in the Denver area, two in Colorado Springs, and one in Southfield, Michigan, installed various radon-resistant features in houses during construction. A sampling of subsequent measurements of indoor radon, adjacent soil gas radon, and soil radium content is summarized in Table 31.6.[36]

The major difference between these data and the Florida survey data in Table 31.3 is that this portion of the NEWHEP data was collected from newly constructed houses where passive radon-resistant construction features were being tested. There are no data on control houses in the same area that did not have those built-in features, making it difficult to compare soil radon measurements with indoor radon concentrations. It appears, however, that passive-only building techniques do not consistently result in indoor radon levels below 4 pCi/L.

31.5.1.3 Variations in Spatial and Temporal Soil Gas Concentrations

Aside from the difficulty in correlating soil radon measurements with indoor radon measurements, various field studies have also shown that obtaining a representative soil gas measurement is difficult. Soil gas radon measurements were made with a permeameter in seven central Florida houses.[42]

TABLE 31.6
Indoor Radon and Soil Radon Measurements in Colorado and Michigan

House No.	Indoor Radon in Basement (pCi/L)	Soil Gas Radon (pCi/L)	Radium-226 in Soil (pCi/g)
HECO 7300	5.9	–	1.3 (90 cm)
HECO 7395	14.5	–	1.3 (surface)
HECO 7395	16.7	–	1.9 (90 cm)
HECO 7419	5.7	710	–
HECO 7423	7.9	1002	1.3 (90 cm)
HECO 7423	–	1779	1.4 (90 cm)
HECO 7425	1.5	620	1.3 (surface)
HECO 7425	–	–	0.7 (90 cm)
HECO 7427	3.0	1430	1.1 (surface)
HECO 7427	–	1316	1.4 (90 cm)
HECO 7448	11.8	930–	
HECO 7455	0.7	1240	0.4 (surface)
HECO 7456	2.3	996	0.6 (90 cm)
HECO 7458	7.2	2030	–
HECO 7458	3.5	388	–
HECO 7459	0.9	1095	1.0 (surface)
HECO 7459	–	1014	1.9 (30 cm)
HEMI 30001	1.8	–	*
HEMI 30002	0.9	–	*
HEMI 30003	4.2	–	*
HEMI 30004	1.7	–	*
HEMI 30005	3.6	–	*

Source: Adapted from U.S. EPA, *Radon-Resistant Construction Techniques for New Residential Construction—Technical Guidance*, EPA/625/2-91/032, U.S. Environmental Protection Agency, Washington, DC, February 1991.

A permeameter is a soil gas and permeability measurement device that allows soil gas to be sampled at various depths. In this study, the radon concentration was the average of samples collected at depths of 60, 90, and 120 cm. Four to six samples were collected from the yard of each house at distances of 0.5–4.5 m from the house foundation. Soil radon concentration measurements in each of the seven yards varied by factors of 1.3–6.4, with an average variation of 3.1. In another study in the Piedmont area of New Jersey,[46] soil radon was measured in the front, side, and backyards of seven houses. Grab samples and 3-month alpha track samples were obtained from a depth of about 1 m. The grab sample radon measurements varied by a factor of 50 between houses and by as much as a factor of 46 between test sites at a single house. The average variation for each of the seven houses was 12.9. The alpha track results showed seasonal variations of approximately an order of magnitude difference between fall and winter/spring soil gas levels. The soil alpha track results did not compare in general with the results obtained by grab sampling. For example, a factor of 30 increase in radon from the front to backyard was observed in one house by grab sample data, while alpha tracks taken in the front and backyards were similar. In a second house, the opposite was observed: grab samples collected in the front and backyards varied by less than a factor of two, while alpha track measurements in the same yards varied by a factor of 14.[46] In another seven-home study in the Piedmont area,[11] a large variability in permeability measurements and soil gas radon concentrations was seen. Spatial variation in soil permeability at individual homes ranges from a factor of 10–10,000. Temporal variations in soil permeability at a given test hole ranged from a factor of 2 to a factor of 90. Spatial variations in soil gas radon ranged from less than a factor of 2 to a factor of 200 in a given site. Temporal variations in soil gas radon ranged from less than a factor of 3 to a factor of 40 for a given test hole.

As indicated from the data, indoor radon concentrations cannot yet be predicted from soil radon values. The possibilities are not promising for designing a device and/or technique that builders can rely on to exclude building sites as potential indoor radon problems. As shown by the Florida and New Jersey data, multiple measurements would be required at each building site, and even those measurements can vary by orders of magnitude. Until the lot has been cleared, rough grading completed, and the foundation hole dug, access to the soil that actually produces the radon gas in the house is difficult, if not impossible. Few builders would decide not to build on a lot after they have incurred the costs of purchasing the lot and digging the foundation. In addition, many houses use fill dirt brought in from other locations. Unless the fill dirt is also characterized, additional radon potential may be missed or, on the other hand, the actual potential for radon entry may be overstated.

In summary, at present, individual building lots cannot be characterized reliably for radon potential, and because of the inherent problems that have been identified, builders should not expect to be able to make these measurements or pay someone else to make them reliable. Work to enhance the accurate prediction of radon-prone areas is continuing within U.S. EPA and among other research organizations.

31.5.2 RADON OBSERVED IN NEARBY BUILDINGS

Another approach for estimating the risk of a radon problem on a particular site is to examine measurements from nearby existing buildings. In U.S. EPA's Radon Reduction Demonstration Program for existing buildings, those with elevated radon levels generally have been identified through prior high-radon measurements in other buildings in the neighborhood. Although it is possible to have isolated pockets of radon gas in the soil beneath a single building, most radon-prone buildings are located in a geological setting common to most other buildings in the general vicinity or region. Because of the many variables that affect radon entry into a building, buildings with elevated radon can be found adjacent to buildings with very little radon. However, statistically, the presence of an elevated radon building in a neighborhood or a significant number of elevated buildings in an area as large as a county increases the likelihood of other elevated-radon buildings in the same area.

A classic example of one elevated radon building leading to the discovery of other elevated-radon buildings in the area occurred in Clinton, New Jersey. A property owner in the Clinton Knolls subdivision read about the radon problem in the Reading Prong area of Pennsylvania and decided to obtain a charcoal canister and measure the radon level in his own house. When he received a very high radon reading, he notified the New Jersey Department of Environmental Protection (NJ DEP). The NJ DEP surveyed the neighborhood, making charcoal canisters available to property owners who were willing to have the radon level checked in their buildings. A survey showed that 101 of 103 properties tested had radon levels above the U.S. EPA action level and over half of the properties had more than 25 times the action level.[47]

The Clinton experience can be contrasted with radon observations in Boyertown, Pennsylvania, where buildings with radon concentrations over 500 times the U.S. EPA action level were found adjacent to buildings below the action level.[48] Therefore, the presence of elevated-radon buildings in a neighborhood is at best only an indication that the probability of having a radon problem has increased.

31.5.3 AIRBORNE MEASUREMENTS

The State of New Jersey has been able to correlate airborne radiation measurements to clusters of buildings with elevated indoor radon.[49] In this study, researchers compared airborne γ-ray spectrometer data with indoor radon data to see if any trends emerged. For the conditions in New Jersey, it was found that areas with airborne anomalies of 6 mg/L equivalent uranium or greater were likely to have clusters of homes with elevated radon. This could be a valuable tool for health officials who are trying to make the greatest public health impact for the most reasonable cost. Inasmuch as it alerts a region to be wary, it is helpful, but it is probably not of much benefit in the assessment of an individual site.

31.5.4 RADON IN WATER

Between 2% and 5% of the radon problems found in the United States can be attributed to radon in water.[50] The most significant radon-in-water problems observed so far in the United States have occurred in the New England states. Houses with individual or community wells seem to have the greatest potential for a problem since the water in those systems is usually not well aerated.

Radon dissolves into groundwater from rocks or soils. When the water is exposed to the atmosphere, some of the dissolved radon is released. As a rule of thumb, there is an increase of about 1 pCi/L in the air inside a house for every 10,000 pCi/L of radon in the household water.[50] Higher radon levels have been observed in individual rooms when water is heated or agitated, such as during shower use.[51] Builders should be aware that houses require groundwater as the house water supply could have a radon problem. The only way to be certain that the groundwater is not a potential radon source is to have the water from the well tested. Some states and private companies provide test kits for this purpose. It should also be noted that radon concentrations in water, like radon concentrations in the air, can vary significantly.

If a well has not been drilled, a nearby well may be an indicator of potential radon problems. Identifying potential radon-in-water problems by using the results from adjacent wells is subject to the same problems that were mentioned earlier. There is no guarantee that the neighbor's well is producing water with the same characteristics as the new well will produce since it may not be from the same stratum. The limited data available on houses with radon-in-water problems indicate that adjacent houses with similar wells sometimes produce similar radon-in-water problems and sometimes do not. However, few isolated radon-in-water problem houses have been observed.

In summary, because of the small percentage of houses with radon-in-water problems, few builders will have to deal with this issue. However, if a house is being built in an area known to have many houses with radon-in-water problems, drilling the well and testing the water supply prior to construction are advised. If a house is built prior to identifying a radon-in-water problem, resolving the problem can be more difficult since space will not have been allowed for the radon-in-water mitigation techniques available.

31.5.5 RADON IN BUILDING MATERIALS

A small percentage of the buildings in the United States with indoor radon concentrations in excess of 4 pCi/L can be attributed to building materials. Most of the building material problems have arisen from the use of known radium- or uranium-rich wastes such as aggregate in block or as backfill around houses. None of the houses studied in the U.S. EPA Radon Reduction Demonstration program have had any identifiable problem associated with radon from building materials.

Builders should be aware that this is a potential problem but, unless building materials have been identified as radium- or uranium-rich, the chances of obtaining radon from building materials are very slim.

31.6 PLANNED VENTILATION: MECHANICAL SYSTEMS

New construction offers the opportunity to plan and install mechanical equipment so that fresh outdoor air is supplied to the living space and the air pressure relationships between the inside of the building and the outside reduce the influx of soil gas. This approach requires a better understanding of moisture and airflow building dynamics than the others covered in this chapter. For example, it is important to understand what effect manipulating interzonal air pressure differences will have on the risk of condensation in the building shell, the entry rate of soil gas, the comfort of the occupants or the risk of increased spillage, and downdrafting of combustion devices. By careful planning, the risk of these and other potential problems can be reduced; however, no systematic research has been carried out to evaluate this approach for radon control. Many variables come into play in trying to design a mechanical system and a building shell that interact with the environment in the ways that are best for the health of the occupant and the building itself.

31.6.1 Interdependence of Mechanical Systems and Climate

Traditionally, residential mechanical equipment has been treated as independent devices that have little or no impact on the rest of the building other than the obvious stated purpose. Bath fans, dryers, and kitchen ranges are assumed to exhaust moisture, lint, and cooking by-products, but to have no impact on the performance of chimneys. Instances have been reported that show that this is not the case in some houses where the fireplaces and other combustion appliances backdraft[52] when one or more of the exhaust fans are in operation. Houses have been reported in which the operation of exhaust devices increases the radon concentration.[53] Houses have been found in which pressure differences between different rooms of the house caused by HVAC distribution fans have increased energy costs,[54] occupant discomfort,[54,55] condensation of the building shell,[55] and radon concentrations in parts of the houses.[29,56] All of these effects are the result of air pressure relationships created by the interaction of equipment, indoor/outdoor temperature differences, wind velocity, and moisture and radon availability.

To a large extent, wind, temperature, moisture, and radon are beyond the control of the residential designer or builder. True, good drainage practice and the techniques outlined earlier in this chapter can divert moisture and radon from a building, but the amount of rainfall or radon produced is independent of anything a builder can do. The pieces of this house dynamics puzzle that the builder or designer can affect are the mechanical devices used in the building.[57]

31.6.2 Guidelines for Planning Mechanical Systems

Specific guidelines for planning mechanical systems so that they minimize problems resulting from their interaction with each other and other climate-driven building dynamics are impossible to determine. The major reason for this is that buildings constructed on different sites in different climates have very different behavior. For example, a ranch house built in Florida has a warm, humid climate with which to work. This means that the space conditioning system is probably dominated by air conditioning and may also incorporate dehumidification. If the same house were located in Arizona, the cooling need would be there but there would be no need for dehumidification. If the same house were built in Minnesota, the space conditioning would be a heating system and might require dehumidifying in the summer and humidifying in the winter. In the Florida house, a case can be made for locating a vapor barrier on the outside skin of the building because the risk of condensation of the building shell is near the cooler indoor surface. In Arizona, there is seldom the risk of condensation because of the small amount of water present in the environment. In Minnesota, the risk of condensation of the building shell would be at the cool outside surface near the siding. In terms of risk of condensation it would be acceptable to pressurize the Florida house to control radon, because, as the outgoing cool interior air is warmed up, the risk of condensation decreases. Pressurizing the house in Minnesota is almost certain to result in condensation during the winter months, as the warm interior air cools down on the way through the building shell.

At this time, a cohesive body of knowledge that has enough depth to make recommendations for different site conditions within the several U.S. climatic regions does not exist. However, many individuals do have enough insight to design intelligently for their own regions, and there are guiding principles that are general enough to apply for all situations:

1. *Preserve the intended purpose of all mechanical devices:* A heating system should still deliver the required amount of heat in a short amount of time. Exhaust fans should remove the moisture, fumes, and contaminants.
2. *Be sure that applicable codes and standards are followed:* Begin with the life and safety codes. The intent of this chapter is to reduce the risk resulting from radon, but not in a way that increases other risks. Especially important in this regard are the National Fuel Gas Code,[58] National Fire Protection Code (NFPA1), and National Electric Code.[59] Also the CABO One and Two Family Dwelling Code[32] will be very helpful. There are thousands of code jurisdictions in the United States; therefore many issues will have to be dealt with locally.
3. *Plan to reduce soil gas entry:* If possible, plan the mechanical systems so that soil gas is not drawn in by lower air pressure in the basement or ground floor rooms (slab-on-grade and crawlspace). Efforts along these lines can be made by minimizing the amount of air drawn from those rooms by exhaust fans, conditioned air return ductwork leaks and grills and sealing bypasses that penetrate floors. Air can also be supplied to these spaces to make up for the amount of air exhausted. If the exhaust air rate equals the supply air rate for a single zone, then pressure differences should be minimized. Supply air can cautiously be increased to pressurize these spaces and prevent soil gas entry, but the effect on moisture dynamics, combustion equipment, and code acceptability must be kept in mind. An example of this is the relatively common practice of opening warm or cool air supply grills in a conditioned basement. This uses conditioned air and the air circulation blower to pressurize the basement (or at least reduce the negative pressures).
4. *Plan to supply air to the areas of the house that need fresh air:* A planned mechanical system also allows the builder to direct fresh air into the living spaces. This will reduce radon concentrations by diluting it with outdoor air depending on how it is supplied; it may also reduce the driving forces that draw soil gas into the building. Supply air will be drawn in by the mechanical devices, stack effect, and wind pressures that exhaust air from the building. The incoming air will enter either through the unintentional cracks and holes left in the building or through passive vents that can be installed in the building shell. Passive vents allow the builder to let the fresh air in where it is wanted. Bedroom closets are a typical location. Supply air can also be powered by a fan and ducted to the areas where it is wanted. Heat recovery ventilators are a well-established method of doing this. In either case, fresh air will be added and the pressure difference between the inside and outside will be reduced.
5. *Take no risks with carbon monoxide:* This is a special warning to carefully ensure that combustion products are properly exhausted from the house. Of course, the place to begin is with the appropriate codes (UMC, NFUC, CABO, and NFC), but keep in mind that even if something is not against any codes it may still be dangerous. For example, a system that backdrafts a fireplace because it removes air from the upstairs of a house might not violate any codes, but is certainly a hazard. Many new heating plants either are power vented or have dedicated outdoor combustion air.

The two most generally applicable and useful guidelines for planning are

1. Air moves from higher to lower pressures.
2. Lowering the temperature increases the relative humidity.

These two rules help predict the effect of air exhaust and supply on the transport of radon and moisture and whether or not to expect increased or decreased risk of condensation.

31.6.3 TWO ILLUSTRATIONS

Here are two situations illustrating the issues involved in trying to understand the interactions between the mechanicals and the climate. These are illustrations. They do not apply to every house in the climates described.

First, consider a house in a cold, humid climate. The way it ordinarily operates is as follows. The warm inside air exits through cracks and holes at the top of the building. The warm air leaving through these cracks and holes cools down as it leaves, increasing the possibility of condensation. The suction placed on the lower part of the building increases the flow of radon-laden soil gas into the basement where it is drawn into the leaks in the cold air return and distributed to the rest of the house by the warm air circulation system. All of the pieces in this scenario are likely to occur. Other things that could present problems might be bathroom fans that do not have much airflow or are vented into the attic.

If the upstairs portion of the house had the area of cracks and holes into the attic and walls reduced, then exhausting a small amount of air from the house would draw outdoor air in through the remaining cracks and holes. This would reduce the risk of condensation in the building shell because the air being pulled in would become warmer, lowering its relative humidity. However, exhausting air from a tighter house might increase the amount of furnace downdrafts and the influx of radon.

Using a furnace that draws combustion air from outdoors or that is power-vented solves the downdraft problem and probably has little effect on the radon influx when compared with a furnace that uses indoor air for combustion purposes. If it is desirable for the upstairs part of the house to run slightly negative to eliminate moisture, ensure that the heating system has been designed so that backdrafting will not occur when bathroom, laundry, and kitchen fans are used. If a centralized exhaust ventilation system is used, remember to vent dryers and kitchen ranges separately. It is poor practice to have grease-soaked lint with a fan blowing air over it in the event of a fire.

If the air exhausted from the upstairs part of the house is diverted into the basement, the basement might be slightly pressurized and the influx of soil gas stopped. If the air leaks between the basement and upstairs and the basement and outside have been sealed, then a smaller volume of air will be able to pressurize the house. If the basement is insulated along the perimeter walls, it would be possible to use the air distribution ductwork to pressurize the basement and depressurize the upstairs. This could be done by planning the distribution ductwork so that it is easy to seal the joints and then opening grills in the supply ductwork. For this to be an effective radon control, the fan would have to run all the time. A two-speed distribution fan could be used that would run on low speed all the time and be boosted to high speed when heating or cooling is called for.

Ventilation systems could further reduce indoor radon levels by dilution with outdoor air and, depending on how it is distributed, could reduce driving forces that draw in soil gas. If outdoor supply air is added to the return air side of the ductwork, then some (50–100 cfm) ventilation air would be introduced and distributed to the house whenever the fan was running. Some new heating systems combine heat recovery ventilation (HRV) with warm air space conditioning. This would add about 200 cfm of fresh air whenever the HRV was operating and 50 cfm whenever the circulation fan was running. The American Society of Heating Refrigeration and Air Conditioning Engineers has revised their residential ventilation guidelines to recommend the capability of providing one-third of an air change per hour (ACH) for residences. An HRV would provide that for a 4500 ft^2 house with 8 ft ceilings, and makeup air for the return ductwork would meet that for a 1100–2200 ft^2 house with 8 ft ceilings. In addition to radon control, this amount of ventilation has the benefits of control of the unavoidable contaminants released by washing, cooking, and body functions. In a heating climate where there is moderate to heavy rainfall, powered ventilation in the winter can be used for humidity control.

To summarize, a mechanical system that is planned to control indoor air contaminants (including humidity, radon, combustion gases, and body odors) and reduce the risk of condensation in the building shell in a cold humid climate should include

1. Power-vented or dedicated outdoor combustion air heating systems.
2. Depressurized upstairs/pressurized basement (possibly using the distribution system).
3. Air supplied to the building with or without heat recovery.
4. Tightened building shell to minimize the amount of air needed to pressurize the basement and to lower the neutral pressure plane.

Situation two is a house constructed in a warm humid climate. It is a single story slab-on-grade house with air conditioning in the attic. There is a single return air grill located in the hallway that leads to the bedrooms. When the air handler is not moving air, the conditioned indoor air mass tends to create a reverse stack effect preventing soil gas from entering. When the air handler is running the house at 2 Pa negative pressure, it overwhelms the reverse stack effect because the supply ducts in the attic are far more extensive than the returns and have more leaks. When the bedroom doors are closed the entire living area goes to about 10 Pa negative pressure. In both of these lower indoor air pressure conditions, soil gas is drawn in through the many cracks and penetrations of the floor slab. Space heat, when it is needed, is supplied by a heat pump cycle through the air conditioning ductwork. In the summertime, when it is warm and humid outdoors, the negative pressure in the building draws air in through the cracks and holes in the building shell. As the air gets adjusted to the cool interior, the relative humidity increases, and the risk of condensation of the building shell near the interior sheetrock increases.

Pressurizing the house would reduce both the soil gas entry and the chances of condensation occurring. This could be accomplished by planning the ductwork so that it could be easily sealed to reduce losses, running a more extensive return air system, and using dampers so that more air is supplied to the house than is exhausted. The difference between supply and exhaust will be lost through the building shell. By making the building shell as airtight as possible, the amount of air it takes to do this will be smaller. If more air is supplied to the building than is removed by the return air ducts, then the difference must come through leaks in the return air ductwork. It is possible that an outdoor air supply duct will have to be run to the return air side of the air handler to make the pressurization (and coincidentally ventilation) air available. The incoming air must be cooled down to house temperature resulting in a sensible and latent heat gain energy penalty. In this case, two approaches could be to reduce the cooling energy penalty. First a high-efficiency cooling coil using dehumidifying heat pipe technology could be used to precondition the incoming air. Second, a heat pump domestic hot water heater could be used to precool the incoming air and heat the hot water at the same time.

The bathroom, laundry, and kitchen exhausts would have to operate as normally installed and enough pressurization air would have to be added so that the intermittent operation of these exhausts would not overcome the time-averaged benefits of house pressurization. Combustion products are probably not an issue because there is no combustion device in the house.

The system is summarized as follows:

1. Pressurize the house using the air-handling system (concurrently adding ventilation air).
2. Reduce the cooling load penalty by preconditioning the incoming air (reducing the indoor humidity and/or heating the domestic hot water).

31.6.4 CONCLUSIONS

Radon is an invisible, odorless, and tasteless gas, with no immediate health symptoms, that comes from the breakdown of uranium inside the earth. Simple test kits can reveal the amount of radon in any building. Buildings with high levels can be fixed with simple and affordable venting techniques.

U.S. EPA estimates that one in every 15 homes nationwide has a high radon level at or above the recommended radon action level of 4 pCi/L per liter of air. Radon is the second leading cause of lung cancer. Breathing in high levels of radon can lead to lung cancer; yet it is easy to avoid. Radon can be easily detected and fixed through well-established venting techniques.

It is obvious that an approach in new construction that matches mechanical system design and installation to the multiple needs of occupant health, safety, and comfort and to building longevity requires an understanding of how the climate and the building interact. This approach is both more comprehensive in effect and complex in design and installation than the other techniques outlined in this chapter. This line of attack should only be pursued by qualified people who have training and experience in mechanical systems, because it is too easy to overlook an important aspect of the interconnections involved. In many ways it is a more sophisticated control strategy than soil depressurization or mechanical barriers.

Anyone who is buying or selling a real estate property, the real estate and relocation professionals, property inspectors, and others are referred to U.S. EPA's booklet: *Home Buyer's and Seller's Guide to Radon*.[60] For the determination of an appropriate radon reduction method and the maintenance of radon reduction systems one can refer to the *Consumer's Guide to Radon Reduction: How to Reduce Radon Levels in Your Home*.[61] For listings of radon measurements and radon mitigation professionals, laboratories, mitigation devices, and chambers of commerce approved radon training courses, refer to the official website of the National Radon Safety Board.[62] Commercial and industrial property owners should read this chapter and are referred to CRC Press publication[57,63] for proper radon control.

For further promotion of Radon Awareness, the U.S. EPA has designated January 2009 as National Radon Action Month. The aim of National Radon Action Month is to increase the public's awareness of radon, promote radon testing and mitigation, and advance the use of radon-resistant new construction practices. U.S. EPA also emphasizes the effects radon can have on children and young workers as part of the Healthy Environmental Program. Young people are more sensitive to radon because their lungs are smaller and their respiratory rates are twice as high. The readers may view, listen to, and/or order one of the Agency's TV, radio, or print ads; please visit http://www.epapsa.com.[64]

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32 Treatment of Battery Manufacturing Wastes

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CONTENTS

32.1 INTRODUCTION

32.1.1 HISTORICAL, CULTURAL, AND BATTERY TECHNOLOGY DEVELOPMENT

The existence and use of batteries is thought to have roots in prehistoric times, whereby, through archeological discoveries, it was discovered that prehistoric people had created an electrochemical cell that would qualify, under today's definition, as a battery. A curiosity found in Baghdad in 1932 was probably representative of battery technology dating as far back as 2500 years.[1] Such a primitive battery cell comprised an iron rod that fits into a copper cylinder. Presumably some fluid, which served as an electrolyte, escaped preservation. Notwithstanding its simplicity, such a cell would have provided current to permit primitive jewelers to electroplate precious metals and make copper shine either like gold or as silver.[1] Although such archeological evidence provides us with some glimpse into the far past, the history of modern-day battery development begins in the 1780s with the discovery of "animal electricity" by Luigi Galvani (1737–1798), which he published in 1791. This Italian anatomist and physician observed that muscles of a frog's leg would contract when jolted with a static electrical spark delivered from a Leyden jar. In further experiments in bioelectrogenesis, as the knee-jerk reaction came to be called, Galvani noticed that the frog's leg would also react to two different metals being applied to the muscle.[1] This behavior was also observed when a dead frog's leg was used in the experiment. From these series of experiments, Galvani deduced that the muscle was producing electricity. It is therefore not surprising that his name has since become intimately associated with electricity to the extent that the process of producing electricity by chemical reaction is termed galvanism.[1]

More important to the history of the current battery was another Italian physicist, one of Galvani's correspondents, Alessandro Volta (1745–1827). Volta realized that the frog's moist tissue may be replaced by cardboards soaked in salt water, and the frog's muscular response could be replaced by another form of electrical detection. Volta came to believe that contact between his dissimilar metals created the electricity that caused the frog's muscle to contract, thus opposing Galvani's deduction.[1] Having already studied the electrostatic phenomenon of capacitance, which required measurements of electric charge and electrical potential, Volta was able to detect electric current flowing through his system, now called the voltaic cell. In its simple construction, the voltaic cell comprised two bowls filled with a salt solution. The bowls were linked together with arcs of metal, one end of the arcs being copper and the other zinc. Besides, each bowl had two ends of two different metal arches in it. The device, the first modern battery, produced electricity by the chemical reactions of the metals in solutions.[1]

In 1799, Volta invented the battery by placing many voltaic cells in series, literally piling them one above the other. This voltaic pile gave a greatly enhanced electromotive force (emf) for the combination, with a voltage of about 50 V for a 32-cell pile. By 1800, Volta had simplified the arrangement of his bowl-battery into a stack of small disks, alternating zinc and copper with a disk of leather saturated with salt solution separating each metal disk, which generated a substantial electric current (Figure 32.1). In honor of volta's ground-breaking accomplishment, the unit of electrical potential, the volt, was named after him.[1] Unfortunately, these early batteries were only useful in limited experimental applications, but were impractical for a large current drain. Such limitations prompted further improvement of the voltaic battery technology. For instance, in 1836, a British chemist John Frederic Daniell improved Volta's cell by moving the copper and zinc into a bath of sulfuric acid to create the gravity or Daniell's cell. However, Daniell's cell did not last long as it suffered from hydrogen accumulation at the cathode. Three years later, William Robert Grove added an oxidizing agent to prevent hydrogen accumulating at the cathode from reducing the voltage the cell produced as it operated. Grove's construction comprised a two-part cell involving a porous pot containing sulfuric acid in which an amalgamated zinc anode was placed. The porous pot was, in turn, placed in a second vessel containing nitric acid and a platinum cathode. In 1841, a German chemist, Robert Wilhelm Bunsen, improved Daniell's cell by substituting cheap carbon for the expensive platinum cathode.[1]

However, the first enduring invention came from Gaston Planté; then working in France, he developed the first lead–acid storage batteries in 1859 (Figure 32.2a) for use in telegraph equipment.[1,2] Notably, Planté's device was not only the first successful storage cell, but was also rechargeable. Further refinement of his battery has, up to date, not been on its electrochemistry, but rather, on the packaging. This battery type is in use today in automobiles and the gelled-electrolyte batteries used in uninterruptible power systems.[1] Inasmuch as Planté's device was a great success, yet many other scientists continued in their search for better designs, as well as electrochemical

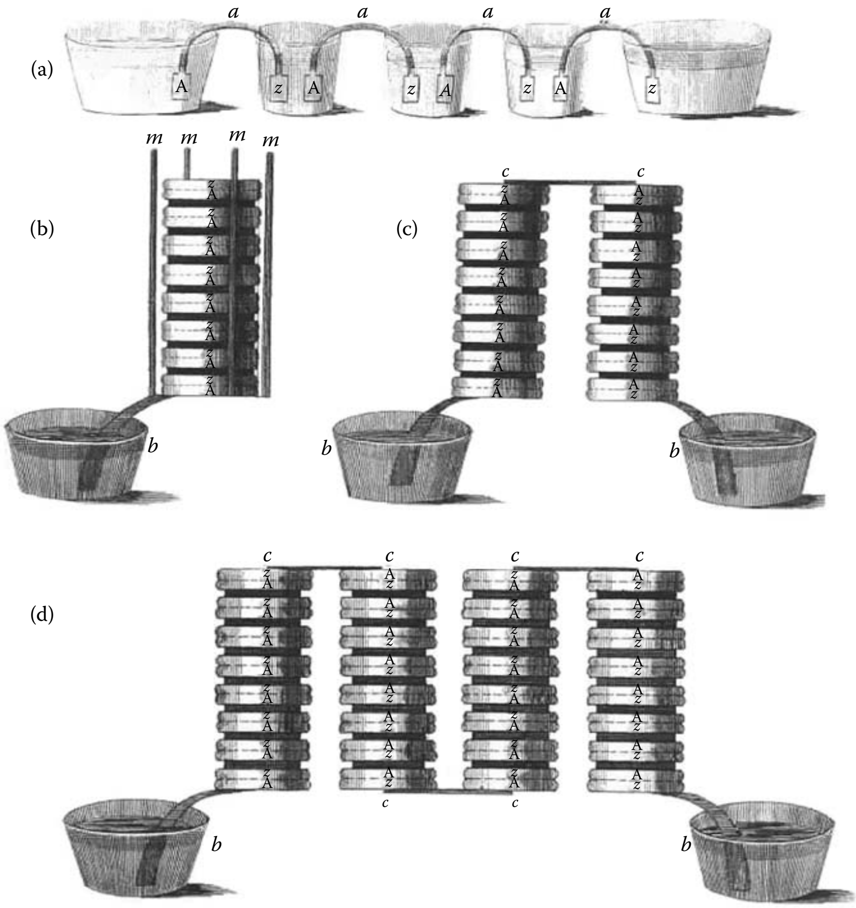

FIGURE 32.1 Volta's 1800 illustration of the voltaic cell from its early development as a series of buckets (a) to a series of cell piles (b–d).

systems. Such efforts yielded more dividends as further contribution to battery development was made by yet another French engineer, George Leclanché, when he developed his wet cell in 1866. In his design, Leclanché used a cathode of manganese dioxide mixed with carbon and an anode of zinc in the form of a rod (Figure 32.2b).

The electrolyte was a solution of ammonium chloride that bathed the electrodes. Like Planté's electrochemistry of the lead–acid battery, Leclanché's electrochemistry survives until now in the form of zinc–carbon dry cells and the use of gelled electrolyte.[1,2] In their original wet form, the Leclanché electrochemistry was neither portable nor practicable to the extent that several modifications were needed to make it practicable. This was achieved by an innovation made by J. A. Thiebaut in 1881, who through encapsulating both zinc cathode and electrolyte in a sealed cup avoided the leakage of the liquid electrolyte. Modern plastics, however, have made Leclanché's chemistry not only usable but also invaluable in some applications. For example, Polaroid's Polar Pulse disposable batteries used in instant film packs use Leclanché chemistry, albeit in a plastic sandwich instead of soup bowls.[1]

The progress of battery technology could not wait for the development of plastics. Scientists continued to look for ways of solving the problem of fussy liquids entirely. This came to fruition when battery chemistry was further modified to produce the dry cells. This breakthrough made

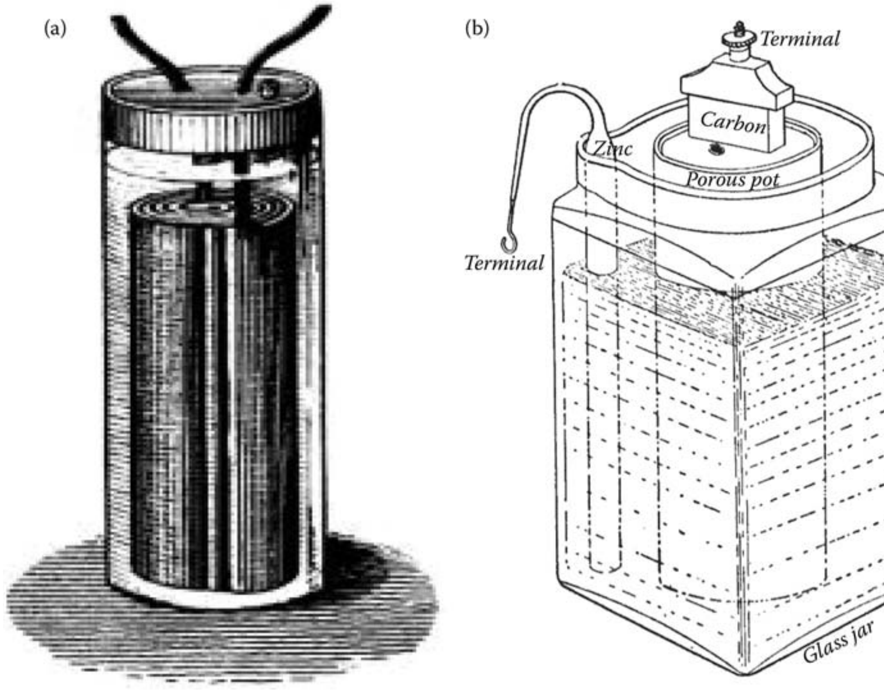

FIGURE 32.2 Early designs of Planté's (a) and Leclanché's (b) cells.

batteries the convenient power source they are today. Credit goes to Carl Gassner of Mainz, Germany, who patented this technology in 1887.[1] In constructing his dry cell, Gassner mixed ammonium chloride with plaster of paris to create a paste, with a bit of zinc chloride added to extend the shelf life. The manganese dioxide cathode was dipped in this paste, and both were sealed in a zinc shell, which also acted as the anode. Unlike previous wet cells, Gassner's dry cell was more solid, did not require maintenance, did not spill, and could be used in any orientation. It provided a potential of 1.5 V, and its first mass production was under the brand name the Columbia dry cell. This type of cell was first marketed by the National Carbon Company (NCC) in 1896.

In 1899, the nickel–cadmium battery, the first alkaline battery, was invented by a Swedish scientist named Waldmar Jungner. The special feature of this battery was its potential to be recharged. In construction, nickel and cadmium electrodes in a potassium hydroxide solution, it was the first battery to use an alkaline electrolyte. This battery was commercialized in Sweden in 1910 and reached the Unites States in 1946. The first models were robust and had significantly better energy density than lead–acid batteries, but nevertheless, their wide use was limited because of the high costs.

Although the technology has been refined by over a century of development, the concepts and chemistry are the same as Gassner's first dry cells. Most of today's exotic rechargeable battery systems such as nickel–cadmium, nickel–metal hydride, and the variety of lithium-based cells are twentieth-century developments. It is therefore notable that new chemistries are no longer being discovered through experimentation as the principles of battery design and operation are well known, but rather, new efforts in battery design focus on making the optimal chemistries work in practical cells.[1] The growth of battery technology has since revolutionalized and several models of long-lasting battery life have been developed. These range from the nickel metal-hydride battery of the late 1980s to the lithium and lithium-ion batteries of the 1970s and 1990s.

32.2 OVERVIEW OF THE MANUFACTURING PROCESS

Batteries are made up of a positive electrode, a negative electrode, and an electrolytic solution. Battery types differ from each other in the chemical processes involved in the conversion of chemical energy into electrical energy. In essence, the manufacturing process of all batteries covers the making of the positive and negative electrodes, the electrolyte materials, the separators, and the materials that would be used as housing of a complete battery. In addition, the process of conversion of chemical energy into electrical energy in all battery types involves the charge and discharge reactions. During these two reactions the electrolyte plays an active role in the two electrodes. For instance, when lead–acid cells are discharged, the lead dioxide (PbO_2) of the positive electrode and sponge lead (Pb) of the negative electrode are both converted to lead sulfate ($PbSO_4$). On charge, the lead sulfate in the positive electrode is converted to lead dioxide (PbO_2) and the lead sulfate in the negative electrode is converted to sponge lead. The electrolyte, sulfuric acid, is an active component in the reactions at both electrodes. The basic process of battery manufacture may be performed either manually or by using highly automated machines. The type of process used depends on the size of the company, and its manufacturing capacity. Further, various methods are used all over the world in the manufacture of different parts of a battery, which are firmly linked to the type and electrochemistry of the battery being manufactured. While a few of the major battery manufacturers make their own alloy, oxides, separators, and containers/covers, most of them purchase rather than fabricate these materials.[3]

32.2.1 MANUFACTURING PROCESS

In a number of battery types, the anode may be a pure metal, an alloy, or a metal salt, while the cathode may be metal oxide or a mixture of oxides of metals and other elements. Therefore, production of electrodes involves various raw materials that must be processed to the required standards. Although batteries differ in the fine details, they are virtually manufactured following similar process steps. In this chapter, the manufacturing steps are hereby described using, as an example, the production process of the lead–acid reserve battery. The manufacturing process as briefly described by Dahodwalla and Herat[3] can be divided into the following sections:

32.2.1.1 Oxide Milling

This is the process in which soft lead (99.97% pure) is converted into lead oxide. To achieve this, solid bars of soft lead are melted at 400–425°C and the molten lead is oxidized to form lead oxide. The lead oxide so formed, along with some percentage (about 26%) of free lead, is then passed into a cyclone separator and a bag filter. This step is important as it allows the particles of lead oxide to be separated from the air stream in these equipments. The separated lead oxide is then transferred using screw conveyors into storage tanks, called silos. However, air emissions from the bag filter contain lead particles, a source of pollution.

32.2.1.2 Grid Casting

Grid casting involves melting bars of lead alloy in a lead melting pot. This is followed by pumping molten lead into the grid molds, which are subsequently cooled by means of cooling water. After the mold has cooled the alloy, it opens to discharge the grid, which is subsequently trimmed to remove the excess lead. The resultant cuttings are then recycled into the lead pot. All these operations take place in one machine, which is completely automated. During this process, different types of lead alloys are used for casting of grids. They may have different thicknesses depending on the thickness of the alloys used. Furthermore, grids are classified on the basis of the type of alloy used and the thickness of the grid casted. It should also be noted that melting of lead causes dross formation as well as generation of some solid wastes. Nevertheless, rejected grids are remelted in the lead melting pot and recycled.

32.2.1.3 Paste Manufacturing

Two types of pastes are manufactured, one for positive plates and the other for negative plates. For the lead–acid batteries, the materials required for paste manufacturing are lead oxide, sulfuric acid, water, and other additives. These additives are different for positive and negative pastes. The ingredients, in the paste mixer, are mixed together in a fixed ratio (ratio of various ingredients depends on the type of grid to be used for plate manufacturing) to form the paste, which is then pasted on the grids. Lead oxide is the major ingredient used in paste manufacture accounting for about 85% of the paste. During paste formation, losses occur due to evaporation and the vapors resulting from the process are treated in a scrubber and then discharged through a stack.

32.2.1.4 Grid Pasting

Plates are formed as a result of applying paste onto grids using machines. The pasting machine is divided into four sections, namely, feeding, pasting, drying, and collection. The grids are fed onto the conveyor belt by a feeding mechanism and the paste is applied on them. The pasted grids are passed between rollers where even spreading of paste occurs. Subsequently, the paste is dried in a flash drier and the dried plates are collected and stacked at the extreme end of the pasting machine. The plates are moved into different sections, namely, pasting, drying, and collection, with the help of the belt conveyor system. Finally, the plates are classified depending on the thickness of paste on a particular type of grid. Reject plates and excess paste applied onto the grids are generated in this section. Also, washing of equipment generates wastewater streams, which are contaminated with "paste," which essentially contains lead.

32.2.1.5 Plate Curing

Curing is the process of exposing plates pasted positive and negative to a regime of (a) controlled time (minimum 32 h), (b) temperature (30–35°C), and (c) relative humidity (≥90%). This process converts the free lead into lead oxide, using oxygen from the surrounding air. The plates are allowed to cure for a minimum of 32 h. Care is also taken to ensure that the maximum temperature of the plate does not exceed 60°C. The cured plates are then parted.

32.2.1.6 Plate Parting

This operation is also performed using machines. The cured plates are fed into the parting machine by mechanical means. The plates are parted in the machine and then collected when the operation is completed manually. The parted plates are thereafter stacked for use in battery assembly. More rejects are also generated in this section as well as some lead dust. The ventilation system in this area ensures that the lead dust generated is removed from the work area and discharged into the atmosphere through a baghouse filter.

32.2.1.7 Battery Assembly

The first operation in this area is that of enveloping of positive plates. This envelope, which may be a polythene sheet, acts as a separator that electrically isolates the positive and negative electrodes. A mechanical vacuum system is used to feed positive and negative plates for automatic stacking. The positive and negative plates are stacked together in the desired sequence and encased. However, before the plates are encased, several other processes such as lug brushing, melting of lugs, cast-on strap, intercell welding, and fixing covers are carried out. After the plates are assembled in the container, they are mounted on a conveyor for the finishing operations that involve a shear test, heat sealing, terminal burning, and leak testing. The product at this stage is called a dry uncharged battery. The number and types of positive and negative plates in each battery depend on the type of battery being manufactured. Nevertheless, for a particular type of battery having a specified capacity, the number and types of positive and negative plates are generally fixed. The activities in this section generate rejects of plates, dross, and lead dust. The vacuum system generates lead dust due to feeding of plates, which is discharged to the atmosphere through a baghouse filter.

32.2.1.8 Charging

The dry uncharged battery now needs to be charged by the addition of an electrolyte, which in the case of the lead–acid battery is sulfuric acid. Accordingly, the battery is filled with sulfuric acid (a specific gravity of 1245–1255 at 25°C) and placed on tables and then cooled with water. The operations of filling and emptying sulfuric acid from the battery are performed automatically using machines. Acid is filled by gravity flow into the cell to a level considerably above the plate tops. The positive and negative terminals of the battery are connected to the electric connections and the electric current is passed for a fixed duration of time during which the battery is charged. Different batteries have different currents for charging and different charging systems are, therefore, used. Charging is indicated as complete when there is no change in specific gravity over a 3-h period. Thereafter, the sulfuric acid is emptied from the batteries, a new solution of sulfuric acid is filled, and the battery is washed, labeled, tested, and packed. It should be noted here that the quantity of sulfuric acid filled in a battery varies with the type of battery manufactured. In case it is a wet-charged battery, it would be ready at this stage for distribution and use. Wastewater streams are generated in this section as a result of charging and washing the batteries. This wastewater is acidic and contains sulfuric acid.

32.3 BATTERY CHEMICAL SYSTEMS

Among the most important factors in designing products around batteries (and batteries themselves) is the amount of power a battery of a given size and weight can produce. After all, the energy source for a device should not handicap the ready use of that device. The chemical reactions in the cell are the most important factor constraining energy density and the usefulness of batteries. In fact, the entire history of battery technology has been mostly a matter of finding and refining battery chemistries to pack more energy in ever-smaller packages. Today's batteries use a variety of chemical systems, some dating from the late nineteenth century as mentioned previously, and some hardly a decade old. The diversity results from each having distinct benefits for particular applications. The following battery chemistries are the most popular for portable computer, cell phone, power system, and peripheral applications.

32.3.1 BATTERY CLASSIFICATION

Batteries are broadly divided into two main classes, namely: (a) primary batteries or cells, which irreversibly (within limits of practicality) transform chemical energy into electrical energy. This happens because of the exhaustion of the initial supply of reactants to the extent that energy cannot be readily restored to the battery by electrical means. In other words, primary batteries are one-way batteries that create new electricity from chemical reaction that permanently transforms the cells. As a consequence, the anode, cathode, and electrolyte are permanently and irreversibly changed and the batteries are disposed of. For this reason, primary batteries are often also referred to as either disposable or nonrechargeable batteries.[1,4] (b) Secondary batteries or cells, which may be recharged when their chemical reactions are reversed by applying electrical energy to the cells, thereby restoring their original composition. In essence, rather than operating as producers of power, the secondary batteries merely store it. For that matter, they are often called storage batteries or simply rechargeable batteries. Despite this seemingly inexhaustible capacity to store energy, secondary batteries are not indefinitely rechargeable. This loss of rechargeability is due to dissipation of the active materials, loss of electrolyte, and internal corrosion.[1]

32.4 DESCRIPTION OF BATTERY SUBCATEGORIES IN THE BATTERY INDUSTRY

32.4.1 SUBCATEGORIES/SUBDIVISION OF BATTERIES

Based on the anode material employed, eight (8) subdivisions (A–H) have been developed by the U.S. EPA.[5] As may be noted (Table 32.1), the zinc anode is divided into two groups (subcategories D and G) based on the electrolyte types. This difference is also reflected in the substantial differences in the manufacture, as well as the waste generated by the two groups. Although a subcategory of nuclear batteries is indicated, hardly any data exist that describes its construction, leave alone the waste characteristics. Similar paucity in information exists on thermal batteries (such as calcium batteries), whose production and use are limited to few operations, especially in

TABLE 32.1
Battery Subcategories, Types, and Construction Materials

Subcategory	Anode Materials	Cathode Materials	Battery Type	Examples
A—Cadmium	Cadmium anode	Nickel, mercury, and silver	Secondary	Nickel–cadmium, mercury–cadmium, and silver–cadmium
B—Calcium	Calcium anode	N.G.	N.G.	Thermal batteries for military and atomic applications
C—Lead	Lead anode	Lead oxide	Secondary	Lead–acid batteries used for starting, lighting, and ignition (SLI)
D—Leclanché	Zinc anode	Carbon, silver chloride, and air	Primary and secondary	Zinc–air batteries, carbon–zinc batteries, and silver chloride–zinc batteries
E—Lithium	Lithium anode	Iodine, sulfur dioxide, thionyl chloride, and iron disulfide	Secondary	Lithium–iron disulfide batteries, lithium–ion batteries, and lithium polymer batteries
F—Magnesium	Magnesium anode	Carbon, vanadium pentoxide, and magnesium chloride		Magnesium-based thermal batteries
G—Zinc	Zinc anode, alkaline electrolyte	Manganese dioxide, nickel hydroxide, mono- and divalent oxides of silver, atmospheric oxygen	Primary and secondary	Nickel–zinc batteries and alkaline manganese cells
H—Nuclear	Radioisotopes	N.G.	N.G.	N.G.
Other types	Variable	Variable	Primary and secondary	Nickel–metal hydride cells, sodium–sulfur batteries, redox batteries, and unusual batteries

Source: Rosch, W., *Batteries: History, Present, and Future of Battery Technology*, EXTREMETECH. Available at http://www.extremetech.com/, June 2001; U.S. EPA, Battery Manufacturing, U.S. Environmental Protection Agency, Washington, DC, 1981.

N.G. = Not given.

military and space exploration programs. Therefore, these two subcategories are out of the scope of this chapter. However, in the subsequent paragraphs, brief descriptions of other subcategories are provided.

32.4.2 SUBCATEGORY A: CADMIUM

Subcategory A encompasses the manufacture of all batteries in which cadmium is the reactive anode material. Cadmium anode batteries currently manufactured are based on nickel–cadmium, silver–cadmium, and mercury–cadmium couples (Table 32.1). The manufacture of cadmium anode batteries uses various raw materials, which comprises cadmium or cadmium salts (mainly nitrates and oxides) to produce cell cathodes; nickel powder and either nickel or nickel-plated steel screen to make the electrode support structures; nylon and polypropylene, for use in manufacturing the cell separators; and either sodium or potassium hydroxide, for use as process chemicals and as the cell electrolyte. Cobalt salts may be added to some electrodes. Batteries of this subcategory are predominantly rechargeable and find application in calculators, cell phones, laptops, and other portable electronic devices, in addition to a variety of industrial applications.[1,4] A typical example is the nickel–cadmium battery described below.

32.4.2.1 Nickel–Cadmium

The most popular rechargeable/storage batteries in consumer electronic equipment are nickel–cadmium cells, often called NiCads. As the name implies, these batteries use cathodes made from nickel and anodes from cadmium. Their most endearing characteristic is the capability to withstand a huge number of full charge/discharge cycles, often in the range of 500–1000 cycles, without deteriorating past the point of usefulness. NiCads also are of relatively lightweight, have a good energy storage density (although about half that of alkaline cells), and tolerate trickle charging (when properly designed). On the downside, cadmium is toxic, thus the requirement for warning labels that implore the user to be cautious with them and properly dispose of them.[1] In most batteries the output voltage declines as the battery discharges. This is so because the reactions within the cell increase its internal resistance. This is, however, not the case with NiCads. The NiCads batteries have a very low internal resistance, meaning they can create high currents that change little as the cell discharges. Consequently, the NiCad cell produces a nearly constant voltage until it becomes almost completely discharged, at which point its output voltage falls precipitously. This constant voltage is an advantage to the circuit designer because fewer allowances need to be made for voltage variations. However, the constant voltage also makes determining the state of a NiCad's charge nearly impossible. As a result, most battery-powered computers estimate the remaining battery power from the time they have been operating and the known battery capacity rather than actually checking the battery state. NiCads are known for another drawback: memory. When some NiCads are partly discharged, then later recharged, they may lose capacity. Chemically, recharging NiCads before they are fully discharged often results in the formation of cadmium crystals on the anodes of the cell. The crystals act like a chemical memory system, marking a second discharge state for the cell. When the cell gets discharged to this secondary discharge state, its output abruptly falls despite further capacity being available within the cell. In subsequent cycles, the cell remembers this second discharge level, which further aggravates the situation by reinforcing the memory of the second discharge state. The full capacity of the cell would only be recovered by nudging the cell past this second discharge state. This should erase the memory and restore full cell capacity. This situation would soon change as newer NiCads are free from memory effects.

Another problem encountered by manufacturers and users of NiCads batteries is the breakdown, by electrolysis, of water. This ought to be prevented; otherwise the cells may explode. As with lead–acid batteries, NiCads are also prone to electrolysis-mediated breaking down of water in the electrolyte into potentially explosive hydrogen and oxygen. Battery manufacturers take great steps to reduce this effect. Commercially available NiCads are sealed to prevent leakage. They are also designed so that they produce oxygen before hydrogen, which reacts internally to shut down the electrolysis reaction. To prevent sealed cells from exploding should gas somehow build up inside them, their designs usually include resealable vents. As a matter of fact, there is a great risk of getting an explosion if a NiCad cell is encased in such a way that it cannot vent. Cadmium anode batteries are produced in a broad range of sizes and configurations corresponding to varied applications (Table 32.2). They range from a cylindrical cell with capacities of <1 A-h to large rectangular batteries for industrial applications with capacities in excess of 100 A-h.[1]

32.4.3 SUBCATEGORY C: LEAD

The lead subcategory encompasses the lead–acid reserve cells and more familiar lead–acid storage batteries. This subcategory of batteries is the largest both in terms of number of plants and in volume of production, as well as the total volume of wastewater generated. The raw materials for all lead anode battery types include lead, lead oxide, lead alloys, sulfuric acid, material for making separators, as well as battery cases, covers, and filter caps. Carbon, barium sulfate, and some fibrous materials may be used as additional materials in the manufacture of electrodes.[5] Although lead anode batteries are manufactured using similar materials and employing the same basic chemistry, they differ significantly in configuration depending on the end use. For instance, lead–acid battery products include cells with immobilized electrolyte for use in portable tools, lanterns; conventional rectangular batteries for use in automotive SLI applications; sealed batteries for SLI use, and a wide variety of batteries designed for industrial applications. Like the NiCads, lead anode batteries are also rechargeable. Besides, these types of batteries may be described as wet charged such as the SLI or dry charged such as damp-charged batteries (damp batteries) and dehydrated plate batteries (dehydrated batteries). Damp and dehydrated batteries may sometimes be described as gelled lead–acid cells.[1] Dehydrated batteries are manufactured by charging the electrodes in open tanks (open formation), which is subsequently followed by rinsing and dehydration processes. Thereafter the batteries are assembled and shipped to various destinations. The wet-charged batteries, on the other hand, may be manufactured by either closed formation processes or open formation processes. Of the three categories, the dehydrated plate batteries afford significantly longer shelf life than wet and damp batteries. Most uninterruptible power systems rely on gelled lead–acid cells for their power reserves. In this application, they require little maintenance. A typical example, described below, is the wet-charged lead–acid battery.

TABLE 32.2
Standard Designs, Shapes, and Sizes

Design Type	Shape	Height (mm)	Diameter (mm)
AAAA	Cylindrical	42.5	8.3
AAA	Cylindrical	44.5	10.5
AA	Cylindrical	50.5	14.5
C	Cylindrical	50.0	26.2
D	Cylindrical	61.5	34.2
J	Rectangular	48.5	33.5 × 9.2
N	Cylindrical	29.35	11.95
9 V	Rectangular	48.5	26.5 × 17.5

Source: Rosch, W., *Batteries: History, Present, and Future of Battery Technology*, EXTREMETECH. Available at http://www.extremetech.com/, June 2001.

32.4.3.1 Lead–Acid Battery

The most common storage batteries in the world are the lead–acid batteries used to start automobiles, which are not only the heirs to Planté's first designs but are also almost identical. They have anodes made from porous lead and cathodes made from lead oxide, both soaked in a sulfuric acid electrolyte. The lead in the cells and the highly corrosive sulfuric acid electrolyte not only make these batteries inherently heavy but also cumbersome and dangerous. Furthermore, the acid and its fumes are capable of damaging nearby objects (particularly metals), while overcharging cells results in electrolysis of the water component of the internal acid to release hydrogen. The hydrogen released by the electrolysis is highly combustible and if mixed with air and exposed to a spark, an explosion may occur. Besides, the breakdown of the water in the cells also has another effect: it reduces the overall amount of water in the cell. As a result, too little water is available, which reduces the reaction area inside the cell, thereby reducing its capacity. Eventually, the cells would deteriorate by atmospheric action and the electrodes may either flake or possibly shut out a cell entirely, thereby reducing its capacity to zero.[1]

Early lead–acid cells consequently required regular maintenance to keep the water/acid inside the cell at the proper level. Since only the water electrolyzes in the battery, it is the only one needed to be replaced regularly. To avoid contaminating the battery chemistry, manufacturers recommend the use of distilled water in replenishing the battery. In stationary applications, lead–acid batteries were once encased in glass. Not only would such designs resist the internal acid, but also they would allow maintenance workers to quickly assess the condition of the cells. For automotive applications, however, a more shatterproof case is required for which engineers developed hard rubber or plastic enclosures. In addition, the convenience of using lead–acid batteries is immensely increased by sealing the cells. The result is the so-called *maintenance-free battery*. Since the vapors within the sealed cell cannot escape, electrolysis losses are minimized. For this reason, maintenance-free batteries never need water. But on the downside, maintenance-free batteries are not entirely trouble-free. They still have acid sloshing around inside them, which may leak out through the battery vent, thereby either damaging the battery compartment or the equipment in which the battery is located. To overcome these shortcomings, two ways of eliminating the slosh have been developed. One way is to keep the liquid acid (electrolyte) inside a plastic separator (typically a microporous polyolefin or polyethylene) between cell electrodes. The second alternative is to chemically combine the liquid electrolyte with other compounds that turn it into a gel (a colloidal form like gelatin), which is less apt to leak out.

Having had over 150 years of technical development behind them, lead–acid batteries can be custom-tailored to specific applications, such as those requiring deep discharge cycles (e.g., where the batteries are used as the sole power source for electrical equipment) and for battery backup uses such as in large uninterruptible power supply systems in data centers. Moreover, lead–acid cells not only have low internal resistance but also experience no memory effect as do some more exotic cell designs, such as NiCads. This enables these cells to produce enormous currents and have a moderately long, predictable life.[1]

32.4.4 SUBCATEGORY D: LECLANCHÉ

The Leclanché battery subcategory is a type of zinc battery that uses an acidic electrolyte and zinc anode. The major raw materials used in the manufacture of batteries in this subcategory include zinc, mercury, carbon, manganese dioxide, ammonium chloride, zinc chloride, silver chloride paper, starch, flour, and pitch (or similar materials) for sealing cells. Plastics are also used in producing flat cells for photographic use. The zinc is most often obtained as sheet zinc preformed into cans, which serve as both cell anode and container. However, some facilities form and clean the cans on-site. Zinc powder may also be used in one such type of cells. Where mercury is used to amalgamate the zinc and to reduce internal corrosion in the battery, it is generally added with the cell electrolyte or the separator. It amounts to approximately 1.7% by weight of the zinc contained in these cells. Plants involved in the manufacture of cells in this subcategory produce conventional carbon–zinc Leclanché cells as well as silver chloride–zinc and carbon–zinc air cells. All of these batteries have in common the use of an acidic (chloride) electrolyte and a zinc anode. In this respect they differ from subcategory G, which, although it has a zinc anode, uses an alkaline electrolyte.

A wide variety of cells and battery configurations and sizes are produced in this subcategory comprising cylindrical cells in sizes from AAA to No. 6, flat cells, which are stacked to produce rectangular 9-V transistor batteries, various rectangular lantern batteries, and flat sheet batteries for photographic applications. Cells of this subcategory are of the primary type (Table 32.1). Although the above cell configurations are used in the construction of this cell subcategory, there are some differences in the manufacturing process. These differences arise from the differences in the cell separators chosen, that is, cooked paste, uncooked paste, or paste paper. Another notable difference may arise from the electrolyte used. For instance, among carbon–zinc air batteries, only dry cells, which use ammonium chloride in the electrolyte, are included in this subcategory; otherwise carbon–zinc air depolarized batteries, which use alkaline electrolyte, are not included in the Leclanché subcategory, but rather, included in subcategory G, the zinc battery. Typical examples described below are the carbon–zinc and zinc–air battery types.

32.4.4.1 Carbon–Zinc

Carbon–zinc cells are probably the most common batteries in the world, known under a variety of names including dry cell and flashlight battery. When you think of batteries, it is likely that carbon–zinc cells first come to mind. One company alone, Energizer, sells over 6 billion carbon–zinc cells each year. They are the lowest-priced primary cells. They also have the lowest storage density of any common battery. In the basic carbon–zinc cell, the "carbon" in the name is a cathode current collector, which is a carbon rod in the center of the cell. The actual materials used in the manufacture of the cathode are a mixture of manganese dioxide, carbon conductor, and electrolyte. The zinc, in addition to serving as the anode, forms the metal shell of the battery. The electrolyte is a complex mixture of chemicals that typically include ammonium chloride and manganese dioxide. Therefore, the electrolyte is the chief difference between Leclanché and zinc cells of subcategory G that use alkaline electrolytes.[1]

32.4.4.2 Zinc–Air

Of the current battery technologies, the one offering the densest storage is zinc–air. One reason is that one of the components of its chemical reaction is external to the battery. Zinc–air batteries use atmospheric oxygen as their cathode reactant, hence the "air" in the name. Small holes in the battery casing allow air to react with a powered zinc anode through a highly conductive potassium hydroxide electrolyte. Originally created for use in primary batteries, zinc–air batteries were characterized by long stable storage life, at least when kept sealed from air and thus inactive. A sealed zinc–air cell loses only about 2% of its capacity after a year of storage. Once air infiltrates the cell, zinc–air primary cells last only for months, whether under discharge or not. Some battery makers have adapted zinc–air technology for secondary storage. Zinc–air cells work best when frequently or continuously used in low-drain situations. The chief drawback of zinc–air batteries is, however, its high internal resistance, which means zinc–air batteries must be huge enough to satisfy high current needs as for notebook PCs, which means an auxiliary battery pack about the size of the PC itself. Zinc–air secondary cells have been only crudely adapted to portable PC applications. One of the first products, the PowerSlice XL, developed jointly by Hewlett-Packard Co. and AER Energy Resources Inc., demonstrated the shortcomings of zinc–air technology for high-current computer use. The product developed for the HP OmniBook 600 notebook PC weighed 7.3 lb, more than the computer itself, but could power the OmniBook only for about 12 h. Energizer has also adapted zinc–air technology to small button cells aimed at hearing aids. Charging a battery is not simply a matter of preventing a dead battery from sucking in the entire output of a power plant (as would be its natural tendency). Cell chemistry is extremely sensitive to the electricity applied to it. If the voltage applied is too low, the cell will output current instead of accepting it. If too high, undesirable reactions would take place, which would, in turn, destroy the cell. This is so because raising the voltage inevitably raises the current to such high levels that it would eventually cause the cell to overheat. In addition, trying to charge a cell beyond its capacity can result in the production of explosive gases and an explosion itself.[1]

32.4.5 SUBCATEGORY G: ZINC BATTERY

Batteries of this subcategory resemble the Leclanché cells in having a zinc anode, while they differ inasmuch as the electrolyte is alkaline. As such, batteries in this subcategory may be referred to or described as zinc anode alkaline electrolyte batteries. These batteries are at present manufactured using six different cathode reactants, namely, manganese dioxide, mercury oxide, nickel hydroxide, monovalent and divalent oxides of silver, and atmospheric oxygen (Table 32.1). The raw materials used in producing these batteries include zinc, zinc oxide, mercury, manganese dioxide, carbon, silver, silver oxide, silver peroxide, mercury oxide, nickel and nickel compounds, cadmium oxide potassium hydroxide, sodium hydroxide, steel, and paper. Zinc and zinc oxide are used to manufacture anodes, while mercury is used both to manufacture mercuric oxide cell cathode material and to amalgamate zinc anode to limit corrosion and self-discharge. Other cathode materials may be made from (a) manganese dioxide, which is blended with carbon to form cathodes for alkaline manganese cells; (b) silver, which is used to produce silver oxide and silver peroxide cathodes as well as wire screens that serve as support grids for cell electrodes; and (c) nickel and nickel compounds, which are used to produce cathodes for nickel–zinc batteries. The electrolytes used in these cells are either potassium hydroxide or sodium hydroxide. Finally, the batteries are encased in steel material, while paper and plastics, respectively, are used as separators and insulating components.

Typically, the alkaline zinc batteries construction (as opposed to chemistry) differs significantly from ordinary carbon–zinc cells. Alkaline cells are effectively turned inside out. Unlike the zinc battery of subcategory D, the shell of the alkaline battery is nothing more than a protective shell, which does not play a part in the overall chemical reaction. The anode of the cell is a gelled mixture of powered zinc combined with the electrolyte (which itself is a mixture of potassium hydroxide and water), and the combination is linked to the negative terminal of the cell by a brass spike running up the middle of the cell. The cathode, a mixture of carbon and manganese dioxide, surrounds the anode and electrolyte, separated by a layer of nonwoven fabric, such as polyester. This is the construction of a Duracell alkaline battery.[1] Depending on the application, alkaline cells can last for 4–9 times the life of more traditional carbon–zinc cells. The advantage is greatest under heavy loads that are infrequently used, that is, something that draws heavy current for an hour once a day rather than a few minutes of each hour. In this respect, an alkaline zinc anode cell is better than typical carbon–zinc cells, which nominally produce 1.5 V, a voltage only available when little current is drawn from the cell during its initial discharge. As the load increases the voltage of the cell diminishes and the charge of the cell also decreases.

A wide range of cell sizes, electrical capacities, and configurations are manufactured in both primary (nonrechargeable) and secondary (rechargeable) categories. Ordinarily, alkaline batteries cannot be recharged because the chemical reactions in the cell to cannot be readily reversed. If one attempts to recharge an ordinary zinc cell, it acts more like a resistor than a storage cell, turning the electricity applied to it into heat, which may cause the cell to heat up enough to explode. For this reason, it is advisable never to attempt to recharge ordinary alkaline zinc anode batteries. The Renewal batteries produced are currently the rechargeable type of this subcategory. The Renewal design relies on a two-prong attack on carbon–zinc technology. The Renewal cell is fabricated

TABLE 32.3
Nominal Voltage and Storage Density of Various Battery Types

Battery Type	Nominal Voltage (V)	Storage Density (wh/kg)
Lead acid	2.1	30
Nickel–cadmium	1.2	40–60
Nickel–metal hydride	1.2	60–80
Circular lithium ion	3.6	90–100
Prismatic lithium ion	3.6	100–110
Polymer lithium ion	3.6	130–150

Source: Rosch, W., *Batteries: History, Present, and Future of Battery Technology*, EXTREMETECH. Available at http://www.extremetech.com/, June 2001.

differently from a standard cell, with a special battery charger and a microprocessor. More importantly, in recharging Renewal batteries, the Renewal charger adds power in a series of pulses, while a microprocessor in the charger monitors how each pulse affects the cell to prevent overheating. However, even with such a novel charger, Renewal cells have a limited life, typically between 25 and 100 charge–discharge cycles (Table 32.3). Accordingly, Renewal cells cost only about twice as much as standard alkaline cells.[1]

32.4.6 SUBCATEGORY E: LITHIUM BATTERY

This subcategory encompasses the manufacture of batteries, which employ lithium as the reactive anode material. However, this classification may not account for the recent developments in lithium battery technologies, which use either the lithium ion or the lithium polymer not as anodes but rather as cathodes and "complexed" electrolytes, respectively.[1] Therefore, in addition to the traditional lithium anode batteries, these newly developed variants are conveniently classified under the lithium battery subcategory and their construction is described in detail under Sections 32.4.6.2 and 32.4.6.3, respectively. A variety of cathode materials that have been applied earlier in the manufacture of lithium cells include iodine, sulfur dioxide, thionyl chloride, and iron disulfide, which were predominant in the 1970s and 1980s (Table 32.1). Lithium battery technology has greatly developed to various designs based on lithium ion as well as lithium polymer battery technologies, respectively.[1] Typical examples described below are the lithium–iron disulfide, lithium-ion, and lithium polymer battery types.

32.4.6.1 Lithium–Iron Disulfide

The lithium–iron disulfide battery, also known as *voltage-compatible lithium* battery, is a sandwich of a lithium anode, a separator, and an iron disulfide cathode with an aluminum cathode collector. Unlike other lithium technologies, lithium–iron disulfide cells are not rechargeable. Compared to the alkaline cells, lithium–iron disulfide cells are lighter (weighing about 66% of same-size alkaline cells), higher in capacity, and longer in life. Even after 10 years of shelf storage, lithium–iron disulfide cells still retain most of their capacity. Lithium–iron disulfide cells operate best under heavier loads. In addition, they can supply power for about 260% the time of a same-size alkaline cell, when used under high-current applications. On the contrary, this advantage is lost at lower loads and at very light loads where such a capacity may disappear entirely. Lithium–iron disulfide cells may be used wherever zinc–carbon batteries are used, although they are cost effective only under high-current loads such as in flashlights, motor-driven devices, and powerful electronics. They are not a wise choice for clocks and portable radios.[1]

32.4.6.2 Lithium Ion

Batteries based on lithium metal were developed and manufactured in the 1970s, and in the 1980s some companies introduced commercial rechargeable cells based on metallic lithium. Such batteries quickly earned a reputation for doubtful safety. To prevent problems caused by reactive metallic lithium, battery makers refined their designs to keep the lithium in its ionic state. In this way, they were able to reap the electrochemical benefits of lithium-based cells without the safety issues associated with the pure metal. In lithium-ion cells, the lithium ions are absorbed into the active material of the electrodes rather than being plated out as metal. The typical lithium-ion cells use carbon for its anode and lithium cobalt dioxide as the cathode. The electrolyte is usually based on a lithium salt in solution. Lithium batteries offer higher storage densities than nickel–metal hydride cells (Table 32.3). Besides, lithium-ion cells also lack the memory effect that plagued early NiCads. On a downward side, however, current lithium cells have a higher internal resistance than NiCads and consequently cannot deliver high currents.[1] Moreover, the life of lithium cells is more limited than that of nickel-based designs, although lithium-ion cells withstand hundreds of charge/recharge cycles. Since lithium-ion cells use a liquid electrolyte (although one that may be constrained in a fabric separator), cell designs are limited to the familiar cylindrical battery form.

32.4.6.3 Lithium Polymer

The *lithium solid polymer cell* is today's brightest new battery technology and is a refinement of the familiar lithium chemistry. As a matter of fact, most battery makers and computer makers are switching to the lithium solid polymer cell design. A typical lithium polymer cell substitutes the liquid electrolytes required in conventional lithium-ion cells by a solid polymer, polyacrylonitrile containing a lithium salt, which is integrated into a polymer plastic separator between the anode and the cathode. Since there is no liquid electrolyte, the solid polymer cell does not require the chunky cylindrical cases of conventional batteries. Instead, the solid polymer cells can be formed into flat sheets or *prismatic* (rectangular) packages that are better able to fit the nooks and crannies of notebook computers. Although the energy density of solid polymer cells is similar to ordinary lithium-ion cells, PC manufacturers can shape them to better fit the space available in a PC, squeezing more capacity into each machine. For example, simply by filling the empty space that would appear in the corners around a cylindrical cell, a solid polymer battery can fit in about 22% more chemistry and energy capacity. In addition, solid polymer batteries are lighter and environmentally friendly because they have no metal shell and contain no flammable solvent.[1]

32.4.7 SUBCATEGORY F: MAGNESIUM

The magnesium subcategory encompasses such batteries as magnesium–carbon batteries, magnesium–vanadium pentoxide thermal cells, ammonia-activated magnesium anode cells, magnesium–air batteries, and several different types of magnesium reserve cells that use metal chloride cathodes. A wide variety of raw materials are used in the manufacture of magnesium anode batteries and such materials are in tandem with the diversity of cell types manufactured. While the anode is magnesium in each case, various raw materials are used for cathode manufacturing including magnesium dioxide, barium chromate, lithium chromate, magnesium hydroxide and carbon (for magnesium–carbon batteries), vanadium pentoxide (for thermal batteries), copper chloride, lead chloride, silver and silver chloride (for magnesium reserve cells), and *m*-dinitrobenzene (for ammonia-activated cells). As for the electrolyte, raw materials such as magnesium perchlorate, magnesium bromide, and ammonia are used. Separators, on the other hand, are most often made from either Kraft paper or cotton.[6,7] This battery system is characterized by its good shelf life in inactivated state and its capability to operate well at extremely low temperatures of the order of −60°C and below. The battery system gives nearly flat discharge over 75% of its total discharge capacity and can be activated with water. Basing on the above characteristics, this battery system finds application in meteorological equipment such as Radiosonde or Rawin Transmitter, Radio reporting, and ozone sonde, among others, which are used for monitoring the climatic conditions at high-altitude regions where the ambient temperature is of the order of −80°C. The batteries are also required to operate the instruments for <3 h only. Besides operating much more efficiently at extremely low temperatures and possessing a long shelf life, a 112-V battery pack weighs nearly half as much as a Leclanché cell pack of the same power output.[8]

32.4.8 OTHER BATTERY TYPES

Apart from the classical subcategories described above, there are other cell subcategories that do not fit into the above classification. Such cells include (a) the sodium/sulfur battery that uses liquid sulfur for the positive electrode, (b) redox batteries, (c) unusual batteries such as the urine battery, ampoule battery, thin-film battery, and homebrew battery,[9] and (d) nickel–metal hydride batteries, which have, as one of the electrodes, metal alloys that have a very high capacity to store atomic hydrogen, and hence called hydrides. Although the technologies for the sodium/sulfur, redox, and unusual batteries are very interesting, their practical applications are still limited, and therefore no further discussion is devoted to them in this chapter. However, the metal-hydride technology is finding such an application in the manufacture of rechargeable batteries that are currently used in a number of devices. This technology development shall be explored briefly by looking at the nickel–metal hydride battery.

32.4.8.1 Nickel–Metal Hydride

Nickel–metal hydride (NiMH) batteries are related to sealed nickel–cadmium batteries (Table 32.4) and only differ from them in that, instead of cadmium, hydrogen is used as the active element at a hydrogen-absorbing negative electrode (anode). This electrode is made from a metal hydride, usually alloys of lanthanum and rare earths ($LiNi_5$ or $ZrNi_2$) that serve as a solid source of reduced hydrogen that can be oxidized to form protons.[1,10,11] In properly designed systems, hydrides can provide a storage sink of hydrogen that can reversibly react in battery cell chemistry. The most common cells that use hydride cathodes carry over the nickel anodes from NiCad cell designs. These cells typically have an electrolyte of a diluted solution of potassium hydroxide, which is alkaline in nature. Substituting hydrides for cadmium in battery cells has several advantages: (a) the environmentally undesirable cadmium is eliminated, which, in turn, removes the constraints on cell manufacture, usage, and disposal imposed because of concerns over cadmium toxicity; (b) the elimination of cadmium also means that the cells are free from the memory effect that plagues NiCad cells; (c) hydrogen is so much better as a cathode material that cells based on nickel and metal hydrides have a storage density about 50% higher than NiCads. In practical terms, it means that cells of the same size and about the same weight can power a notebook computer for about 50% longer; and (d) its incorporation into products currently using NiCads because of the many design similarities between the two chemistries is possible.[1,11]

Cells based on nickel and metal hydrides are not perfect. Their chief drawback is that most of such cells have a substantially higher self-discharge rate than do NiCad cells. Some NiMH cells lose as much as 5% of their capacity per day, although this figure is coming down with more refined cell designs. As with NiCads, NiMH cells have a nominal output voltage of 1.2 V that remains relatively flat throughout the discharge cycle, falling precipitously only at the end of the useful charge of the cell. In many ways NiMH cells are interchangeable with NiCads. They have a similar ability to supply high currents, although not quite as much as NiCads. NiMH cells also endure many charge/discharge cycles, typically up to 500 full cycles, but they are not a match for NiCads. Although the discharge characteristics of NiMH and NiCads are similar, the two cell types react differently during charging. Specifically, NiCads are essentially endothermic while being charged and NiMH cells are

TABLE 32.4
Summary Comparison of Nickel–Metal Hydride Application Features

Application Feature	Comparison of Nickel–Metal Hydride with Nickel–Cadmium Batteries
Nominal voltage	Same (1.25 V)
Discharge capacity	NiMH up to 40% greater than NiCd
Discharge profile	Equivalent
Discharge cutoff voltages	Equivalent
High-rate discharge capability	Effectively the same rates
High-temperature (>35°C) discharge capability	NiMH slightly better than standard NiCd cells
Charging process	Generally similar; multiple step constant current with overcharge control recommended for fast charging NiMH
Charge termination techniques	Generally similar but NiMH transitions are more subtle. Backup temperature termination recommended
Operating temperature limits	Similar, but with NiMH, cold temperature charge limit is 15°C
Self-discharge rate	NiMH slightly higher than NiCd
Cycle life	Generally similar, but NiMH is more application dependent
Mechanical fit	Equivalent
Mechanical properties	Equivalent
Selection of sizes/shapes/capacities	NiMH product line more limited
Handling issues	Similar
Environmental issues	Reduced with NiMH because of elimination of cadmium toxicity concerns

Source: *Energizer: Nickel–Metal Hydride Application Manual*, June 2001, Eveready battery Co. Inc., www.data.energizer.com.

exothermic, that is, they produce heat. As the NiMH cell approaches full charge, its temperature can rise dramatically. Consequently, chargers are best designed for one or the other type of cell.

32.5 WASTEWATER CHARACTERIZATION

As may be noted from the foregoing description of a typical battery manufacturing process (Section 32.2.1), water is used in preparing reactive materials and electrolytes, in depositing reactive materials on supporting electrode structures (grids), in charging electrodes, and removing impurities, as well as washing finished cells, production equipment, and manufacturing area/work places. As a consequence, wastewater flow, pattern of water use, and waste characteristics are similar among the subcategories, albeit varying widely among different battery manufacturing units.[5] Table 32.5 summarizes the prominent constituents of wastewater streams generated from various battery subcategory plants. For instance, high levels of lead, oxides of lead, sulfates, and suspended solid (SS) material and the low pH due to the acidic electrolyte used, that is, sulfuric acid, characterize lead acid manufacturing plants.[3] Wastewater characterized by high levels of cadmium, nickel, silver, zinc, and mercury are the most dominant pollutants in cadmium anode, zinc anode, Leclanché cells, lithium anode, and calcium thermal battery plants.[5] In addition, barium, zirconium, asbestos, and chromium represent the unique pollutants of thermal battery plants such as the calcium battery plant and lithium anode plants. Several oxides of various metals used in the cathode manufacture are also generated in all battery manufacturing plants of all subcategories, although to levels that may not be detrimental to the environment. Of all the metals and their released oxides, heavy metals such as cadmium, lead, and mercury[4] and to a less extent nickel, silver, and zinc[12] are considered as both health and environmental hazards.

TABLE 32.5
Principal Wastes or Pollutants in Wastewater Streams from Various Battery Manufacturing Plants

Battery Subcategory	Waste Streams Characteristics	Management Strategies
A—Cadmium	Cadmium, nickel, silver, and zinc Wastewater is alkaline and high in suspended solids	Chemical precipitation for removal of dissolved metals Settling or filtration to remove SS Ion exchange for silver recovery
B—Calcium	Cadmium, barium, and chromium Other potential pollutants based on raw materials are zirconium, asbestos, and iron *Note*: Process water use and discharge in this category are limited	Chemical reduction of chromium Settling
C—Lead	Lead, iron, sulfates, and suspended solids Wastewater is acidic. *Note*: Process water use and discharge in this category are limited	pH adjustment and settling Chemical precipitation settling Cleaner production option
D—Leclanché	Zinc, manganese, mercury, oil and grease, and total suspended solids (TSS) The wastewater is slightly alkaline *Note*: Process water use and discharge in this category are limited	Chemical precipitation Oil skimming Settling
E—Lithium	Cadmium, barium, and chromium *Note*: Process water use and discharge in this category are limited	pH adjustment and settling
F—Magnesium	*Note:* Most process operations are accomplished without the use of process water No wastewater characterization data available	Settling and filtration pH adjustment and SS removal
G—Zinc	Anode production (zinc, mercury, TSS, oil, and grease) Cathode production (copper, chromium, zinc, lead, silver, nickel, mercury, and TSS) Electrolyte preparation (arsenic, selenium, and zinc) pH is slightly alkaline	pH adjustment Sulfide precipitation Carbon adsorption Amalgamation Sedimentation Filtration

Source: U.S. EPA, *Battery Manufacturing*, U.S. Environmental Protection Agency, Washington, DC, 1981.

32.6 HEALTH AND ENVIRONMENTAL EFFECTS OF BATTERY MANUFACTURE

Batteries are recognized as the source of heavy metals and hazardous substances such as lead, cadmium, mercury, nickel, zinc, copper, manganese, lithium, and cobalt, among others.[4] Among the toxic heavy metal constituents of battery wastewater, mercury, lead, and cadmium, often referred to as the big three, are in the limelight due to their major impact on the environment[12,13] and are closely regulated in terms of disposal and handling procedures, as well as special battery recycling treatments.[4]

Heavy metals and to some extent their derivatives are among the indestructible pollutants that are neither subject to bacterial attack nor other breakdown or degradation processes and are thus permanent additions to the environment.[12,14] Accordingly, their concentrations most often exceed the permissible levels normally found in the environment: soil, water ways, and sediments, ending up in the food chains. Following these events, heavy metals and/or their derivatives accumulate in the plant and animal life where they profoundly disrupt biological processes, causing various diseases.[12] Furthermore, while some metals are toxic at sufficiently high concentrations, metals such as silver, mercury, cadmium, and copper are markedly more toxic even at very low levels.[12,15] This section explores the toxicological effects of the three most hazardous heavy metals in battery wastewater: lead, cadmium, and mercury, respectively.

32.6.1 LEAD TOXICOLOGY

Lead (Pb) is the main pollutant in the lead–acid battery manufacturing industry (BMI). Lead is present in air, in the form of fine particles, in solid form, and in water, in suspended and dissolved form. In addition, sulfates of lead are present in air emissions and in wastewater. As pointed out earlier, lead will end up in various foods, through which it reaches man. As a matter of fact, almost all food, water, and air contain a certain amount of lead. For this reason, even if a person never worked with lead, he/she would still consume or inhale some of it during the course of his/her daily activities.[16] Up to 50% of inhaled inorganic Pb may be absorbed in the lungs, while 10–15% is taken up through food among adults. In children, Pb is absorbed up to 50% via the gastrointestinal tract.[17] In blood, Pb is bound to the erythrocytes (where it interferes with the synthesis of heme), and eliminated slowly and principally via urine. If it is accumulated in the skeleton, Pb is even more slowly released from the body. For instance, while the half-life of blood Pb is about 1 month, in the skeleton it is 20–30 years.[17] There is a normal body-load of lead above which Pb poisoning will ensue. This normally occurs when absorption is unchecked, resulting in the accumulation of lead in the body at a faster rate than it can be eliminated. Pb forms complexes with oxo-groups in enzymes, thereby affecting virtually all steps in the process of hemoglobin biosynthesis (manifesting in anemia) and porphyrin metabolism.[12,18] In addition, toxic levels of Pb in human have been associated with encephalopathy, seizures and mental retardation,[19] constipation, abnormal sperm, lack of appetite, weight loss, nausea, abdominal pain, muscle aches, as well as joint tenderness. Lead also affects nerve conduction and at high lead levels, kidneys may be affected. Children and the young of other species are more susceptible to lead poisoning. For instance, there is evidence showing that chronic exposure to lead significantly affects the intelligence and neuropsychological performance of children.[3,20] As a matter of fact, elevated blood Pb levels in children ($\geq 70\,\mu g/dL$) can lead to mental retardation due to brain injury.[21,22] The vulnerability of children to the devastating effects of Pb seems to emanate from their inability to prevent passage of Pb through their less developed blood–brain barrier, coupled with the higher gastrointestinal uptake of Pb compared with adults.[17]

Lead may also interact detrimentally with aquatic life. Once lead deposits in soil, it sticks to soil particles and is only displaced by rain water, ending up in water sources where it affects the aquatic life. Some plants accumulate Pb from both contaminated soils and water sources or more specifically water in the rhizosphere. Besides, contaminated soils are liable to remain polluted with lead; this will affect soil fertility.[3,4] The fact that large changes in the lead content of soil are required to produce changes in the aerial parts of the plants as compared to changes in aerial lead concentration is closely reflected in the leaf lead concentration. Accumulation of Pb in grasses remains a potential hazard to livestock.[3]

32.6.2 CADMIUM TOXICOLOGY

Cadmium (Cd) anode cells are at present manufactured based on nickel–cadmium, silver–cadmium, and mercury–cadmium couples. Thus wastewater streams from cadmium-based battery industries carry toxic metals: cadmium, nickel, silver, and mercury, of which Cd is regarded the most hazardous. It is estimated that globally, manufacturing activities add about 3–10 times more Cd to the atmosphere than from natural resources such as forest fire and volcanic emissions. As a matter of fact, some studies have shown that NiCd batteries contribute almost 80% of cadmium to the environment,[4,23] while the atmosphere is contaminated when cadmium is smelted and released as vapor into the atmosphere.[4] Consequently, terrestrial, aquatic, and atmospheric environments become contaminated with cadmium and remain reservoirs for human cadmium poisoning.

Accumulation of cadmium in agricultural soils leads to increased cadmium uptake by crops and vegetables, grown for human consumption.[17]

The most severe form of Cd toxicity in humans due to long-term exposure is "itai-itai (ouch-ouch)." This disease, first reported from Japan, is characterized by excruciating pain in the bone caused by a combination of osteomalacia and osteoporosis.[12,17] Furthermore, whereas high concentrations of cadmium in the human body have been demonstrated to cause serious damage to lungs, long-term exposure to low levels causes severe damage to kidneys. The disastrous effects of Cd poisoning on kidneys may be a direct consequence of its long residence time in the kidneys, about 20–30 years. Unfortunately, up to now, no medical treatment can reduce the amount of cadmium, once it is stored in kidneys. Other health implications of Cd in humans include hepatic damage, hypertension, as well as being weakly associated with some forms of lung cancers.[4,17]

32.6.3 MERCURY TOXICOLOGY

Mercury is released in wastewater from plants that manufacture cells based on the cadmium–mercury couple. Such cells include many household batteries, especially the button cell batteries. As with other hazardous heavy metals, Hg may get into the environment through poor wastewater management practices and eventually ends up in the food chain, that is, plants, aquatic life, and animals, that are themselves food for human. It has been shown by several investigators that, after entering into the aquatic environment, inorganic Hg is transformed into methyl-Hg compounds (organic mercury) through microbial activities and bioaccumulates in aquatic food chains.[24–28] Furthermore, in the vapor and organic forms, however, mercury becomes very poisonous. It attacks the lungs, kidneys, and the brain, where it causes nervous disorders, cancer, brain damage, difficulty in vision, hearing, walking, tremors, coma, and even death.[28,29–33] The vapor, which is mainly produced during the production process, may cross the blood–brain barrier and also accumulate in the blood stream.[12] On a positive side, such damages are reversible once exposure to the metal has stopped. It has also been possible to detect proteinuria at relatively low levels of occupational exposure. Furthermore, metallic mercury is an allergen that has been linked to eczema, while mercury from amalgam fillings may give rise to oral lichen, as well as the so-called amalgam disease. This linkage, however, remains controversial, although some studies have claimed proof of symptom relief after removal of dental amalgam fillings.[17]

32.6.4 OTHER HEAVY METALS

Although cadmium, mercury, and lead have been singled out as the most hazardous, other heavy metals have also been shown to cause detrimental effects when they accumulate in the human body. For instance, chromium in the hexavalent Cr(VI) oxidation state is very toxic . It owes its toxicity to its [Cr(VI)] ability to move readily through soils and aquatic environments, where it acts as a strong oxidizing agent capable of being absorbed readily through the skin.[34] Hexavalent chromium, Cr(VI), is released during many industrial processes, including electroplating and battery manufacturing.[35] Several factors that make hexavalent chromium pollution a matter of intense concern include its toxic, mutagenic,[36] carcinogenic,[37] and teratogenic[38] effects. In addition, Cr(VI) also forms stable anions, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$; the fraction of any particular species is dependent on the chromium concentration and pH,[39] which in turn affects the toxicity and bioavailability.[12] Copper in larger amounts is extremely toxic to living organisms. The toxicity of copper(Cu) is due to the deposition of copper(II) ions in brain, skin, liver, pancreas, and myocardium.[40] Nickel (II) ion at toxic levels may be released in wastewater streams of various battery manufacturing plants that use the nickel metal in any production process step(s). The nickel would end up in the soil or sediment where it may strongly get attached to particles containing iron or manganese. Under acidic conditions, nickel is more mobile in soil and may seep into groundwater. One may be exposed to nickel by drinking water, eating food, and by skin contact with soil, water, and metals containing nickel. Toxic effects of nickel have been demonstrated in a number of animal models. Based on such studies, it has been found that large amounts of nickel in rats and mice food cause lung disease and affect the stomach, blood, liver, kidneys, and immune system. Effects on reproduction and birth defects were also found in rats and mice eating or drinking very high levels of nickel. However, the most common adverse health effect of nickel in humans is an allergic reaction to nickel. The most common reaction is a skin rash at the site of contact.[41] Besides the effect of individual metal intoxication, mixed metal contaminations seem to exert a synergistic effect on the overall toxic effects. For example, a high degree of DNA fragmentations of splenic macrophages on exposure to multimetals indicates that a greater number of cells undergo apoptosis on heavy metal exposure and thus disturb their functional integrity.[42]

32.7 TREATMENT OF BATTERY MANUFACTURING WASTE

Effluent treatment processes are designed to ensure that when wastewaters are discharged into natural water courses, any adverse effects are reduced or prevented.[43] Some of the methods rely on the use of the adsorptive capacity of the adsorbate on the adsorbent. For instance, adsorptive removal of heavy metals has been achieved on activated carbon or activated alumina, as well as polymer resins.[13] Whereas activated carbon exhibits an extremely large surface area and intrinsic adsorption to many chemicals, polymer resins have been found to form complexes with the heavy metal ions and are therefore prominently being used in the treatment of heavy metals in wastewater-loaded streams. Typical examples of such polymers include silica gel, active alumina, zeolite, and metal oxides[44] and find application in many processes for the removal of heavy metals from wastewater such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, filtration, reverse osmosis, ion exchange, and membrane technologies.[12] Therefore, several technologies for treating heavy metal-bearing wastewater, such as precipitation, reduction, solvent extraction, and membrane processes, have been used.[43] In addition to the use of adsorptive polymer resins, chemical precipitation may also be achieved by either pH adjustment or salting out, and has been used to remove dissolved metals. On the other hand, settling coupled with filtration has also been used to remove precipitates as well as SS. In some instances, as in the recovery of silver, ion exchange chromatography on suitable resins may be used, while adsorption has been used to remove dilute pollutants.[12,43] Table 32.5 summarizes the various treatment options that have, until recently, been used by the respective battery manufacturing plants. These methods, however, have had several disadvantages such as incomplete metal removal and toxic sludge generation. On the other hand, although the use of artificially prepared ion exchange resins is effective, it is nonetheless too expensive to be applied on industrial scale. For this reason, the potential of a new method of removing heavy metals by biological biosorbents presents an important breakthrough.[43]

32.7.1 USE OF BIOSORBENTS IN THE TREATMENT OF BATTERY WASTEWATER

It has been recognized that the physicochemical methods such as those briefly outlined in the foregoing (Section 32.6) are either ineffective or expensive especially when the heavy metal ions are in solutions and at concentrations of the order of 1100 mg of dissolved heavy metal ions/L. For instance, activated carbon is only able to remove around 30–40 mg/g of Cd, Zn, and Cr in water and is nonregenerable, making it quite costly when used in wastewater treatment. In addition, the precipitation method often results in sludge production, while ion exchange, which is considered a better alternative technique, is not economically appealing because of high operational cost. As a result of these, biological methods such as biosorption/bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physicochemical methods.[12]

Biosorption strategies consist of a group of applications involving the detoxification of hazardous substances such as heavy metals instead of transferring them from one medium to another by means of biosorbents, which may be either microbes or plants. Biosorption options are generally characterized as being less disruptive and may henceforth be carried out on-site, thereby eliminating the need to transport the toxic materials to treatment sites.[12] Biosorption is a very cost-effective method because biosorbents are prepared from naturally abundant biomass, which include, among others, nonliving plant biomass materials such as maize cob and husk, sunflower stalk, *Medicago sativa* (Alfalfa), cassava waste, wild cocoyam, sphagnum peat moss, sawdust, chitosan, Sago waste, peanut skins, shea butter seed husks, banana pith, coconut fiber, sugar-beet pulp, wheat bran, sugarcane bagasse,[12] and *Cassia fistula*.[43] Several studies have shown that these biomass materials are effective in the removal of trace metals from the environment. Typically, *C. fistula* has been studied for possible application as a very promising biosorbent for the removal of Ni(II) from synthetic aqueous solutions. The feasibility of using *C. fistula* as a biosorbent lies in its numerous ionizable chemical groups comprising carboxyl, carbonyl, alcoholic, and amino groups. Such groups make it a good option for use as a biosorbent in metal biosorption.[45]

In their study to explore the ability of *C. fistula* waste biomass to remove Ni(II) from industrial effluents, Hanif and coworkers found that *C. fistula* biomass is very effective in removing Ni(II) from wastewater produced by various industries. These ranged from ghee industry (GI), nickel chrome plating industry (Ni–Cr PI), BMI, tannery industry: lower heat unit (TILHU), tannery industry: higher heat unit (TIHHU), textile industry: dying unit (TIDU), and textile industry: finishing unit (TIFU). In these industries, the initial Ni(II) concentration in their industrial effluents was found to be 34.89, 183.56, 21.19, 43.29, 47.26, 31.38, and 31.09 mg/L in GI, Ni–Cr PI, BMI, TILHU, TIHHU, TIDU, and TIFU, respectively. After biosorption, the final Ni(II) concentration in industrial effluents was found to be 0.05, 17.26, 0.03, 0.05, 0.1, 0.07, and 0.06 mg/L in GI, Ni–Cr PI, BMI, TILHU, TIHHU, TIDU, and TIFU, respectively. Accordingly, the percentage (%) sorption Ni(II) ability of *C. fistula* from seven industries included in their study was in the order: TILHU (99.88) > GI (99.85) ≈ BMI (99.85) > TIFU (99.80) > TIHHU (99.78) > TIDU (99.77) > Ni–Cr PI (90.59). Due to the unique high Ni(II) sorption capacity of *C. fistula* waste biomass, it can be concluded that it is an excellent biosorbent for Ni(II) uptake from industrial effluents.[43]

In a separate study, Igwe and Abia[46] determined the equilibrium adsorption isotherms of Cd(II), Pb(II), and Zn(II) ions and detoxification of wastewater using unmodified and ethylenediamine tetraacetic acid (EDTA)-modified maize husks as a biosorbent. This study established that maize husks are excellent adsorbents for the removal of these metal ions, with the amount of metal ions adsorbed increasing as the initial concentrations increased. The study further established that EDTA modification of maize husks enhances the adsorption capacity of maize husks, which is attributed to the chelating ability of EDTA. Therefore, this study demonstrates that maize husks, which are generally considered as biomass waste, may be used as adsorbents for heavy metal removal from wastewater streams from various industries and would therefore find application in various parts of the world where development is closely tied to affordable cost as well as environmental cleanliness.[46]

32.7.2 CLEANER PRODUCTION OPTIONS FOR BATTERY MANUFACTURE

The major aim of cleaner production (CP) options is to prevent or reduce the amount of waste generated in production processes. For that matter, the prevention or reduction of the amount of waste as a result of manufacturing activities of batteries is increasingly becoming the major focus of both battery plants and environmental protection agencies. This is in recognition of the importance of minimizing the volume and quantity of waste (solid and liquid) released into the environment and their detrimental effects on flora and fauna. For this reason, good housekeeping practices or CP techniques such as changing manufacturing processes, better process control, on-site recycling, and other methods may be used as alternatives to achieve the prevention or reduction of the amount of waste generated at manufacturing plants.[3] Therefore, using these techniques of CP and waste reduction, battery manufacturers aspire to the "cleaner production philosophy." In conforming to this philosophy, for some time now, an increasing number of the forward-looking manufacturers have been accredited with ISO 9002 for outstanding quality, while others are now certified with ISO 14001 in recognition of their "environmental management systems." As a consequence of ISO

14001 accreditation among battery manufacturers, more and more facilities are conforming to sound environmental practices [Wilson, The International Lead Management Center (ILMC)]. As pointed out earlier (Section 32.2), although batteries differ in the fine details, they are virtually manufactured following similar process steps. In the following subsections, the application of CP options in the various manufacturing steps are described using, as an example, the production process of the lead–acid reserve battery.[3]

32.7.2.1 CP Options for Scrap Plates

During grid pasting, grid parting, and battery assembly operations, scrap plates are generated. Taking the grid pasting operation, scrap plates may come from improper feeding of grids. After the pasting and drying of the plates, they may be rejected for improper pasting, increasing the volume of scrap. Furthermore, the moisture content of the paste on the plates is determined frequently. The plates used for testing are also scrapped. In the plate parting operation, improper feeding of the plates into the parting machine leads to the rejection of plates that are eventually scrapped. Besides, feeding of the parted plates in the enveloping machine further causes scrap generation in the battery assembly area. Once again, improper feeding of the plates is the cause of scrap generation in assembly areas. The following CP options are suggested for the prevention/reduction of scrap plates:

a. *Cast grid as a single unit*: Grids, which are cast in pairs, are separated into two after the curing operations to facilitate assembly into the battery. The grids can be cast as one unit with one lug. Since the parting of the grids would generate scrap, casting them as a single unit with lug at one end will be beneficial as it would eliminate the plate parting operation as well as the wastes generated in this unit operation. However, even when this is a desirable CP option, it is still held back with regard to its implementation. First of all, the feeding mechanisms in a pasting machine and various equipment used for handling of grids from grid-casting stage to grid-parting stage are of such design and mechanism that lugs at two ends would be required to handle the grids. For this reason, grids with one lug would make the above operations difficult to conduct. Therefore, if grids are manufactured singularly they will need to have two lugs, whereby one of the lugs will have to be cut for the plate to be used in the battery. A singular unit, therefore, would also require parting operation. Moreover, if grids are to be cast as single units with one lugs, the existing equipment (molds, feeding, and handling mechanism/equipment of grids) would become redundant and new equipment would have to be installed. The costs involved in achieving these requirements may be prohibitive.[3]

b. *Refeed the plates*: The plates rejected in the grid pasting operation may be recycled into the feeding end of the pasting machine. This would bring about a reduction in the quantity of scrap plates generated due to improper pasting. However, it is currently not technically possible to apply this CP option as the plates once fed cannot be refed. This is so because the feeding mechanism would get affected and thereby obstruct more plates in the rotation mechanism. As a result, more waste would be generated, making this option not feasible.[3]

c. *Washing and recycling of plates in the grid pasting section*: After the drying operation some plates that are rejected due to improper application of paste may be collected in a tank or container. These plates can then be washed using a water jet and the grids can be separated from the water. After the grids are dried and the water is allowed to settle, the paste that settles can be reused in the pasting operation in a fixed ratio with the virgin paste. As for the clear water from the top of the tank or container, it can be used as process water to mix with the paste or for cleaning purposes. The dried grids can be melted and fresh grids cast in the casting section. Assuming all plates were recycled, implementation of this CP option would lead to savings on raw materials and reduction in the volume of scrap. As this option has no environmental impacts and no major capital investment, the returns are beneficial both financially and environmentally. However, the feasibility of recycling of paste removed from the plates needs to be investigated as it may not be possible to recycle all the paste into the paste mixer. Furthermore, the moisture content of the paste would be a critical parameter for monitoring prior to recycling.[3]

d. *Recycling of plates from the plate parting and battery assembly section*: The scrapped plates from the grid parting and battery manufacturing section cannot be recycled in the same manner as mentioned above (option c). Instead, the plates can be washed, the grids dried and recycled, while the wash water can be allowed to settle suspended particles and the clear water can be recycled. However, unlike the CP option in (c) above, the sediment of the settled paste cannot be recycled, as this is unusable as paste. This is so because in the curing operation, the reaction has already taken place and changed the nature of the paste. It has, therefore, to be disposed of as sludge. It should also be noted that the removal of paste from the plates after it has been cured is difficult as compared to removal of paste after the pasting operation. Thus, the washing of plates would involve washing using a jet spray. Besides, physical breaking of the paste would also be required before water is sprayed for removal of paste. All these barriers should make implementing CP option at this operation difficult. However, if implemented, it does bring about saving of grids, although it creates another waste stream of sludge. It still is, thus, worth considering and if found feasible should be implemented.[3]

32.7.2.2 CP Options for Sludge from the Trade Waste Treatment Facility

Sludge, which is a mixture of paste and salt precipitates of various metals, is generated in a number of operations. First, the paste is spilled on the floor of the grid pasting area from where it is washed into the drain. The paste-containing wastewater is then transferred to the trade waste treatment facility. This waste stream is settled in a pit in the trade waste treatment facility, where sludge is formed. Sludge is also formed in the wastewater treatment facility due to chemical precipitation reaction. From the settling pit, the settled sludge is removed and stored in drums on-site. Even then, the sludge is once again allowed to settle in these drums, and water decanted, and drums filled with the sludge are then shipped to the smelter. To prevent/reduce the generation and transportation of sludge, the following options are suggested:

a. *Dewatering of sludge*: The sludge may be dewatered using either a belt press, a plate, and a frame filter press or centrifuges. This CP option would not only greatly reduce the volume of the waste generated, but also the volume of sludge being transported to the smelter for off-site recycling. Besides, the water from the filter press can be treated and recycled on-site. Since the reduction in the volume of sludge depends on the equipment selected for dewatering, the saving in transportation costs would likewise depend on the volume reduction achieved. This saving, however, may be offset by the equipment purchase and maintenance costs. This is seen as a barrier to the exploration of this CP option.[3]

b. *Segregation of paste from precipitates*: The paste sludge would be segregated from the metal-salts precipitates (formed due to chemical precipitation reaction in the wastewater treatment facility) by using different pumps for pumping paste sludge and metal-salts precipitates. The paste sludge may then be dewatered (using a filter press or belt press) and subsequently the dewatered paste used in the grid pasting section. This CP option would not only facilitate reduction in the quantity of sludge sent for off-site disposal but would also reduce the quantity of paste to be manufactured, due to the possible recycling activity. As much as this CP option is promising, its implementation faces one major challenge: since this paste is a mixture of positive and negative pastes, it would only be mixed in the negative paste mixer. This, in turn, would limit the amount of recycled paste that can be added into the negative paste mixer in this manner, that is, a ratio of recycled paste to the new paste should be put into consideration. Nonetheless, it ought to be explored.[3]

c. *Segregation at source*: It should be recalled (Section 32.2.1.6) that the positive and negative pastes are pasted on different machines. For that matter, the paste which is spilled on the floor when executing these two operations may be collected separately onto separate pits of positive and negative paste, respectively, before pumping into the dewatering equipment (one type of paste for each cycle). The resultant dewatered paste or cake may then be recycled into the paste mixer. This CP option would be of benefit as the paste (collected and dewatered) can be reused in both the positive paste mixer (recycled positive spilled paste) and the negative paste mixer (recycled negative spilled paste). Accordingly, the quantity of paste required to be manufactured would further be reduced. Moreover, since the waste paste is not settled in the trade waste treatment facility, operating costs of the trade waste facility would also be reduced. Therefore, implementation of this option would reduce the quantity of sludge to be sent for off-site recycling. Inasmuch as this CP option offers better solutions compared to option (b) above, it faces two major challenges: firstly, the moisture content of the paste is important and a certain percentage has to be maintained for reuse in paste mix. Thus, the filter press selected (for dewatering of sludge) should be able to maintain this percentage. Secondly, even though recycling of both positive and negative pastes can be achieved by this CP option, it would be difficult to segregate the positive and negative paste spills on the plant floor. This would result in the generation of a mixture of positive and negative pastes again. This would, in turn, result in recycling the paste in only the negative paste mixer thereby making this option similar to option (b) above. Besides, this option also requires investment in dewatering equipment.[3]

32.7.2.3 CP Options for Loss of Oxide in Paste

Loss of oxide in paste may result from both improper feeding of grids into the pasting machines and cleaning of hoppers during maintenance. Normally a distance is maintained between two successive grids, that is, a time lag exists between the feeding mechanism of grids into the pasting machine and the successive step where the grids from the previous step are then fed into the pasting hopper. Within this gap, a small amount of paste is deposited. When it is dropped off the conveyor belt and collected, the paste may be recycled back into the hopper. Cleaning and maintenance of the pasting machine also causes generation of sludge. When the plates are being transferred using conveyors, the paste tends to stick on the rollers as they are used to evenly spread paste on grids. This necessitates the washing of the rollers to remove the sticky paste. After washing off the paste, it ends up into sludge, and finally into the wastewater treatment facility.[3] The various prevention/reduction options in this case are as follows:

a. *Hopper operation*: This involves making improvements in operating procedures, control operations, and the maintenance done in the hopper operation (i.e., from the feeding of paste on conveyor belts, and its being applied onto grids). If implemented, this CP option would reduce the amount of paste being wasted and would bring about reduction in the operation costs of trade waste treatment facility as the quantity of wastewater to be treated would reduce.[3]

b. *Material of construction*: Material construction may be improved by making the hoppers and rollers have a nonstick coating on them. This would prevent the sticking of the paste on the equipment. Furthermore, a collection tank may be placed below the rollers to collect excess paste that falls off during the operations. The collected paste in tanks would then be recycled. The benefit of such options may be appreciated in the reduction in the quantity of paste ending as sludge as no sludge would be stuck to the equipment. This would also further reduce water consumption as less cleaning would be required. The quantity of paste ending up in the trade waste treatment facility would also be greatly reduced, thus leading to reduced operating costs.[3]

c. *Improved process control*: Automation of the process of applying paste on the grids may reduce the waste being generated during this process. This is so because such outcomes as thickness of paste would be controlled if the pasting operation was automated. Accordingly, automation would not only prevent the generation of excess paste as sludge, but would also reduce the number of plates being scrapped after the grid pasting process. The benefits of this CP option hinge on the fact that it would not only reduce the quantity of plates scrapped but also would reduce the amount of paste sludge generated, thereby leading to reduced operation costs. However, since this CP option is a preventive as well as a long-term option, it may require a large capital investment and several changes in the existing equipment.[3]

32.7.2.4 CP Options for Metal Dust in Air

Manufacturing operations that include, among others, the collection of pasted plates in the pasting section, the collection of parted plates in the grid parting section, and the collection of enveloped plates in the battery assembly, are some of the major sources of metal dust. Besides, paste mixing causes evaporative losses, which contain metal oxides. In the oxide milling section, for example, the conversion of the metal into metal oxide and the subsequent separation of the two (metal from its oxide) may lead to the generation of additional metal particles that are released as dust. Furthermore, the vacuum suction feeding system in the battery assembly section also generates polluted air. Since it is the handling of the plates that is of major concern with regard to generation of metal pollution, there is nothing much that can be done to prevent or reduce it. Thus, treatment of the pollutant is the best solution in this case. In addition, the use of face masks by operators and ventilation systems may also be the best practical option to deal with metal dust particles. In view of the fact that the collected filter dust has no use on-site, leave alone its not being recyclable on-site, the only best option is to deposit it to the smelter. The only CP option would be to replace the vacuum system. Replacing the vacuum system used for feeding of plates in the battery assembly section would not only reduce the amount of air pollution in terms of metal particulate, but also reduce the volume of air that should be treated in the baghouse filters of the mechanical system. The immediate benefit of this CP option would be the improved workplace environment owing to the reduction in generation of metal dust. Conversely, using a nonvacuum system for feeding of plates in the battery assembly section would need the replacement of existing equipment, in addition to the installation of three baghouse filters at the treatment facility of the metal dust discharged from the ventilation system. This may not only impact on the costs for changing the operation arrangement, but also the replacements may not be as effective as envisaged.[3]

32.7.2.5 CP Options for Metal Particles in Stormwater

The metal particles, which are emitted from the stacks after the baghouse filtration process, tend to settle on-site. Recall that the baghouse filters are used as pollution control equipment for metal dusts generated in the facility. After settling, these particles are then washed away in the event known as storm, thereby causing the metal pollution of stormwater. Sample analysis of the selected stormwater drains has often indicated the presence of metals in various forms. Prevention/reduction options in this case should aim at either preventing or reducing the metal particles from entering the stormwater drain, and the collection/treatment facility of stormwater. Two CP options may be explored: (1) improve the efficiency of pollution control equipment and (2) filtration and recycling of stormwater.[3]

a. *Improve the efficiency of pollution control equipment*: Improving the efficiency of the pollution control equipment (baghouse filters) would reduce the amount of metal emitted from the stacks. As a result of improved efficiency of pollution control equipment, the metal particles settled on-site and the corresponding concentration in stormwater would reduce. Since the baghouse filters are operating at removal efficiencies (of particulate matter) of greater than 95%, improving the efficiency of the pollution control equipment further would involve very high costs and could require replacement of the existing equipment. This is a major drawback of this CP option.[3]

b. *Filtration and recycling of stormwater*: In order to recycle the stormwater, fine metal particles as well as other SS should be removed. To achieve this, another CP option ought to be introduced. In this option, the stormwater may be collected into a tank and then passed through a filter to remove fine particles. The resultant filtered stormwater would then be recycled on-site. The major benefit of adding a filtration system lies in the improvement of the quality of water to a level that would make it suitable for mixing with paste and being used as process water. This would greatly reduce water usage as well as achieving reduction in stormwater pollution. Either a cartridge or a valveless autowash gravity (VAG) filter may be used for this purpose. The advantage of using the VAG filter is the fact that it involves no instrumentation and maintenance and it backwashes automatically. In this regard, it is more suitable for this application when compared to the cartridge filter. However, the cost of VAG filters is substantially higher than those of cartridge filters. However, this option would create waste streams (that of particles collected at the filter media and backwash water used for cleaning of filter media), which should have to be managed suitably. Besides, the collection and filtration of stormwater may prove to be an added expense when compared to the cost of water purchased from the authorities. This may be a pitfall as this CP option is being considered. Nevertheless, a detailed design of the stormwater collection and filtration system should enable quantification of the cost of stormwater, as well as enable operationalizing it.[3]

32.8 CONCLUSIONS AND FUTURE PROSPECTS

Although the development of the battery technology was achieved as early as a century ago, several advances are continually being made in the designs and modifications in the chemistry of a particular battery. These changes have made the battery a companion that is required in many hand-held devices and therefore popularized further the use of batteries. With these developments has also come the battery wastes burden, which is also complicated by the inefficient and in most cases costly battery waste treatment methods. The present and the future lies in the development of efficient, cheaper, and environmentally friendly approaches to the management of battery wastewater streams, which contain hazardous metal ions. Promise in this direction lies in the development and adopting CP options and exploring the use of biosorbents.

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Environmental Engineering

HANDBOOK OF ADVANCED INDUSTRIAL AND HAZARDOUS WASTES TREATMENT

EDITED BY
LAWRENCE K. WANG
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NAZIH K. SHAMMAS

Most industrial and hazardous waste management resources cover the major industries and provide conventional in-plant pollution control strategies. Until now, however, no book or series of books has provided coverage that includes the latest developments in innovative and alternative environmental technology, design criteria, managerial decision methodologies, and regional and global environmental conservation. The **Handbook of Advanced Industrial and Hazardous Wastes Treatment**–together with its predecessor, the Handbook of Industrial and Hazardous Wastes Treatment–forms a complete and up-to-date resource that contains all the necessary technical information on hazardous industrial waste treatment.

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