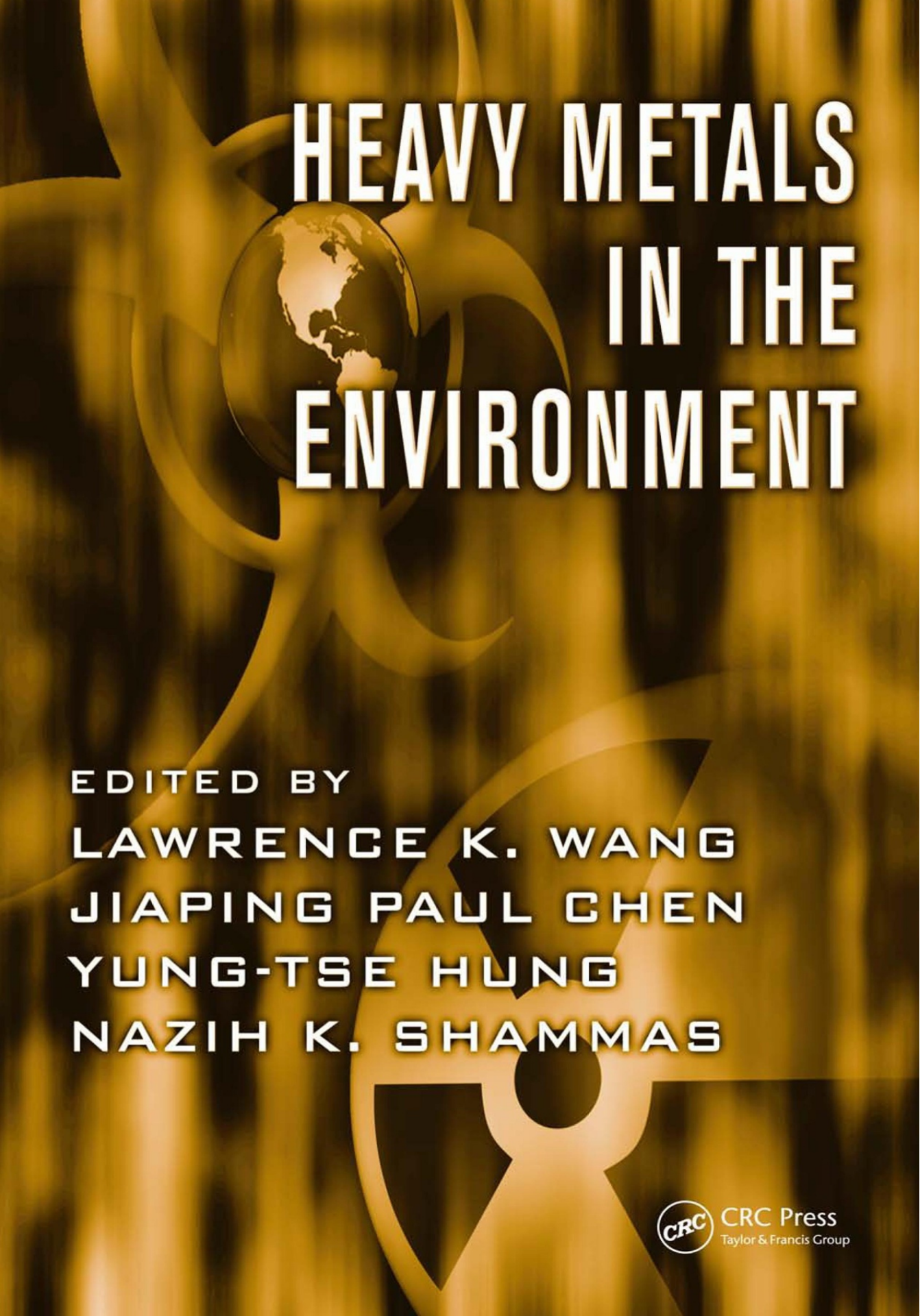




HEAVY METALS IN THE ENVIRONMENT

EDITED BY
LAWRENCE K. WANG
JIAPING PAUL CHEN
YUNG-TSE HUNG
NAZIH K. SHAMMAS



CRC Press
Taylor & Francis Group

HEAVY METALS IN THE ENVIRONMENT

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CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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CRC Press is an imprint of Taylor & Francis Group, an Informa business

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-1-4200-7316-4 (Hardcover)

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Library of Congress Cataloging-in-Publication Data

Heavy metals in the environment / edited by Lawrence K. Wang ... [et al].
p. cm. -- (Handbook of industrial and hazardous wastes treatment ; no. 3)
Includes bibliographical references and index.
ISBN-13: 978-1-4200-7316-4
ISBN-10: 1-4200-7316-8
1. Heavy metals--Environmental aspects. I. Wang, Lawrence K. II. Title. III. Series.

TD196.M4H4325 2009
628.5'2--dc22

2008053175

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>
and the CRC Press Web site at
<http://www.crcpress.com>

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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. Taylor & Francis and CRC Press have developed this timely book series entitled *Advances in Industrial and Hazardous Wastes Treatment*, which emphasizes 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 or commercial operation, and 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.

Heavy Metals in the Environment is the third book in the *Advances in Industrial and Hazardous Wastes Treatment* series. The importance of metals, such as lead, chromium, cadmium, zinc, copper, nickel, iron, and mercury, is discussed in detail. They could be important constituents of most living animals, plants, and microorganisms, and many nonliving substances in the environment. Some of them are essential for growth of biological and microbiological lives. Their absence could limit growth of small microorganisms to large plants or animals. However, the presence of any of these heavy metals in excessive quantities will be harmful to human beings, and will interfere with many beneficial uses of the environment due to their toxicity and mobility. Therefore, it is frequently desirable to measure and control the heavy metal concentrations in the environment.

In a deliberate effort to complement other industrial waste treatment and hazardous waste management texts published by Taylor & Francis and CRC Press, this book, *Heavy Metals in the Environment*, covers the important results in research of metals in environment. In the first two chapters, the recent research trends and the toxicity and sources of heavy metals are covered. The processes and mechanisms on metals in the environment are covered in [Chapters 3–7](#); they are the environmental behavior and effects of engineered metal and metal oxide nanoparticles, environmental geochemistry of high arsenic aquifer systems, nanotechnology application in metal ion adsorption, biosorption of metals, and heavy metal removal by exopolysaccharide-producing cyanobacteria. In [Chapters 8–14](#), technologies for metal treatment and management are addressed. These cover technologies for metal bearing effluents, metal contained solid wastes, metal finishing industry wastes, metal finishing brownfield sites, and arsenic contaminated groundwater streams. Metal in the atmosphere can greatly affect health of human beings. [Chapter 15](#) addresses control, treatment, and management of metal emissions from motor vehicles.

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

This book, *Heavy Metals in the Environment*, is to be used as a college textbook as well as a reference book for the environmental professional. It features the major hazardous heavy metals in air, water, land, and facilities that have significant effects on the public health and 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 heavy metal or metal-related industrial waste treatment or practice should be invaluable to environmental managers or researchers who need to trace, follow, duplicate, or improve on a specific industrial hazardous waste treatment practice.

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

Lawrence K. Wang, New York
Jiaping Paul Chen, Singapore
Yung-Tse Hung, Ohio
Nazih K. Shammas, Massachusetts

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 19 books, and is credited with 24 U.S. patents and 5 foreign patents. He received his BSCE degree from the National Cheng-Kung University, Taiwan, his MS degrees from both the Missouri University of Science and Technology and the University of Rhode Island and his PhD degree from Rutgers University, New Jersey.

Jiaping Paul Chen is an associate professor of environmental science and engineering at the National University of Singapore. His research interests are physicochemical treatment of water and wastewater and modeling. He has published more than 80 journal papers and book chapters. He has received various honors and awards, including Guest Professor of the Hua Zhong University of Science and Technology, and Shandong University of China, and Distinguished Overseas Chinese Young Scholar of National Natural Science Foundation of China. He is recognized as an author of highly cited papers (chemistry and engineering) of ISI Web of Knowledge. Professor Chen received his ME degree from the Tsinghua University, Beijing and his PhD degree from the Georgia Institute of Technology of Atlanta, Georgia.

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 eight 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 the National Cheng-Kung University, Taiwan, and his PhD degree from the University of Texas at Austin. He is the editor of *International Journal of Environment and Waste Management*, *International Journal of Environmental Engineering*, and *International Journal of Environmental Engineering Science*.

Nazih K. Shammass 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 Krofta Engineering Corporation, Lenox, Massachusetts. Dr. Shammass is the author of over 250 publications and eight 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.

Contributors

Rajasekhar Balasubramanian

Division of Environmental Science and
Engineering
National University of Singapore
Singapore

Changlun Chen

Institute of Plasma Physics
Chinese Academy of Science
Beijing, China

Yamin Deng

School of Environmental Studies and
MOE Key Laboratory of Biogeology
and Environmental Geology
China University of Geosciences
Wuhan, China

Roberto De Philippis

Department of Agricultural Biotechnology
University of Florence
Florence, Italy

Mohammad I. El-Khaiary

Chemical Engineering Department
Alexandria University
Alexandria, Egypt

Veysel Eroglu

Minister of Environment and Forestry
Istanbul Technical University
Istanbul, Turkey

Ferruh Erturk

Yıldız Technical University
Istanbul, Turkey

Wen Xin Gong

School of Environmental Science and
Engineering
Shandong University
Shandong, China

Jun He

Division of Environmental Engineering
and Science
National University of Singapore
Singapore

Yuh-Shan Ho

Department of Environmental
Sciences
Peking University
Beijing, China

Huijuan Liu

Research Center for Eco-Environmental
Sciences
Chinese Academy of Sciences
Beijing, China

Ruiping Liu

Research Center for Eco-Environmental
Sciences
Chinese Academy of Sciences
Beijing, China

Yue Ma

School of Environmental Science and
Engineering
Shandong University
Shandong, China

Ernesto Micheletti

Department of Agricultural
Biotechnology
University of Florence
Florence, Italy

Ghinwa M. Naja

Department of Chemical
Engineering
McGill University
Montreal, Quebec, Canada

Bernd Nowack

Materials, Products and the
Environment Group
Swiss Federal Laboratories for Materials
Testing and Research
St. Gallen, Switzerland

Jiuhui Qu

Research Center for Eco-Environmental
Sciences
Chinese Academy of Sciences
Beijing, China

Nazih K. Shammass

Lenox Institute of Water Technology
Krofta Engineering Corporation
Lenox, Massachusetts

Xue Fei Sun

School of Environmental Science
and Engineering
Shandong University
Shandong, China

Bohumil Volesky

Department of Chemical Engineering
McGill University
Montreal, Quebec, Canada

Laurence K. Wang

Krofta Engineering Corporation
Zorex Corporation
Lenox Institute of Water Technology
Lenox, Massachusetts

Shu Guang Wang

School of Environmental Science
and Engineering
Shandong University
Shandong, China

Xiangke Wang

Institute of Plasma Physics
Chinese Academy of Science
Beijing, China

Yanxin Wang

School of Environmental Studies and
MOE Key Laboratory of Biogeology
and Environmental Geology
China University of Geosciences
Wuhan, China

Gaosheng Zhang

Yantai Institute of Coastal Zone Research
for Sustainable Development
Chinese Academy of Sciences
Shandong, China

1 Metal Research Trends in the Environmental Field

Yuh-Shan Ho and Mohammad I. El-Khaiary

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1.1 INTRODUCTION

It has long been known that, in the right concentrations, many metals are essential to life and ecosystems [1–4]; chronic low exposures to metals can lead to severe environmental and health effects. Similarly, in excess, these same metals can be poisonous [5–9]. The main metal threats are associated with heavy metals such as lead, arsenic, cadmium, and mercury. Unlike many organic pollutants, which eventually degrade to carbon dioxide and water, heavy metals will tend to accumulate in the environment, especially in lake, estuarine, or marine sediments [10]. Metals can also be transported from one environment compartment to another [11], which complicates the containment and treatment problem.

Heavy metals are closely connected with environmental deterioration and the quality of human life, and thus have aroused concern all over the world. More and more countries have signed treaties to monitor and reduce heavy metal pollution [12]. Moreover, this field of research has been receiving increasing scientific attention due to its negative effects on life [9,10,13,14]; it was found that metals accumulate in animal and plant cells, leading to severe negative effects. The transport and accumulation of heavy metals by air [15], water [14,16], and soil [17,18] have also been a hot topic for research. It was found that in some cases contamination was circulated on a global range. Another related research topic was the monitoring of metal pollution and predicting critical levels and loads, which distilled into national and international regulations such as the European Union's Dangerous Substances Directive [19], the U.S. EPA [20] for water, the EU Air Quality Framework Directive [21], and the World Health Organization [22] for air.

A large body of research that deals with the treatment of metal pollution by different methods such as adsorption [23–26], activated sludge [27,28], phytoextraction [29–32], electrokinetic methods [33], electroosmosis [34], and ion exchange [35] has also been published.

Today, researchers are carrying out more comprehensive studies on metal pollution, leading to the unusual breadth of topics. Despite increasing interest, there have been few attempts at gathering systematic data on the nature and extent of metal pollution research. Garfield indicated that recent research focus could be detected by publication output [36]. A common research tool is the bibliometric method, which has already been widely applied to many fields of science and engineering. Furthermore, the Science Citation Index (SCI), from the Institute for Scientific Information (ISI), Web of Science databases, is the most important and frequently used source database of choice for a broad review of scientific accomplishment [37–39].

1.2 DATA SOURCES AND METHODOLOGY

Data were based on the online version of the SCI, Web of Science. SCI is a multidisciplinary database of the ISI, Philadelphia, USA. According to *Journal Citation Reports* (JCR), it indexes 6166 major journals with citation references across 172 scientific disciplines in 2006. One hundred and ninety-five journals listed in the three ISI subject categories of environmental engineering ($n = 35$), environmental sciences ($n = 144$), and water resources ($n = 57$) were considered in this study. The online version of SCI was searched under the keyword “metal or metals” to compile a bibliography of all papers related to metal research from 1991 to 2006. Articles originating from England, Scotland, Northern Ireland, and Wales were reclassified as being from the United Kingdom. Besides, the reported impact factor (IF) of each journal was obtained from the 2006 JCR. Collaboration type was determined by the addresses of the authors, where the term “single country” was assigned if the researchers’ addresses were from the same country. The term “international collaboration” was assigned to those articles that were coauthored by researchers from multiple countries.

1.3 RESULTS AND DISCUSSION

The total number of publications that met the selection criteria was 25,449. These publications were divided into 13 document types. The most frequently used document type (96%) was articles (24,409), followed distantly by reviews (609; 2.39%). Other document types of less significance were notes (108; 0.42%), letters (108; 0.42%), and editorial material (104; 0.41%). Since peer-reviewed journal articles represent the majority of documents within this field, 24,409 articles were further analyzed in this study. The emphasis of the following discussion is to determine the pattern of scientific production; research activity trends that consist of authorship, institutes, and countries; and also the trends in the research subjects addressed.

1.3.1 LANGUAGE OF PUBLICATION

Written languages of all metal-related articles in the environmental field were grouped. The results showed that English had a clear monopoly, making up 99% of all article publications. Other languages were French (0.26%), German (0.25%), and Spanish (0.025%). French articles were published in *Environmental Technology* ($n = 32$), *Houille Blanche-Revue Internationale de l'Eau* ($n = 14$), *Water Quality Research Journal of Canada* ($n = 8$), *Journal of Environmental Engineering and Science* ($n = 6$), *Water Research* ($n = 3$), and *Science of the Total Environment* ($n = 1$). German articles were published in *Gefahrstoffe Reinhaltung der Luft* ($n = 34$), *Acta Hydrochimica et Hydrobiologica* ($n = 27$), and *Isotopes in Environmental and Health Studies* ($n = 1$). Only one journal published Spanish articles: *Ingenieria Hidraulica en Mexico* ($n = 6$). For all practical purposes, English was the international language of choice in metal research, at least according to the SCI database. We leave the debate of whether or not English was the lingua franca of international scientific communication to other commentators [40].

1.3.2 ARTICLE OUTPUT AND DISTRIBUTION IN JOURNALS

Figure 1.1 shows the article output results from 1991 to 2006. The number of articles per year increased from 550 in 1991 to 2871 in 2006, reflecting the increasing interest in this field of research. More than 55% of the records were published during the period 2001–2006. In total, 24,409 articles were published in 173 journals. Six core journals contained 34% of the total articles. Figure 1.2 shows the trend of article publication in these six journals from 1991 to 2006. It is noticed that *Applied Catalysis A—General* rose from the sixth rank in 1991 to the first rank in 2006; also *Chemosphere* rose from the fifth rank in 1991 to the second rank in 2006.

1.3.3 PUBLICATION PERFORMANCE: COUNTRIES, INSTITUTES, AND AUTHORSHIP

Among the 24,409 articles produced in 145 countries, the top 20 most active countries produced 23,062 articles (95%), whereas the remaining 125 countries produced 1347 articles. Table 1.1 shows that the most active country was the United States (6081; 25%). The United States also produced the most independent publications (4859; 24%). Moreover, the seven most industrialized countries (G7: Canada, France, Germany, Italy, Japan, the United Kingdom, and the United States) collectively held the major portion (59%) of the world's publication. Figures 1.3 and 1.4 show the trend of article production in the top 10 countries from 1991 to 2006. The numbers of articles produced per year seem to increase at similar rates for most countries, except for China (whose rank changed from tenth in 1991 to second in 2006) and Spain (whose rank changed from ninth in 2001 to third in 2006).

The top 20 most productive institutes are listed in Table 1.2. There are seven institutes from the United States, three from Canada, two from China, and one each from Spain, Italy, France, Taiwan,

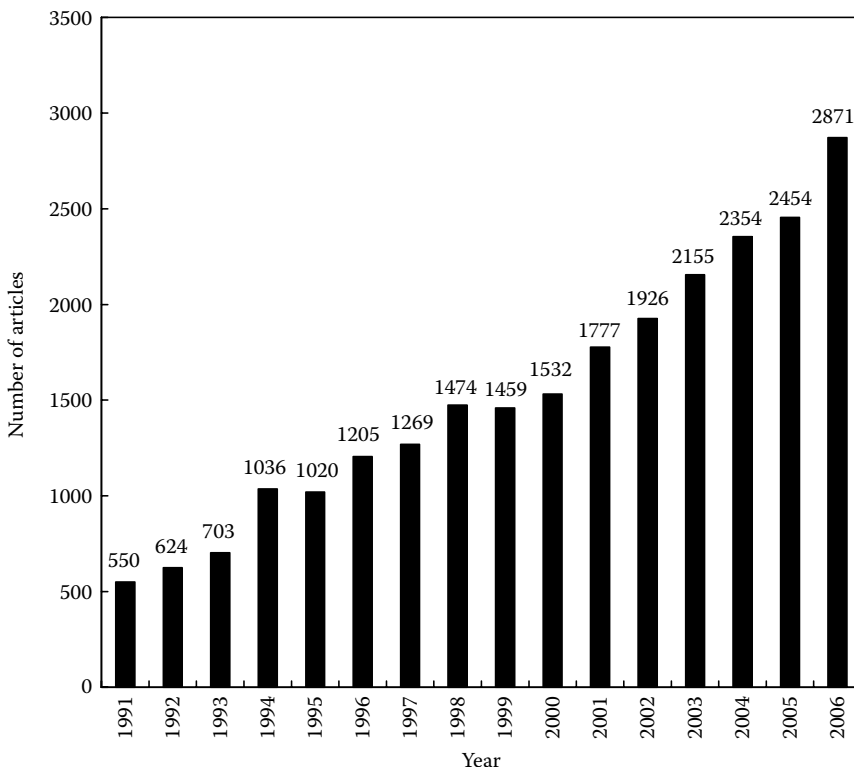


FIGURE 1.1 Publication outputs per year for the period 1991–2006.

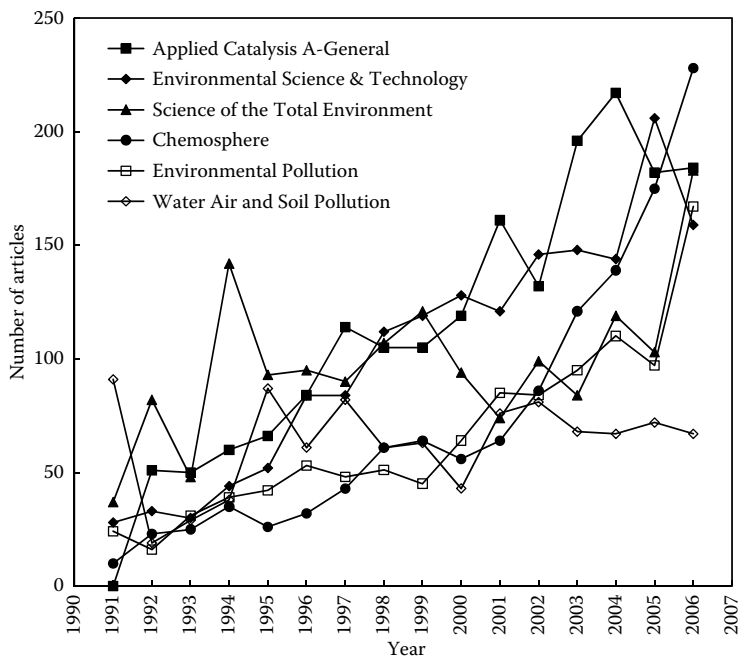


FIGURE 1.2 Comparison of the growth trends of articles in the top six active journals during the period 1991–2006.

TABLE 1.1
Top 20 Most Productive Countries of Articles during 1991–2006

Country	TP	%TP	SP	R (%)	CP	R (%)	FP	R (%)	RP	R (%)
United States	6081	25	4854	1 (24)	1227	1 (30)	5448	1 (22.4)	4925	1 (22)
United Kingdom	1809	7.4	1140	2 (5.6)	669	2 (17)	1432	2 (5.9)	1285	2 (5.7)
Canada	1569	6.4	1103	3 (5.4)	466	5 (12)	1353	3 (5.6)	1212	3 (5.3)
France	1298	5.3	822	7 (4.0)	476	3 (12)	1037	6 (4.3)	941	7 (4.1)
Italy	1297	5.3	1042	4 (5.1)	255	9 (6.3)	1159	4 (4.8)	1126	4 (5.0)
Spain	1263	5.2	939	6 (4.6)	324	7 (8.0)	1101	5 (4.5)	1038	5 (4.6)
Germany	1154	4.7	682	9 (3.4)	472	4 (12)	881	8 (3.6)	828	8 (3.6)
India	1109	4.6	950	5 (4.7)	159	19 (4.0)	1035	7 (4.2)	945	6 (4.2)
China	1076	4.4	642	10 (3.2)	434	6 (11)	861	9 (3.5)	826	9 (3.6)
Japan	1010	4.1	730	8 (3.6)	280	8 (7.0)	853	10 (3.5)	795	10 (3.5)
Australia	647	2.7	432	13 (2.1)	215	11 (5.3)	528	12 (2.2)	501	12 (2.2)
Netherlands	638	2.6	417	15 (2.1)	221	10 (5.5)	505	15 (2.1)	445	16 (2.0)
Sweden	634	2.6	429	14 (2.1)	205	13 (5.1)	527	13 (2.2)	496	13 (2.2)
Turkey	574	2.4	516	11 (2.5)	58	31 (1.4)	549	11 (2.3)	536	11 (2.4)
Poland	568	2.3	399	16 (2.0)	169	15 (4.2)	499	16 (2.0)	492	14 (2.2)
Taiwan	546	2.2	480	12 (2.4)	66	28 (1.6)	510	14 (2.1)	491	15 (2.2)
Belgium	498	2.0	288	19 (1.4)	210	12 (5.2)	380	17 (1.6)	369	17 (1.6)
South Korea	454	1.9	293	18 (1.4)	161	17 (4.0)	367	18 (1.5)	359	18 (1.6)
Hong Kong	434	1.8	252	22 (1.2)	182	14 (4.5)	367	18 (1.5)	350	19 (1.5)
Finland	403	1.7	281	20 (1.4)	122	22 (3.0)	340	20 (1.4)	328	20 (1.4)

Notes: TP, total publications; SP, independent publication; CP, international collaborative publication; %TP, share in publication; R, ranking; FP, first author publication; and RP, corresponding author publication.

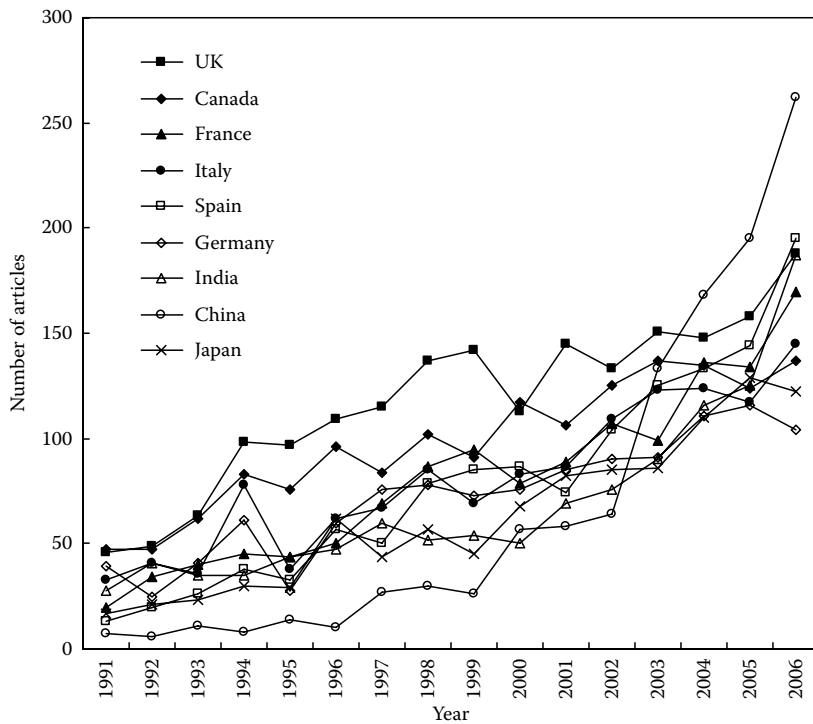


FIGURE 1.3 Comparison of the growth trends of articles in active countries (ranking as second to ninth) during the period 1991–2006. Noted that United States is ranked as the first country and its growth trend is given in Figure 1.4.

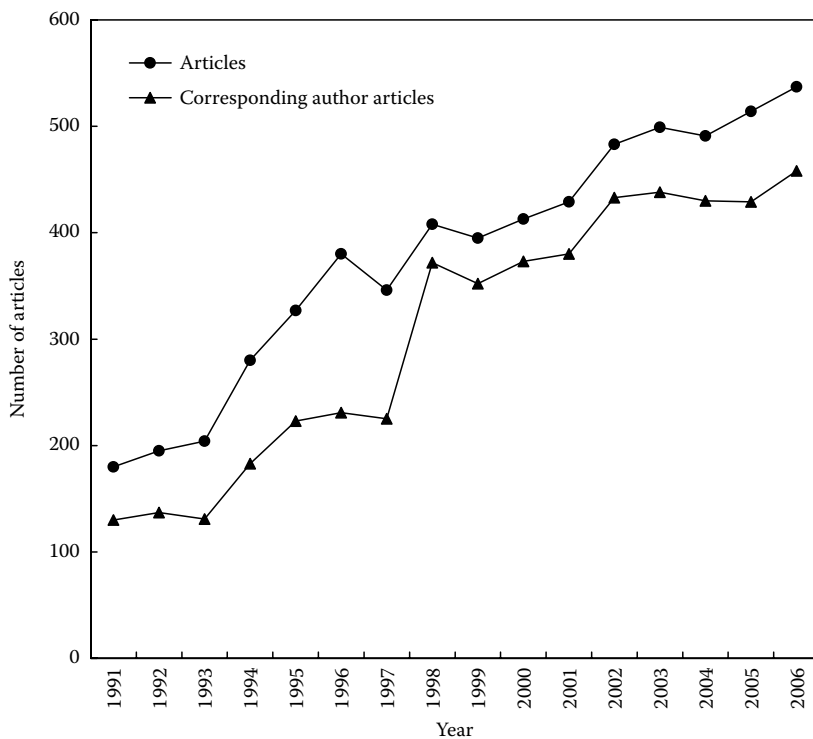


FIGURE 1.4 The growth trends of articles in the United States during the period 1991–2006.

TABLE 1.2
Top 20 Most Productive Institutes of Articles during 1991–2006

Institute	TP	TP R (%)	SP R (%)	CP R (%)	FP R (%)	RP R (%)
U.S. Environmental Protection Agency, USA	375	1 (1.5)	4 (0.7)	1 (2.5)	3 (0.85)	2 (1)
Chinese Academy of Sciences, China	330	2 (1.4)	1 (0.99)	2 (1.8)	1 (0.99)	1 (1.0)
Consejo Superior de Investigaciones Científicas (CSIC), Spain	316	3 (1.3)	2 (0.96)	3 (1.7)	2 (0.91)	3 (0.9)
United States Geological Survey (USGS), USA	237	4 (0.97)	3 (0.76)	5 (1.2)	4 (0.64)	4 (0.72)
Consiglio Nazionale delle Ricerche (CNR), Italy	211	5 (0.87)	15 (0.4)	4 (1.4)	6 (0.53)	5 (0.57)
Environment Canada, Canada	177	6 (0.73)	26 (0.31)	6 (1.2)	9 (0.46)	7 (0.45)
University of Quebec, Canada	174	7 (0.71)	5 (0.62)	11 (0.82)	5 (0.55)	6 (0.45)
University of Florida, USA	165	8 (0.68)	8 (0.46)	10 (0.93)	7 (0.47)	7 (0.45)
University of Delaware, USA	158	9 (0.65)	19 (0.37)	7 (0.97)	8 (0.46)	11 (0.41)
Rutgers, The State University of New Jersey, USA	149	10 (0.61)	29 (0.30)	7 (0.97)	14 (0.38)	12 (0.41)
University of Georgia, USA	136	11 (0.56)	15 (0.40)	13 (0.74)	15 (0.36)	18 (0.32)
Le Centre National de la Recherche Scientifique (CNRS), France	131	12 (0.54)	98 (0.16)	7 (0.97)	25 (0.29)	24 (0.28)
McGill University, Canada	128	13 (0.53)	13 (0.41)	16 (0.65)	13 (0.39)	13 (0.38)
University of Maryland, USA	123	14 (0.50)	19 (0.37)	14 (0.66)	20 (0.32)	19 (0.31)
National Taiwan University, Taiwan	122	15 (0.50)	18 (0.39)	17 (0.63)	19 (0.34)	16 (0.33)
Hong Kong University of Science and Technology, Hong Kong	120	16 (0.49)	6 (0.60)	67 (0.37)	11 (0.41)	9 (0.43)
Zhejiang University, China	118	17 (0.48)	12 (0.42)	25 (0.56)	10 (0.41)	9 (0.43)
Imperial College of Science, Technology and Medicine, University of London, UK	117	18 (0.48)	15 (0.40)	22 (0.57)	16 (0.35)	20 (0.30)
Universiteit Gent, Belgium	116	19 (0.48)	9 (0.44)	30 (0.52)	17 (0.34)	15 (0.37)
Indian Institute of Technology, India	115	20 (0.47)	7 (0.56)	67 (0.37)	12 (0.40)	14 (0.37)

Notes: TP, total publications; SP, independent publication; CP, international collaborative publication; FP, first author publication; RP, corresponding author publication; and R, ranking.

Hong Kong, the United Kingdom, Belgium, and India. The highest production came from the U.S. EPA (375; 1.5%), followed closely by the Chinese Academy of Sciences (330; 1.4%) and CSIC from Spain (316, 1.3%). The high activity of the latter two institutes is partially responsible for the recent increase in rank of China and Spain.

Collaboration plays an important role in contemporary scientific research, which is manifested in internationally coauthored papers traced by bibliometric tools [41]. Among the 24,365 articles with author address published from 1991 to 2006, 13,080 (54%) were produced by single institutions, whereas 7304 (30%) were produced by intranational collaboration and 4025 (17%) by international collaboration (CP). The United States produced the largest number of CP (1227), which amounts to 20% of the total articles from the United States and 30% of CP produced by all countries. However, Hong Kong ranked number one in the percent of its publications produced by international collaboration (42%), followed by Germany (41%) and China (40%). Other countries that produce a good part of their articles by CP are France (36%), the Netherlands (35%), Sweden (32%), and Finland (30%).

It is usually assumed that the corresponding author is the seniormost among the research group. Hence, articles without corresponding author address information on the ISI Web of Science were excluded from the analysis. The analysis comprised a total of 22,698 articles with 13,310 corresponding authors. Among these corresponding authors, 9222 (41%) published only one article and 4348 (19%) published two articles as corresponding author. The most active corresponding author

was Burger J. from Rutgers State University, USA, who published 68 articles as corresponding author, 68 articles as first author, and 78 articles in total. This was followed by Wang W.X. from Hong Kong University of Science & Technology, who published 52 articles as corresponding author, 12 articles as first author, and 63 articles as author. Regarding corresponding author countries, the United States ranked at the top (4925; 22%) followed by the United Kingdom (1285; 5.7%), Canada (1212; 5.3%), and Italy (1126; 5.0%). Table 1.2 shows that the ranking of institutes according to the number of corresponding author articles is not the same as the ranking according to the total number of articles. The Chinese Academy of Sciences (233; 1.0%) and the U.S. EPA (227; 1.0%) are almost equally at the top, followed closely by CSIC of Spain (205; 0.90%) (Figure 1.5).

On the basis of the assumption that the first author of an article performs most of the research, a distribution of first authors was undertaken. The United States produced the largest number of first author articles (5448; 22%), followed by the United Kingdom (1432; 5.9%) and Canada (1353; 5.6%). However, when it comes to institutes, the top-ranking institute in regard to first author was not from the United States. The institute with the highest number of first author papers was the Chinese Academy of Sciences (241; 0.99%), followed by CSIC (221; 0.91%) and then by the U.S. EPA (207; 0.85%).

A bias would appear in authorship analysis if any two or more authors have the same name or if authors use different names in their publications (e.g., name changes due to marriage). In addition, authors could work for different institutions or countries over time or within the same period of time, which increases the difficulties of analyzing authorship. Therefore, it is strongly recommended that an “international identity number (IIN)” is created, which is offered to an individual person for all authors when they publish their first paper in an ISI-listed journal. We believe that assigning and tracing the IIN will be the only way of accurately recording authorship. Similarly, a bias would also

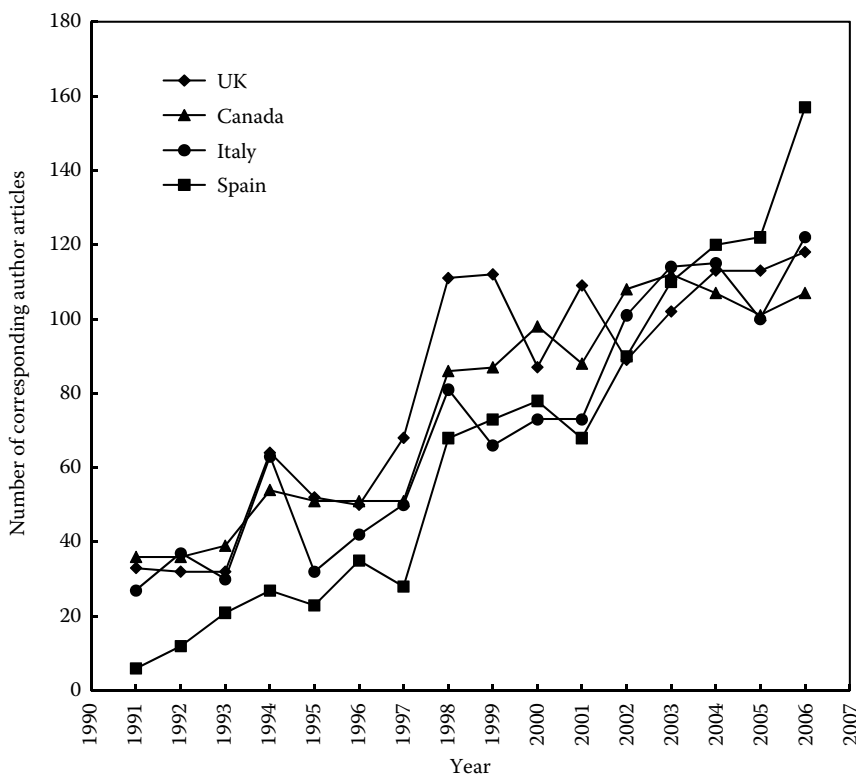


FIGURE 1.5 Comparison of the growth trends of corresponding author articles during the period 1991–2006 in the United Kingdom, Canada, Italy, and Spain.

appear because both the Chinese Academy of Sciences and the Indian Institute of Technology have branches in many cities. In this study the publications of these two institutes were pooled under one heading; dividing the publications among the branches would have given different rankings.

1.3.4 RESEARCH EMPHASIS: AUTHOR KEYWORDS AND KEYWORDS PLUS

The statistical analysis of keywords aimed at discovering the directions of science [42], and proved to be important for monitoring the development of science and programs. The bibliometric method concerning author keywords analysis has been found in recent years [38], whereas using author keywords to analyze the trend of research has been much more infrequent [43]. The examination of author keywords in the period of this study revealed that 32,167 author keywords were used. Of these, 23,741 (74%) appeared only once, 3706 (12%) appeared twice, and 1422 (4.4%) appeared thrice. The large number of once-only author keywords probably indicated a lack of continuity in research and a wide disparity in research focus [39]. Table 1.3 shows the distributions of the top 30

TABLE 1.3
Top 30 Most Frequency of Author Keywords Used during 1991–2006 and 4 Four-Year Periods

Author Keywords	91–06 TP (%)	91–94 R (%)	95–98 R (%)	99–02 R (%)	03–06 R (%)
Heavy metals	2625 (16)	1 (15)	1 (16)	1 (17)	1 (15)
Metals	996 (5.9)	2 (6.9)	3 (6.0)	2 (6.4)	3 (5.4)
Cadmium	994 (5.9)	3 (6.6)	2 (6.3)	3 (5.9)	2 (5.6)
Copper	844 (5.0)	5 (4.9)	4 (5.2)	4 (5.3)	4 (4.7)
Lead	829 (4.9)	4 (5.6)	4 (5.2)	5 (5.0)	5 (4.6)
Trace metals	585 (3.5)	6 (4.7)	6 (4.0)	6 (4.0)	9 (2.7)
Zinc	582 (3.4)	7 (4.1)	7 (3.4)	7 (3.9)	8 (3.1)
Heavy metal	498 (2.9)	23 (1.7)	16 (2.1)	8 (2.9)	6 (3.5)
Adsorption	471 (2.8)	11 (3.3)	13 (2.3)	15 (2.1)	7 (3.4)
Mercury	448 (2.7)	15 (2.3)	8 (3.1)	9 (2.9)	11 (2.4)
Sediment	431 (2.6)	10 (3.4)	10 (2.6)	10 (2.8)	12 (2.3)
Soil	417 (2.5)	16 (2.2)	12 (2.4)	13 (2.3)	10 (2.6)
Toxicity	406 (2.4)	9 (3.6)	9 (2.7)	11 (2.6)	16 (2.0)
Pollution	392 (2.3)	18 (2.0)	11 (2.5)	12 (2.6)	14 (2.2)
Sediments	334 (2.0)	8 (3.8)	14 (2.2)	14 (2.1)	21 (1.5)
Bioavailability	318 (1.9)	24 (1.4)	24 (1.4)	19 (1.8)	13 (2.2)
Bioaccumulation	307 (1.8)	16 (2.2)	18 (1.8)	16 (2.0)	18 (1.7)
Arsenic	297 (1.8)	30 (1.1)	23 (1.5)	20 (1.7)	15 (2.0)
Nickel	291 (1.7)	12 (3.1)	15 (2.2)	17 (1.8)	27 (1.3)
Trace elements	288 (1.7)	19 (1.9)	19 (1.7)	23 (1.4)	17 (1.9)
Speciation	286 (1.7)	14 (2.7)	17 (2.0)	18 (1.8)	23 (1.4)
Chromium	253 (1.5)	22 (1.8)	19 (1.7)	21 (1.6)	27 (1.3)
Biomonitoring	252 (1.5)	36 (0.92)	28 (1.1)	22 (1.6)	19 (1.6)
Sewage sludge	230 (1.4)	19 (1.9)	21 (1.7)	30 (1.1)	25 (1.3)
Kinetics	205 (1.2)	26 (1.3)	26 (1.2)	32 (1.1)	25 (1.3)
Sequential extraction	200 (1.2)	24 (1.4)	33 (1.0)	24 (1.3)	30 (1.1)
Sorption	198 (1.2)	30 (1.1)	37 (0.93)	33 (1.0)	22 (1.4)
Biosorption	196 (1.2)	97 (0.42)	43 (0.86)	27 (1.2)	24 (1.4)
Leaching	194 (1.1)	53 (0.67)	29 (1.1)	26 (1.2)	29 (1.2)
Fish	187 (1.1)	30 (1.1)	25 (1.2)	25 (1.3)	36 (0.96)

Notes: TP, publications in the study period; R (%), the rank and percentage of the articles.

most active author keywords used during 1991–2006 and also in four-year periods. Besides “heavy metals” (16%) and “metals” (5.9%), the most frequently used keywords for all periods were the names of certain heavy metals: cadmium (5.9%), copper (5%), lead (4.9%), and zinc (3.4%). It is interesting to note that the sum of using keywords “adsorption,” “sorption,” and “biosorption” is 5.2%, which reflects the dominance of sorption-related techniques for the treatment of metal pollution. The closest treatment method is “leaching” at 1.1%, whereas other methods of metal removal do not appear in the top 30 list of keywords. Generally, the ranking of most author keywords did not fluctuate distinctly, showing that metal research in the environmental field was basically steady in the past 16 years. However, several keywords such as “bioavailability,” “arsenic,” “adsorption,” “sorption,” and “biosorption” have increased in ranking of frequency, which might be identified as current environmental research hotspots. On the other hand, the use of keywords such as “sediments,” “speciation,” and “nickel” has steadily declined from 1991 to 2006, which might indicate well-established disciplines or that the research trend has moved away from these topics.

Furthermore, keywords plus, which supplied additional search terms, was extracted from the titles of papers cited by authors in their bibliographies and footnotes in the ISI database [42]. Keywords plus analysis is an independent supplement that reveals article contents with more details. In source title analysis, as we segment the title into single words, the result is not repeated and can be statistically analyzed by rule and line; however, it breaks the integrality of phrases in the title. In author keywords analysis, we preserve the intact words that the authors want to convey. Although it makes the same single word or phrase appear in different author keywords, we can compare the discrimination between author keywords or sum up dissimilar keywords with a common phrase or single word for further study. Keywords plus substantially augmented title word and author keyword indexing. In all, 21,783 articles were found to include keywords plus information. Table 1.4 shows the 30 most frequently used keywords plus with their rankings and percentages.

Keywords plus analysis as an independent supplement reveals article contents with more details. There are some similar and dissimilar trends between their statistical results in the study period. The keywords plus “heavy metals,” “metals,” “cadmium,” and “copper” were at the top of the list, in accordance with the frequency of author keywords and title words. It is interesting to note that in author keywords analysis, “cadmium,” “copper,” and “lead” received more or less the same focus in research (5.9%, 5%, and 4.9%, respectively). However, keywords plus tells another story: “cadmium” ranked second at 12% after “heavy metals” (16%), whereas “copper” and “lead” were relatively distant at 8.6% and 7.2%, respectively. On the other hand, “water,” which ranked fifth in keywords plus (7.2%), did not appear at all in the top 30 author keywords. This indicates that the research was more oriented toward metal pollution in aqueous systems, and is corroborated by noticing that the keyword plus “air” ranked 80th (1%). Moreover, the ranking of “water” improved from eighth during 1991–1994 to fifth during 2003–2006, whereas that of air dropped from 55th to 99th in the same time periods. Another disagreement was found in the appearance of “mercury”: in author keywords its ranking improved from 15th (1991–1994) to 8th (1995–1998) and then steadily declined until it held the 11th rank (2003–2006); on the other hand, its ranking in keywords plus dropped from 16th (1991–1994) to 40th (2003–2006). This may be attributed to the global legislations that reduced/eliminated mercury compounds from many products, thus reducing the environmental problems of mercury and consequently diverting the research focus to other pollutants. Other terms that are frequent in keywords plus but not in the top 30 author keywords are “accumulation” (5.8%), “removal” (4.4%), “growth” (2.7%), and “exposure” (2.5%). The frequency of these words has a significance because keywords plus is usually more concerned with the novel research direction than with the mature direction in the field [42]. “Adsorption” and “sorption” increased in keywords plus frequency from 1991 to 2006, corroborating the observed importance of this treatment method. Moreover, the word “removal” increased in ranking and frequency from 24 (2.1%) in 1991–1994 to 10 (6%) in 2003–2006. This increase, in view of the declining frequency of “toxicity,” might indicate that research is moving away from assessing the impact of metal pollution and focusing instead on the treatment of polluted bodies. The treatment of metal pollution by “reduction” increased in ranking from 58th (1991–1994) to 28th (2003–2006), suggesting increased interest in this technique.

TABLE 1.4
Top 30 Frequency of Keywords Plus Used and 4 Four-Year Periods

Keywords Plus	91–06 TP (%)	91–94 R (%)	95–98 R (%)	99–02 R (%)	03–06 R (%)
Heavy metals	3532 (16)	2 (13)	1 (14)	1 (15)	1 (19)
Cadmium	2664 (12)	1 (13)	2 (14)	2 (12)	2 (12)
Metals	1904 (8.7)	3 (11)	4 (9.1)	3 (9.0)	4 (8.0)
Copper	1871 (8.6)	4 (10)	3 (9.3)	4 (8.3)	3 (8.1)
Water	1574 (7.2)	8 (6.7)	5 (8.4)	6 (6.9)	5 (7.1)
Zinc	1568 (7.2)	5 (8.7)	6 (7.6)	8 (6.7)	7 (6.9)
Lead	1522 (7.0)	6 (7.6)	7 (7.0)	5 (7.2)	8 (6.7)
Trace metals	1462 (6.7)	7 (7.0)	8 (6.8)	7 (6.8)	9 (6.5)
Adsorption	1375 (6.3)	10 (5.7)	9 (5.9)	11 (5.7)	5 (7.1)
Accumulation	1264 (5.8)	11 (5.6)	11 (5.6)	10 (5.9)	11 (5.9)
Toxicity	1205 (5.5)	9 (5.8)	10 (5.7)	9 (6.0)	12 (5.1)
Sediments	1103 (5.1)	12 (5.2)	12 (5.2)	12 (5.1)	13 (4.9)
Removal	949 (4.4)	24 (2.1)	24 (2.2)	14 (4.3)	10 (6.0)
Pollution	931 (4.3)	13 (3.8)	13 (4.1)	14 (4.3)	14 (4.5)
Speciation	926 (4.3)	14 (3.4)	14 (4.0)	13 (4.5)	15 (4.4)
Soils	816 (3.7)	15 (3.0)	15 (3.4)	16 (3.5)	16 (4.2)
Sorption	670 (3.1)	44 (1.4)	24 (2.2)	17 (3.1)	17 (3.9)
Contamination	618 (2.8)	35 (1.6)	19 (2.3)	19 (2.7)	18 (3.4)
Plants	599 (2.7)	33 (1.8)	27 (2.1)	23 (2.6)	19 (3.4)
Soil	591 (2.7)	18 (2.6)	23 (2.2)	18 (2.7)	21 (2.9)
Growth	590 (2.7)	17 (2.8)	17 (2.8)	21 (2.6)	25 (2.7)
Kinetics	546 (2.5)	30 (1.9)	31 (2.0)	26 (2.2)	20 (3.1)
Exposure	546 (2.5)	35 (1.6)	36 (1.8)	20 (2.7)	22 (2.9)
Oxidation	537 (2.5)	24 (2.1)	18 (2.4)	30 (2.1)	23 (2.8)
Mercury	523 (2.4)	16 (2.8)	16 (3.0)	22 (2.6)	40 (1.9)
Trace elements	508 (2.3)	39 (1.5)	35 (1.8)	26 (2.2)	24 (2.8)
Iron	477 (2.2)	27 (2.0)	21 (2.3)	25 (2.3)	31 (2.1)
Sewage sludge	454 (2.1)	24 (2.1)	22 (2.3)	32 (2.0)	33 (2.0)
Bioavailability	452 (2.1)	46 (1.3)	44 (1.5)	28 (2.2)	27 (2.5)
Reduction	451 (2.1)	58 (1.1)	31 (2.0)	34 (2.0)	28 (2.4)

Notes: TP, publications in the study period; R (%), the rank and percentage of the articles.

1.4 CONCLUSIONS

In this study, dealing with metal research in the 195 journals listed in the environmental field SCI papers, we obtained some significant points on worldwide research trends throughout the period from 1991 to 2006. The effort provided a systematically structural picture as well as clues on the impacts of metal research. English was by far the dominant language (99%); three other languages were also used, indicating that metal research is globally communicated in English. Apparently more and more authors, institutes, and countries have been engaged in metal research over the years. The G7, with a longer research tradition in this field, has the absolute superiority of production. Besides, China and Spain (both non-G7 countries) have boosted their research in the last few years and hold the second and third ranks, respectively, in 2006. The United States produced the largest number of internationally collaborative articles, but five other countries had more than a third of their production by international collaboration (Hong Kong, Germany, China, France, and the Netherlands). The most frequently used keywords were “cadmium,” “copper,” and “lead,” which

reflects stability in this research field. Among the metal removal methods investigated, adsorption was the most frequent and is still rising. Other significant methods of removal in metal research are “oxidation” and “reduction.”

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2 Toxicity and Sources of Pb, Cd, Hg, Cr, As, and Radionuclides in the Environment

Ghinwa M. Naja and Bohumil Volesky

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2.1 METAL TOXICITY

Out of 106 identified elements, about 80 of them are called metals. These metallic elements can be divided into two groups: those that are essential for survival, such as iron and calcium, and those that are nonessential or toxic, such as cadmium and lead. These toxic metals, unlike some organic substances, are not metabolically degradable and their accumulation in living tissues can cause death or serious health threats. Furthermore, these metals, dissolved in wastewaters and discharged into surface waters, will be concentrated as they travel up the food chain. Eventually, extremely poisonous levels of toxin can migrate to the immediate environment of the public. Metals that seep into groundwaters will contaminate drinking water wells and harm the consumers of that water.

Pollution from man-made sources can easily create local conditions of elevated metal presence, which could lead to disastrous effects on animals and humans. Actually, man's exploitation of the world's mineral resources and his technological activities tend to unearth, dislodge, and disperse chemicals and particularly metallic elements, which have recently been brought into the environment in unprecedented quantities and concentrations and at extreme rates. Man's new technologies involving nuclear fission opened up a whole new area of hope and concern at the same time. Radioactive isotopes of elements and, indeed, new elements have been discovered and handled in historically unprecedented quantities and concentrations. The sneaking and deadly danger of radioactivity associated particularly with long-lived and high-radiation isotopes has cast a shadow over our lives. Actually, the disposal problems concerning radioactive isotopes originating directly or indirectly from the operation of nuclear generating facilities have produced a considerable slow-down in deployment of this technology, which, after all, may only be a transient phase made obsolete by the dangers it generates.

2.1.1 SELECTED HEAVY METALS

Heavy metals can be defined in several ways. One possible definition is the following: Heavy metals form positive ions in solution and they have a density five times greater than that of water. They are of particular toxicological importance. Many metallic elements play an essential role in the function of living organisms; they constitute a nutritional requirement and fulfill a physiological role. However, overabundance of the essential trace elements and particularly their substitution by non-essential ones, such as the case may be for cadmium, nickel, or silver, can cause toxicity symptoms or death. Humans receive their allocation of trace elements from food and water, an indispensable link in the food chain being plant life, which also supports animal life. It is a well-established fact that assimilation of metals takes place in the microbial world as well as in plants, and these elements tend to get concentrated as they progress through the food chain. It has been shown that spectacular metal enrichment coefficients of the order of 10^5 – 10^7 can occur in cells [1]. Imbalances or excessive amounts of a metal species along this route lead to toxicity symptoms, disorders in the cellular functions, long-term debilitating disabilities in humans, and eventually death.

2.1.1.1 Lead

Lead is the most common of the heavy elements. Several stable isotopes exist in nature, ^{208}Pb being the most abundant. The average molecular weight of lead is 207.2. Lead is a soft metal that resists

corrosion and has a low melting point (327°C). From a drinking water perspective, the almost universal use of lead compounds in plumbing fittings and as a solder in water distribution systems is important. Distribution systems and plumbing installed before 1945 were made from lead pipes [2]. Solid and liquid (sludge) wastes account for more than 50% of the lead discharged into the environment, usually into landfills, but lead has been dispersed more widely in the general environment through atmospheric emissions—particularly from car exhausts. With the introduction of unleaded fuel, lead emissions from this source declined. The annual consumption of lead is in the order of 3 million tons, of which 40% is used in the production of electrical accumulators and batteries, 20% is used in gasoline as alkyl additives, 12% in building construction, 6% in cable coatings, 5% in ammunition, and 17% in other usages. It is estimated that approximately 2 million tons are mined yearly. Probably 10% of this total is lost in treatment of the ore to produce the concentrate, and a further 10% is lost in making pig lead. The amount of lead discharged into the environment is equal to the amount weathered from igneous rocks. In global lead level terms, the power storage battery industry may have a relatively low impact on the environment because about 80% of all batteries are recycled.

2.1.1.1.1 Exposure

Lead is present in tap water as a result of dissolution from natural sources or from household plumbing systems containing lead in pipes. The amount of lead from the plumbing system that may be dissolved depends on several factors, including acidity (pH), water softness, and standing time of the water [3]. Food can be contaminated by naturally occurring lead in the soil as well as by lead from sources such as atmospheric fallout or water used for cooking.

The total intakes and uptakes of lead from all sources are 29.5 and 12.5 µg/d, respectively, for children and 63.7 and 6.7 µg/d, respectively, for adults in urban areas [4]. The relative contribution of water to average intake is estimated to be 9.8% and 11.3% for children and adults, respectively. The total intake of lead from three of the four major sources—air, food, and dust—appears to have dropped significantly since the mid-1980s as a result of regulatory and voluntary actions to control lead from air (via gasoline) and food (via cans).

Other sources of lead intake include ceramic ware, activities involving arts and crafts, peeling paint, and renovations resulting in dust or fumes from paint [5]. No allowance was made for the contribution of lead from these sources, because they occur on a highly sporadic basis and because no quantitative data are available. It has been pointed out [5] that old paint has been an important source of excess lead intake for inner-city children living in older housing stock in the United States. Although the lead pollution from mining activities presents a relatively localized problem, its magnitude is significant, and particularly on the water pollution side it is compounded by the occurrence of other heavy metals. The obvious danger of pollution from smelting operations has long been recognized. Pollution control practices, however, leave a great deal to be desired. Primary smelters process the ore material and are usually large but few in number, whereas secondary smelters process scrap from old batteries, cable sheathing, etc. and represent more dispersed point sources of heavy metal pollution.

2.1.1.1.2 Health Effects

Lead can be absorbed by the body through inhalation, ingestion, dermal contact (mainly as a result of occupational exposure), or transfer via the placenta. In adults, approximately 10% of ingested lead is absorbed into the body. Young children absorb from 40% to 53% of lead ingested from food. Once lead is absorbed, it enters either a “rapid turnover” biological pool with distribution to the soft tissues (blood, liver, lung, spleen, kidney, and bone marrow) or a “slow turnover” pool with distribution mainly to the skeleton [6]. Of the total body lead, approximately 80–95% in adults and about 73% in children accumulate in the skeleton. The biological half-life of lead is approximately 16–40 days in blood [6] and about 17–27 years in bones [6].

2.1.1.1.3 *Acute and Chronic Exposure*

Perhaps no other metal, not even arsenic, has had its toxicology so extensively studied as has lead. Lead poisoning has been actually linked to the fall of the Roman Empire. The high lead content in bones from the roman period supports the hypothesis that the use of lead containers for wine and other liquids, the use of lead water pipes, and lead-containing ceramic glazing of earthenware containers contributed to the decimation of the ruling class, who were more able to afford the lead containers [7]. The lead poisoning of children has been linked to contemporary earthenware glazed surfaces and pigments of older paints. The toxicology of lead has been extensively studied. Inorganic lead is a general metabolic poison and enzyme inhibitor (like most of the heavy metals). Organic lead is even more poisonous than inorganic lead. The earliest symptoms of lead poisoning seem to be psychical (e.g., excitement, depression, and irritability). Young children are particularly affected and can suffer mental retardation and semipermanent brain damage. One of the most insidious effects of inorganic lead is its ability to replace calcium in bones and remain there to form a semi-permanent reservoir for long-term release well after the initial absorption. The usual indicator of the degree of inorganic lead poisoning in humans is the content of this element in whole blood. Different authorities suggest safety levels in the range of 0.2–0.8 ppm. The figure 0.2 ppm seems to reflect a worldwide minimum. The disturbing fact is that the natural levels in human blood are already very close to what is considered a reasonable toxicological limit, not leaving us with any margin for exposure to lead.

Lead is a cumulative general poison, with fetuses, infants, children up to six years of age, and pregnant women (because of their fetuses) being most susceptible to adverse health effects. Lead can severely affect the central nervous system. Overt signs of acute intoxication include dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, hallucinations, and loss of memory [8], with encephalopathy occurring at blood lead levels of 100–120 $\mu\text{g dL}^{-1}$ in adults and 80–100 $\mu\text{g dL}^{-1}$ in children. Signs of chronic lead toxicity, including tiredness, sleeplessness, irritability, headaches, joint pain, and gastrointestinal symptoms, may appear in adults with blood lead levels of 50–80 $\mu\text{g dL}^{-1}$ [8]. After one or two years of exposure, muscle weakness, gastrointestinal symptoms, lower scores on psychometric tests, disturbances in mood, and symptoms of peripheral neuropathy were observed in occupationally exposed populations at blood lead levels of 40–60 $\mu\text{g dL}^{-1}$ [9]. At levels of 30–50 $\mu\text{g dL}^{-1}$, there were significant reductions in nerve conduction velocity. Renal disease has long been associated with lead poisoning; however, chronic nephropathy in adults and children has not been detected below blood lead levels of 40 $\mu\text{g dL}^{-1}$. Finally, it has been demonstrated that interactions between calcium and lead were responsible for a significant portion of the variance in the scores on general intelligence ratings, and that calcium had a significant effect on the deleterious effect of lead [10]. Several lines of evidence demonstrate that both the central and peripheral nervous systems are principal targets for lead toxicity. These include subencephalopathic neurological and behavioral effects in adults and electrophysiological evidence of both central and peripheral effects on the nervous system in children with blood lead levels well below 30 $\mu\text{g dL}^{-1}$. The carcinogenicity of lead in humans has been investigated in several epidemiological studies of occupationally exposed workers [11]. The International Agency for Research on Cancer considered the overall evidence for the carcinogenicity of lead to humans to be inadequate [11].

2.1.1.2 **Cadmium**

Cadmium is a silvery-white, lustrous, but tarnishable metal; it is soft and ductile and has a relatively high vapor pressure. Cadmium is nearly always divalent; chemically it closely resembles zinc and occurs in almost all zinc ores by isomorphous replacement [12]. Cadmium is found in natural deposits as ores containing other elements. The greatest use of cadmium is primarily for electroplating, paint pigments, plastics, silver–cadmium batteries, and coating operations, including transportation equipment, machinery and baking enamels, photography, and television phosphors. It is also used in nickel–cadmium batteries, in solar batteries, and in pigments [13]. In one review, it was noted that the use of cadmium products has expanded in recent years at a rate of 5–10% annually, and the

potential for further growth is very high [14]. The whole world's annual production of cadmium is around 20,000 tons. Discharge of cadmium into natural waters is derived partly from the electroplating industry, which accounts for about 50% of the annual cadmium consumption in the United States. Other sources of water pollution are the nickel–cadmium battery industry and smelter operations, which are more likely to be fewer in number but of a greater point source significance, often affecting the environment at distances of a 100 km order of magnitude [15].

2.1.1.2.1 Occurrence

Cadmium is a relatively rare element. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration of between 0.15 and 0.2 mg kg⁻¹ [16]. Cadmium occurs in nature in the form of various inorganic compounds and as complexes with naturally occurring chelating agents; organocadmium compounds are extremely unstable and have not been detected in the natural environment. Industrial and municipal wastes are the main sources of cadmium pollution. The solubility of cadmium in water is influenced to a large degree by the acidity of the medium. Dissolution of suspended or sediment-bound cadmium may result when there is an increase in acidity [17]. The need to determine cadmium levels in suspended matter and sediments in order to assess the degree of contamination of a water body has been pointed out. The concentration of cadmium in unpolluted fresh waters is generally less than 0.001 mg L⁻¹ [16]; the concentration of cadmium in seawater averages about 0.00015 mg L⁻¹ [17]. Surface waters containing in excess of a few micrograms of cadmium per liter have probably been contaminated by industrial wastes from metallurgical plants, plating works, plants manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel–cadmium batteries, or by effluents from sewage treatment plants [17].

High concentrations of cadmium in air are associated with heavily industrialized cities, notably those having refinery and smelting activities [16], where levels may be several hundred times those found in noncontaminated areas [18]. According to the earlier (1969) data from the U.S. National Air Sampling Network, the annual average cadmium concentrations at 29 nonurban stations were all less than 0.000003 mg m⁻³; those for the 20 largest cities ranged from 0.000006 to 0.000036 mg m⁻³ [18].

The presence of cadmium in vegetation may arise from the deposition of cadmium-containing aerosols directly on plant surfaces and by the absorption of cadmium through roots. Plants vary in their tolerance to cadmium in soil and in the amounts they are able to accumulate. Certain shellfish, such as crabs and oysters, may concentrate cadmium to extremely high levels in certain tissues, even if they inhabit waters containing low levels of cadmium. Reported concentrations of cadmium in foodstuffs vary widely; concentrations in most foods average about 0.05 mg kg⁻¹ on a wet-weight basis. Other fresh meats generally contain less than 0.05 mg kg⁻¹; cadmium concentrations in fish are usually less than 0.02 mg kg⁻¹ [18]. In cadmium-polluted areas, cadmium levels may be significantly elevated; rice and wheat from contaminated areas of Japan have been found to contain concentrations near 1 mg kg⁻¹, at least a factor of 10 higher than those for most parts of the world [18].

2.1.1.2.2 Health Considerations

Cadmium is not at present believed to be an essential nutrient for animals or humans. Several studies on human subjects indicate that 4–7% of a single dose of ingested cadmium is absorbed from the intestine. The absorption of cadmium nitrate or cadmium chloride in animal studies ranged from 0.5% to 3% [18]. The total amount absorbed by humans has been estimated as 0.0002–0.005 mg day⁻¹ [19].

Absorbed cadmium accumulates mainly in the renal cortex and liver. The pancreas, thyroid, gall-bladder, and testes can also contain relatively high concentrations. Several studies suggest that accumulation of cadmium in the human body is a function of age [20]; one author claims that there is a 200-fold increase in the cadmium content of the body in the first three years of life, and that in this early period humans accumulate almost one-third of their total body burden. Cadmium accumulates with age until a maximum level is reached at about age 50; the total body burden of a person of 50 years of age ranges from 5 to 40 mg. About half the body burden is found in the kidneys and

liver; the cadmium concentration of the cortex of the kidneys ranges from 0.005 to 0.1 mg g⁻¹. Concentrations of cadmium in the renal cortex are normally 5–20 times those in the liver [17].

2.1.1.2.3 Toxic Effects

Due to its acute toxicity studied only recently, cadmium has joined lead and mercury in the most toxic “Big Three” category of heavy metals with the greatest potential hazard to humans and the environment. Cadmium is one of the metals most strongly absorbed by living cells accumulated by vegetation. It is also among the most toxic to living organisms and more likely to leach from industrial wastes. The acute oral lethal dose of cadmium for humans has not been established; it has been estimated to be several hundred milligrams [21]. Doses as low as 15–30 mg [21] from acidic foodstuffs stored in cadmium-lined containers have resulted in acute gastroenteritis. The consumption of fluids containing 13–15 mg of cadmium per liter by humans has caused vomiting and gastrointestinal cramps.

Acute cadmium poisoning has occurred following exposure to fumes during the melting or pouring of cadmium metal [22]. Fatalities have resulted from a 5 h exposure to 8 mg m⁻³, although some individuals have recovered after exposure to 11 mg m⁻³ for 2 h. Acute pneumonitis resulted from inhalation of concentrations between 0.5 and 2.5 mg m⁻³ for 3 days. Symptoms of acute poisoning include pulmonary edema, headaches, nausea, vomiting, chills, weakness, and diarrhea. Cadmium has been established as a very toxic heavy metal. A disease known as “Itai-Itai” in Japan is specifically associated with cadmium poisoning, resulting in multiple fractures arising from osteomalacia [23]. Symptoms of the disease, which occurred most often among elderly women who had many children, are the same as those of osteomalacia (softening of the bone); the syndrome is characterized by lumbar pain, myalgia, and spontaneous fractures with skeletal deformation. It is accompanied by the classical renal effects of industrial cadmium poisoning: proteinuria, and often glucosuria, and aminoaciduria [18].

Cadmium tends to accumulate in the human body (30 mg in an average American male), with 33% in the kidneys and 14% in the liver. Chronic cadmium poisoning produces proteinuria and causes the formation of kidney stones. There is evidence of a link between cadmium and hypertension. The main problem with cadmium in humans appears to be that the body seldom excretes as much cadmium as is absorbed. There is little general agreement about acceptable safety limits for cadmium intake. In the United States, the safety level of cadmium in drinking water has been set at 10 ppb. Sampling of surface waters revealed some dangerously high cadmium levels. Chronic exposure to airborne cadmium results in a number of toxic effects; the two main symptoms are lung emphysema and proteinuria [22]. Emphysema appears after approximately 20 years of exposure; levels of exposure that result in disability have not been systematically determined. It has been proposed that the minimum critical level of cadmium in the kidney required to produce renal tubular damage is approximately 0.2 mg g⁻¹ [24]. The World Health Organization (WHO) has recommended that the provisional permissible intake of cadmium not exceed 0.4–0.5 mg per week or 0.057–0.071 mg d⁻¹ [24].

2.1.1.3 Mercury

Mercury is a dense, silvery-white metal that melts at –38.9°C. Mercury is present in the Earth’s crust at an average concentration of 0.08 mg kg⁻¹; cinnabar (mercury[II] sulfide, HgS) is the most common mercury ore [25]. Igneous, metamorphic, and sedimentary rocks contain mercury at concentrations up to 0.25, 0.40, and 3.25 mg kg⁻¹, respectively [25]. Mercury and its compounds are used in dental preparations, thermometers, fluorescent and ultraviolet lamps, and pharmaceuticals, and as fungicides in paints, industrial process waters, and seed dressings. The pulp and paper industry also consumes mercury in significant amounts in the form of phenyl mercuric acetate, a fungicide, and in caustic soda, which may contain up to 5 mg kg⁻¹ as an impurity.

2.1.1.3.1 Occurrence

Many mercury compounds are volatile, and most decompose to form mercury vapor. Elemental mercury has a substantial vapor pressure even at ambient temperatures but, except at elevated

temperatures, does not react readily with oxygen in air. Mercury can exist as univalent and divalent ions. Mercury(I) is always in 2+, and all of its compounds are the dimeric form. Mercury(II), Hg^{2+} , forms both covalent and ionic bonds; HgCl_2 , for example, is covalent. This causes a relatively low solubility of HgCl_2 in water and higher solubility in organic solvents. Mercury(II) can also form complexes by accepting pairs of electrons from ligands. The covalent property of mercury(II) allows a stable mercury–carbon bond and the formation of organometallic compounds. The organomercury salts are soluble in organic solvents, and compounds such as dimethyl mercury, $(\text{CH}_3)_2\text{Hg}$, can easily be separated from inorganic salts and even from HgCl_2 , as HgCl_2 can first be complexed to form 2+ with excess chloride. The distribution of mercury between the three oxidation states is determined by redox potential, pH, and the anions present.

Mercury can enter the atmosphere by simple transport as metallic mercury vapor or as volatilized organic mercury compounds. The formation of volatile organomercurials may occur through microbial, animal, or plant metabolic activity. These natural processes result in the constant circulation of significant quantities of mercury in the atmospheric environment. The U.S. Environmental Protection Agency (EPA) has estimated rural concentrations of mercury in air to be $0.000005 \text{ mg m}^{-3}$, urban concentrations $0.00003 \text{ mg m}^{-3}$, and indoor concentrations $0.0001\text{--}0.0002 \text{ mg m}^{-3}$; the average atmospheric concentration was estimated at $0.00002 \text{ mg m}^{-3}$, and it was stated that atmospheric concentrations are unlikely to exceed an average value of $0.00005 \text{ mg m}^{-3}$ [26]. Mercury in air can be washed out by rain. In industrial areas, mercury concentrations as high as 0.0002 mg L^{-1} have been reported in rain. In most surface waters, $\text{Hg}(\text{OH})_2$ and HgCl_2 are the predominant mercury species. In reducing sediments, however, most of the mercury is immobilized as the sulfide. Concentrations of mercury in surface and drinking waters are generally below 0.001 mg L^{-1} [26]. The presence of higher levels of mercury in water is due to effluents from the chlor–alkali industry, the pulp and paper industry, mining, gold, and other ore-recovering processes, and irrigation or drainage of areas in which agricultural pesticides are used.

Inorganic mercury in sediments, under anaerobic conditions, can be transformed by microorganisms into organic mercury compounds, the most common of which is methyl mercury [27]. These compounds can readily associate with suspended and organic matter and be taken up by aquatic organisms. Methyl mercury has high affinity for lipids and is distributed to the fatty tissues of living organisms [28]. Although methyl mercury is estimated to constitute only 1% of the total mercury content of water, more than 90% of the mercury in biota is in the form of methyl mercury [28]. It has been estimated that about 5000 tons of mercury are annually released into the environment by man's activities. Mercury is readily scavenged by organic matter. Mercury salts from industrial effluents deposit in river or lake sediments and are then acted upon by anaerobic bacteria, which convert them into toxic methyl mercury and dimethyl mercury. It is in the hydrosphere that the effects of mercury pollution are most significant. Soluble mercury is readily incorporated into organisms in the aquatic environment and ultimately finds its way into higher members of the food chain such as man. The progress of mercury through the food chain successively increases its concentration to such an extent that natural levels in some commercial fish are close to, or exceed, the lowest level now set by the health authorities in many countries. It is therefore obvious that a small additional "pollution" component can be sufficient to cause a public health hazard under certain circumstances. This situation has already been reached for mercury and lead and may soon apply to cadmium. Analyses of the Greenland ice cap revealed that while mercury levels worldwide had been constant since 800 B.C., since 1950 the amounts present seem to have doubled.

2.1.1.3.2 Health Effects

Absorption of metallic mercury following ingestion is negligible; less than 0.01% of an administered dose of metallic mercury was absorbed in animals, for example. In humans, accidental ingestion of several grams of metallic mercury increased blood mercury levels [29], but only rarely did doses of 100–500 g cause clinical illness (stomatitis and diarrhea). Soluble inorganic mercury(II) salts are absorbed to a limited extent, 7–15% in humans, and sparingly water-soluble mercury(I)

salts are absorbed to an even lesser degree. The mercury(I) ion can be biotransformed to the mercury(II) ion *in vivo*, however. Ingested organic mercury, on the other hand, is readily absorbed [30]; 95% or more is absorbed in humans. Absorption depends on particle size, solubility, and rate of decomposition of the salts in biological fluids. A fraction of inhaled mercury salts will be cleared to the alimentary tract and absorbed by ingestion. Generally, aerosols of inorganic mercury compounds are absorbed to a lesser degree than is mercury vapor.

2.1.1.3.3 *Distribution and Metabolism*

The world's annual consumption of mercury averages about 10,000 tons, and about half of this total is used in the production of chlorine for bleaching paper pulp. As a result of the established mercury threat, the largest man-handling of mercury in chlorine manufacture is being limited by introducing alternative technologies that do not employ mercury electrodes. The next largest mercury consumption (approximately 35%) is in the production of switch gear and batteries.

Inorganic mercury compounds are rapidly accumulated by the kidney, the main target organ for these compounds. Mercury in the kidneys is in the form of a metallothionein-like complex. Binding of the mercury by the protein, metallothionein, is enhanced in the presence of cadmium. Phenyl and methoxyethyl mercuric salts rapidly degrade to mercuric salts and distribute as such in the bodies of humans and animals. The toxicity of these organomercurials is dependent on the rate of their conversion (biotransformation) to inorganic mercury; because this conversion is rapid, the toxicity of these compounds in cases of chronic exposure is similar to that seen after inorganic mercury exposure. Elemental mercury vapor that is inhaled rapidly diffuses through the alveolar membrane; in the body, it is oxidized to mercuric ions, which produce the toxic effects.

Absorption of methyl mercury from food (bound to protein) or water (as chloride salt) is almost complete both in animals and in humans. Methyl mercury has considerable stability in the body and circulates for a time unchanged in the blood. It is distributed in high concentrations to the kidney and somewhat less to the liver. In the kidney, 40% is present in the inorganic form. In humans, methyl mercury has a ratio of 20:1 between red blood cells and plasma, in contrast to the 1:1 ratio after exposure to inorganic or phenyl mercury [26]. The most reliable index of exposure to methyl mercury and of retention in the central nervous system is the finding of methyl mercury in red blood cells. Hair mercury levels reflect past exposure and are dependent on the rate of hair growth. There is an almost linear relationship between the amount of methyl mercury in blood and that in the hair that was formed during exposure; the ratio of hair to blood levels has been consistently found in the range 230–300:1 [26]. At steady state, the level of mercury in blood is proportional to the daily intake of methyl mercury; the constant of proportionality for a 70 kg adult has been estimated to be between 0.3 and 1.0 (units of days per liter).

2.1.1.3.4 *Toxicity*

With the possible exception of lead, mercury as a pollutant has been studied more extensively than any other trace element during the past three decades. Although it had been known for many centuries that mercury is poisonous to animals and humans, it was not until the late 1950s that its extreme toxicity to humans was appreciated as it made headlines worldwide. In 1953, the mysterious death of 52 persons living in fishing villages along Minamata Bay in Japan was unmistakably linked with mercury poisoning. High levels of mercury originating from the nearby plastics factory were found in the shellfish eaten by the villagers. The “minamata disease,” mercury poisoning, has been linked to many more deaths around the globe ever since and symptoms of mercury poisoning crippled countless more. Advanced analytical methods made it possible only relatively recently to monitor low levels of mercury in the environment, which, however, are sufficient to cause these serious problems on the large scale.

A particularly disturbing feature of mercury poisoning is that the effects are not immediately obvious. Methyl mercury is particularly toxic because it readily passes from the bloodstream into the cerebellum and cortex, causing damage that is symptomized by numbness, awkwardness of gait,

and blurring vision. Clinical tests to determine mercury poisoning are based mainly on the levels of this element in whole blood. Identifiable symptoms of mercury poisoning occur with levels of 0.2–0.6 ppm. Such levels would be reached by a daily intake of 0.3–1.0 mg of mercury by a healthy man. The WHO proposed an acceptable daily intake (ADI) of 0.3 mg Hg, of which not more than 0.2 mg should be in the form of methyl mercury. Since most of the environmental mercury is derived from natural sources, man's addition to this load is of critical importance. The appearance, character, and extent of the toxic effects of mercury depend on a number of factors: the chemical form of the mercury; the mercury compound and its ionization potential; the dose, duration of exposure, and the route of administration; and the dietary levels of interacting elements, especially selenium [30]. When given in acute massive doses, mercury, in whatever chemical form, will denature proteins, inactivate enzymes, and cause severe disruption of any tissue with which it comes into contact in sufficient concentration.

The two major responses to mercury poisoning involve neurological and renal disturbances. The former is characteristic of poisoning by methyl and ethyl mercuric salts, in which liver and renal damages are of relatively little significance. The latter is characteristic of inorganic mercurial poisoning. In general, however, acute lethal toxic doses by ingestion of any form of mercury will result in the same terminal signs and symptoms, which consist of shock, cardiovascular collapse, acute renal failure, and severe gastrointestinal damage. After acute administration of ionizable inorganic salts of mercury to animals or humans, the highest levels of mercury are found in the kidney; although acute oral poisoning results primarily in hemorrhagic gastritis and colitis, the ultimate damage is to the kidney. Clinical symptoms of acute intoxication include pharyngitis, dysphagia, abdominal pain, nausea and vomiting, bloody diarrhea, and shock. Later, swelling of the salivary glands, stomatitis, loosening of the teeth, nephritis, anuria, and hepatitis occur. Ingestion of 500 mg mercuric chloride causes severe poisoning and sometimes death in humans. Acute exposure results from inhalation of air containing mercury vapor in the range 0.05–0.35 mg m⁻³. Exposure for a few hours to a concentration of between 1 and 3 mg m⁻³ may give rise to pulmonary irritation and destruction of lung tissue and occasionally central nervous system disorders [30]. Chronic exposure occurs in persons occupationally exposed to large amounts of mercury on occasion and as a result of prolonged therapeutic use. Alkyl compounds of mercury are the most toxic to humans, producing illness, irreversible neurological damage, or death from the ingestion of milligram quantities [31]. Outbreaks of poisonings by these organic derivatives have been the result of accidents or of environmental contamination in a number of countries: Iraq, Guatemala, Pakistan, Japan (Minamata and Niigata), and the United States [31].

Symptoms may occur weeks or months after exposure to toxic concentrations of either methyl mercury or ethyl mercury. Therefore, no clear distinction between acute and chronic symptomatology can be made. In cases of severe poisoning, pronounced weight loss can occur with or without intestinal symptoms. Neurological symptoms include mental deterioration, rigidity and hyperkinesia, and salivation and sweating. Alkyl mercury readily crosses the placenta unchanged and concentrates in fetal tissues. As a result, infants born to exposed mothers may suffer from mental retardation, cerebral palsy, and convulsions. The fetus is far more sensitive to methyl mercury poisoning than is the child, and children below 10 years of age are more susceptible than adults. Although methyl mercury acts on basic genetic systems such as the spindle fiber mechanism and DNA, its mutagenic potential appears to be small. No evidence for genetic, teratogenic, or carcinogenic effects has yet been described for inorganic mercury.

2.1.1.4 Chromium

As any other transition metal, chromium can be found at a degree of oxidation ranging from (–II) to (+VI). However, the most common oxidation states of chromium are (0), (III), and (VI). In natural deposits, chromium is present in complex cubic isomorphous minerals called spinel. Most of the chromium found in nature is in its trivalent state (the most stable one), but small amounts of the hexavalent form have been found along with the divalent oxidation state. Chromium is used in many

industrial applications. It can be either used melted with other metals to produce alloys or plated. Chromium steel alloys provide high corrosion resistance and good hardenability. Other applications of chromium range from tanning agents, paint pigments, and catalysts to impregnation solution for wood or photography. The world production of chromite ore is several millions of tons per year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (aluminothermic process) or by electrolysis of either CrO_3 or chrome alum solutions.

2.1.1.4.1 Chemical Pathways

Chromium concentrations in both air and soil are subject to large variations. In air the concentrations range from 0.3 ng m^{-3} in remote sites to 50 ng m^{-3} in urban areas, and in soil they vary from traces to 250 mg kg^{-1} , where it may be from phosphate fertilizers. Chromium concentrations in natural waters are very limited by the low solubility of Cr(III) oxides. Thus a major part of chromium in waters is in the hexavalent state. Main contaminations are generated by industrial wastewaters. Since the trivalent state is predominant in soils, it is unlikely that even heavily polluted farmland would result in chromium accumulation in the food chain via plants. No common plant used as animal feed or food has been reported with a tendency to concentrate chromium.

2.1.1.4.2 Clinical Effects

Chromium was recognized to be a hazardous element in the early years after it was discovered. No reports indicate that chromium salts (+III) have severe toxic effects. Hexavalent chromium is considered to be lethal for a dose higher than 3 g for adult humans. The first symptoms are vomiting and persisting diarrhea. After a week, hemorrhagic diathesis and epistaxis are commonly observed. Convulsions occur during the final stages of the illness. Repeated occupational inhalation of hexavalent chromium compounds causes perforations of the nasal septum and skin ulceration "chrome holes." The sense of smell and acute irritative dermatitis or allergic eczematous dermatitis have frequently been reported in case of chronic exposure to chromic acid vapors as well as an increased incidence of cancer in the respiratory organs. Bronchial asthma due to chromate dust or chromic acid fumes has been experienced by a number of workers. Environmental contamination with chromium seems trivial compared to mercury or cadmium. Nevertheless, severe toxic effects on plants have been reported at Cr(VI) concentrations of approximately 0.5 mg L^{-1} .

2.1.1.4.3 Monitoring and Legislations

It is accepted that monitoring both atmosphere and biological material from exposed workers is essential. Chromium concentrations can be determined using colorimetry, atomic absorption, or emission spectroscopy. The U.S. Standards Institute listed a maximum acceptable concentration (MAC) of 0.1 mg m^{-3} for chromic acid. The U.S. National Institute of Occupational Safety and Health (U.S.-NIOSH) makes a difference between noncarcinogenic Cr(VI) and carcinogenic Cr(VI). The time-weighted average values at a workplace are $25 \text{ } \mu\text{g m}^{-3}$ for airborne carcinogenic chromium and $50 \text{ } \mu\text{g m}^{-3}$ for noncarcinogenic chromium.

2.1.2 RADIONUCLIDES

2.1.2.1 Uranium

Uranium (U) is a hard, silvery-white amphoteric metal and a radioactive element. In the natural state, it consists of isotopes ^{238}U (99.28%), ^{234}U (0.006%), and ^{235}U (0.714%). Uranium occurs naturally in the +2, +3, +4, +5, or +6 valence states, but most commonly in the hexavalent form. In nature, hexavalent uranium is commonly associated with oxygen as the uranyl ion, UO_2^{2+} . There are over 100 uranium minerals: those of commercial importance are the oxides and the oxyanionic salts. Although uranium has a family of 15 radioisotopes, only three occur naturally. The radiation levels from all three are very low due to two factors: (1) the radiation they emit is not very penetrating

and is emitted at a low rate and (2) the high density of uranium (1.7 times the density of lead and 2.5 that of steel) acts as a shield against its own radiations. Large quantities of natural uranium can therefore be handled without any special precautions such as shielding or remote handling. Uranium is present in water supplies as a result of leaching from natural deposits, its release in mill tailings, emissions from the nuclear industry, and the combustion of coal and other fuels. Phosphate fertilizers, which may contain uranium at concentrations as high as 150 mg kg^{-1} , may also contribute to the uranium content of groundwater.

2.1.2.1.1 Biological Pathways

Uranium occurs in the mammalian body in soluble form only as tetravalent uranium or hexavalent uranium in uranyl complexes. Both hexavalent and tetravalent uranium form complexes with carbonate ions and proteins in the body. Oxidation of tetravalent uranium to hexavalent uranium is likely to occur in the organism. Absorption of uranium salts may occur by inhalation or by ingestion; 95% of uranium retained in the body is deposited in bone. Excretion is mainly via the kidney. As all uranium isotopes are radioactive, the hazards of a high intake of uranium are twofold: chemical toxicity and radiological damage. There is no evidence that uranium has any metabolic function in the mammalian organism.

2.1.2.1.2 Chemical Toxicity

The critical organ for chemical toxicity is the proximal tubule of the kidney. Chemical injury reveals itself, in humans, by increased catalase excretion in urine and proteinuria. Such changes are likely to occur when the uranium concentration in the kidney exceeds 1 mg kg^{-1} . The concentration of uranium in the kidney is mainly dependent on the solubility of the uranium compound to which the individual is exposed. The limiting daily intake of uranium is in the order $1.5 \text{ } \mu\text{g d}^{-1}$, and it is mainly derived from food items such as vegetables, cereals, and table salt. Occupational exposure involves the inhalation of dust particles of varying size and density containing uranium compounds with different solubility.

The most important effect of uranium is the damage to the kidneys. High doses of uranium cause tissue damage in the kidneys, leading to functional loss as indicated by failure to resorb urinary protein, glucose, catalase, phosphate, citrate, and creatinine, causing slow death by suppression of respiration. A high dosage of uranium also affects blood vasculature through the body. Capillary permeability, blood pressure, and edema may increase and clotting ability may decrease. Uranium may damage the capillary membrane, and it is also known to induce some damage to liver and muscle tissue. Its effects on the nervous system may be similar to those from poisoning by other heavy metals. A study of the chemical toxicity of uranium revealed that a body burden of 0.1 mg kg^{-1} of body weight produced a definite nephrotoxic effect. The toxic effects of uranium were reviewed by a panel of prominent uranium toxicologists in 1984 and are summarized in Table 2.1.

TABLE 2.1
Health Effects of Uranium

Health Effect	Uranium/kg Body Weight (mgU kg^{-1})	Uranium (mg) in a 70 kg Person	Uranium Intake (mg) by a 70 kg Person
50% lethality	1.63	114	230
Threshold for permanent renal damage	0.3	21	40
Threshold for transient renal injury or effect	0.058	4.06	8.3
No effect	0.03	2.1	4.3

2.1.2.2 Radon

Radon-222 is a chemically inert gas formed through the radioactive decay of ^{226}Ra . Both are members of the ^{238}U decay series. Although a gas, radon deserves a mention here due to its toxic effects and stealthy presence in habitable structures. Radon is soluble in water, its solubility decreasing rapidly with an increase in temperature (510, 230, and $169\text{ cm}^3\text{ kg}^{-1}$ at 0°C , 20°C , and 30°C , respectively) [32]. Radon is extremely volatile and is readily released from water.

Uranium and radium are present in varying amounts in all rocks and soils. Although most of the radon produced in soil from radium is retained in the Earth, where it decays, a small portion diffuses into the pore spaces and hence into the atmosphere. Other sources of radon include groundwater that passes through radium-bearing rocks and soils, traditional building materials such as wallboard and concrete blocks, uranium tailings, coal residues, and fossil fuel combustion.

2.1.2.2.1 Exposure

Radon is the major source of naturally occurring radiation exposure for humans. Exposure occurs via the ingestion of radon dissolved in water and the inhalation of airborne radon. A U.S. survey estimated geometric mean radon levels in public water supplies, public groundwater supplies, and private wells of 2.5, 4.8, and 34 Bq L^{-1} . Public wells analyzed by King et al. [33] contained radon at an average concentration of about 40 Bq L^{-1} . Nazaroff et al. [34] reported a geometric mean radon concentration of 5.2 Bq L^{-1} in public well water supplies in the United States, based on population-weighted statistics. In Finland and Sweden, the population-weighted average for drinking water from private wells has been estimated at 60 and 38 Bq L^{-1} , respectively [35].

Outdoor radon concentrations vary seasonally and diurnally and are influenced by height above ground level and meteorological conditions such as wind speed and temperature [35]. Enhanced levels will be found in the vicinity of uranium mines and mill and tailings operations. Indoor radon levels are typically much higher and much more variable than outdoor levels. Radon entry into houses and other buildings is primarily from the soil or rock under the structures. Radon in water, building materials, and natural gas can also contribute to indoor levels [35], particularly in confined spaces with low air change rates (e.g., homes that have been tightly sealed for energy conservation).

The relationship between the concentration of radon in the water supply and the concentration of radon in indoor air depends on several factors, including the rate and type of usage of the water (e.g., drinking water, showers, and laundry), the loss or transfer of radon from the water to the air, and the characteristic ventilation of the house. Nazaroff et al. [34], based on measurements in U.S. homes and water supplies, estimated that public supplies derived from groundwater serving 1000 or more persons contribute about 2% to the mean indoor radon concentration for houses using these sources. In general, under normal conditions, the intake of radon from indoor and ambient air far surpasses the intake of radon from drinking water via both the ingestion and inhalation routes.

2.1.2.2.2 Health Effects

Radon consumed in water appears to rapidly enter the bloodstream from the stomach, perfusing all the cells of the body [36]. As it is lipid soluble, it does not distribute evenly throughout the body [37]. Clearance of radon from the bloodstream is relatively rapid, with a half-time on the order of minutes.

Hursh et al. [37] demonstrated that radon is removed from the body primarily through exhalation via the lung. Several studies have found that radon is removed from the body with a primary half-time of between 30 and 70 min, with a smaller component (possibly that associated with fatty tissue) having a half-time on the order of several hours. The rate of radon elimination from a resting person appears to be slower than that for a physically active person [36]. Most radon inhaled with indoor air is exhaled and remains in the lungs for only a short time. The radon daughter ^{218}Po is very reactive and electrostatically attracted to tiny particulates in air. These particulates are inhaled and deposited in the lung. Radon's daughters then decay sequentially, releasing damaging alpha and beta particles. Therefore, it is radon's progeny, not radon, that actually cause damage to the bronchial epithelium, because only the progeny remain in the lungs long enough to decay significantly.

Epidemiological data derived from underground miners of various metal ores have shown a relatively consistent relationship between lung cancer incidence and exposure to radon progeny [38]. Limitations of the miner studies include crude exposure estimates, inadequate follow-up periods [38], and the inability to account for the confounding factor of cigarette smoking. Comparatively few epidemiological studies have investigated the exposure to natural background radon levels, and those that are available show no significant increase in lung cancer death rate from inhalation exposure to normally occurring levels of radon and radon progeny [38]. Also, there are no experimental or epidemiological data available that link ingested radon with any known health impacts in humans [38]. It has been concluded that there is no need to establish a MAC for radon in drinking water. However, anyone whose indoor air radon concentrations exceed acceptable levels (800 Bq m^{-3} as an annual average concentration in the normal living area) should investigate the possibility that their groundwater also contains high levels of radon. Individuals who attempt to remove radon from their water supply using point-of-use devices containing activated carbon should be cautioned regarding the difficulties of disposing of the used radioactive carbon.

2.1.3 ARSENIC POLLUTION

Highly poisonous arsenic is widely distributed in nature and occurs in the form of inorganic or organic compounds. The most toxic form of arsenic is its trivalent cation As^{+3} . Arsenic contamination has been reported from many parts of the world, including the United States, United Kingdom, Canada, and Australia; however, in terms of severity of the problem, Bangladesh tops the list, followed by India and China. In what has been dubbed “the largest poisoning in the history of mankind,” an estimated 40–60 million people suffer from different degrees of acute arsenic poisoning in Bangladesh and Eastern India alone. Well-known health problems caused by acute arsenic poisoning exist on a large scale in those parts of the world where high levels of arsenic are naturally present in a widespread aquifer tapped for drinking and irrigation.

2.1.3.1 Arsenic Speciation and Toxicity

Arsenic is a poisonous chemical that is widely distributed in nature and occurs in the form of inorganic or organic compounds. It is ranked as twentieth in abundance among the elements in the Earth’s crust. Arsenic can exist in four valence states: -3 , 0 , $+3$, and $+5$. Under reducing conditions, arsenite, As(III) , is the dominant form; arsenate, As(V) , is generally the stable form in oxygenated environments. Elemental arsenic is not soluble in water. Arsenic salts exhibit a wide range of solubilities, depending on pH and ionic environment.

Inorganic compounds consist of water-soluble arsenite (As III), the most toxic form, and arsenate (As V), the less toxic form, and such pollutants have been associated with many health problems such as skin lesions, keratosis (skin hardening), lung cancer, and bladder cancer [39–41] (Figures 2.1 and 2.2). Organic arsenic species, abundant in seafood, are much less harmful to health, and are readily eliminated by the body. The release of arsenic into the environment occurs in a variety of ways through industrial effluents, pesticides, wood preservative agents, combustion of fossil fuels, and mining activity [39–41]. Indeed, arsenical insecticides have been used in agriculture for centuries, and particularly lead arsenate was quite extensively used in Australia, New Zealand, Canada, and the United States [41,42].

2.1.3.2 Arsenic-Contaminated Countries

Arsenic contamination has been reported from many parts of the world, including the United States, United Kingdom, Canada, and Australia; however, in terms of severity of the problem, Bangladesh tops the list, followed by India and China (Figure 2.3) [40]. In these countries, arsenic has been released in the groundwater by oxidation of the arsenopyrites/pyrites (arsenic is present in more than 200 mineral species, the most common of which is arsenopyrite) from the subsoil or oxyhydroxide reduction. It has been estimated that about one-third of the atmospheric flux of arsenic is of natural origin. Volcanic action is the most important natural source of arsenic, followed by low-temperature



FIGURE 2.1 Health effects of arsenic. Skin lesions and keratosis due to arsenic poisoning (hands).



FIGURE 2.2 Health effects of arsenic. Skin lesions and keratosis due to arsenic poisoning (feet).

volatilization. Inorganic arsenic of geological origin is found in groundwater used as drinking water in several parts of the world, for example Bangladesh [41].

Besides the drinking of contaminated groundwater, people in such countries use this water for crop irrigation. Therefore, arsenic compounds find their way into soils used for rice (*Oryza sativa*) cultivation through polluted irrigation water, and through historic contamination with arsenic-based pesticides [43]. Arsenic contamination poses a particular challenge, as this pollutant can enter plants through their phosphate transporter [44] and its contamination is invisible and has no taste or smell.

2.1.3.3 Clinical Effects

Skin disorders, including hyper/hypopigmentation changes and keratosis, are the most common external manifestations, although skin cancer has also been identified. Around 5000 patients have

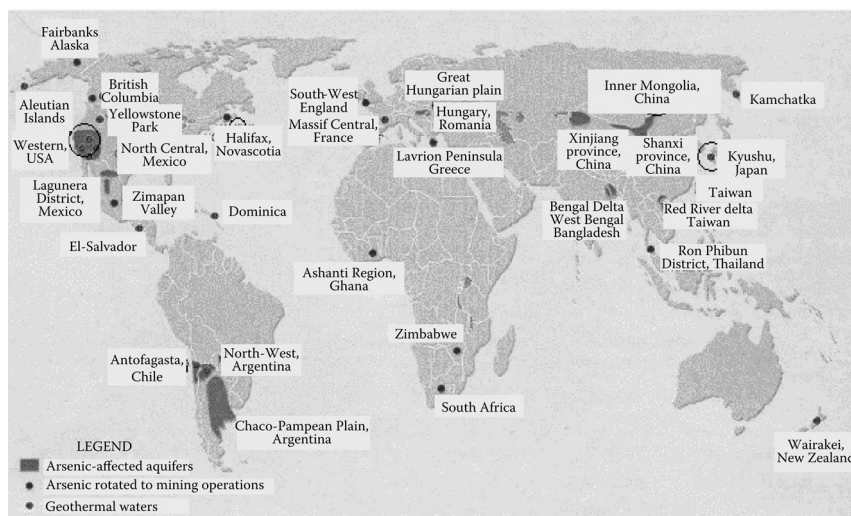


FIGURE 2.3 Arsenic geographic occurrence.

been identified with As-related health problems in West Bengal (including skin pigmentation changes), although some estimates put the number of patients with arsenicosis at more than 200,000 [45]. In some areas in Bangladesh, groundwater arsenic concentrations can reach 2 mg L^{-1} (2 ppm) [41,46], whereas the WHO provisional guideline value for drinkable water is only 0.01 mg L^{-1} (10 ppb) [43]. An estimated Bangladesh population of 65 million is exposed to the threat of arsenic poisoning through drinking water [40], and surprisingly at least 32 million Americans consume water containing more than 2 ppb of arsenic. The U.S. EPA is now considering a new standard in the range of 2–20 ppb.

2.2 METALS IN GROUNDWATERS

While the interest in groundwater has mainly focused on the supply of water, a shift of concern to groundwater quality has occurred. At present, the reservoir of freshwater found beneath the surface is gradually degrading due to man's activities. This is placing a strain on drinking water supply, especially in rural areas where tapping into the ground for water is a common practice. Regulations and introduction of standards concerning water quality have been counteracting this deterioration. However, groundwater contamination goes more frequently undetected or is largely undetectable due to heterogeneities underground, until the damage is widespread. Hope for the future lies in understanding the movement of water and contaminants in aquifers, a porous and permeable type of geological formation that holds and conducts the flow of groundwater.

Focus on inorganic contaminants has been relatively recent since organics are more used in industry and seem to have posed a more eminent problem. Many inorganic contaminants, specifically heavy metals, are toxic and pose a great health and environmental concern in quite low concentrations. Due to the progressive mobilization of heavy metals above the water table caused by man's increasing technological activities, the metals reach underground aquifers in increasing quantities. While some metals may be partially removed by ion exchange with the soil components before they reach the aquifer, the danger of contaminating the latter has been well established. The movement of heavy metals in aquifers depends on how the heavy metals act in aqueous environment. These considerations involve pH, hydrolysis, redox potential, and formation of complexes. Metal mobility generally tends to decline with pH where a solid, typically a metal hydroxide, a metal carbonate, a metal sulfide, or other complexes, becomes a more dominant phase.

2.2.1 HEAVY METALS IN AQUIFERS

The transport of solutes in porous materials, such as aquifers, can be considered as flow through a fixed volume element that can be reflected in the following mass balance:

$$\begin{aligned} (\text{net rate of change of mass within element}) &= (\text{flux of solute out of the element}) \\ &\quad - (\text{flux of solute into the element}) \\ &\quad \pm (\text{loss or gain of solute mass due to reaction}). \end{aligned}$$

Processes that dictate the flux in or out are advection and hydrodynamic dispersion. Advection is a component of solute movement attributed to transport by flowing groundwater. Dispersion refers to the spreading of the contaminant caused by the fact that not all of the contaminant actually moves at the same speed as the average linear velocity [47]. The average linear velocity ($\bar{v}$) is given by (v/n) , where v is the specific discharge and n is the porosity. The dispersion–advection equation, Equation 2.1, describes the transport of dissolved constituents that are reactive in saturated isotropic and porous media:

$$\frac{d}{dx} \left(T_x \frac{dh}{dx} \right) + \frac{d}{dy} \left(T_y \frac{dh}{dy} \right) = S \frac{dh}{dt} - R + L, \quad (2.1)$$

where $L = (-K'h_{\text{source}} - h) / b'$ [48].

This equation is based on the basic assumption that water in the aquifer tends to flow horizontally, that is, in the x and y directions, and vertically as leaks through confining beds. Hydraulic conductivity is the ability of an aquifer to transmit water and transmissivity (T) is the average transmission. T_x and T_y are the components of transmissivity, h is the hydraulic head, S is the storage coefficient, R is a sink/store term, and L is the leakage through the confining bed. K' is the vertical hydraulic conductivity of the confining bed, b' is the thickness, and h_{source} is the head in the reservoir on the other side of the confining bed.

A confined aquifer is overlain by a unit of porous material that tends to slow down water movement and its transmissivity will remain constant if the aquifer is both uniform in thickness and homogeneous in nature, which rarely is the case. To simplify the advection–dispersion further, the case of flow for nonreactive dissolved constituents in saturated, homogeneous isotropic material at steady state is taken. The advection–dispersion equation then becomes

$$D_1 \frac{d^2 C}{dl^2} - \bar{v}_l \frac{dC}{dl} = \frac{dC}{dt}, \quad (2.2)$$

where l is a curvy linear coordinate taken to be in the directions of the flow line, D_1 is the coefficient of hydrodynamic dispersion in the longitudinal direction, which depends on the dispersivity and properties of the porous media, and C is the solute concentration. Even with this simplified equation, the flow of contaminant with water through the aquifer is dependent on many variables.

A good visualization of the one-dimensional advection–dispersion equation is passing of a non-reactive tracer (C_0) through a homogeneous granular medium and looking at its relative concentration in the outflow as seen in Figures 2.4 and 2.5. The assumption of plug flow would have the solute exiting as a step function, indicated by the line marked “position of advection front.” In reality, mechanical dispersion and molecular diffusion cause flow to deviate from this; some molecules will move faster and some slower than the average linear velocity ($\bar{v} = Q/nA$), which is the flowrate divided by the product of porosity and cross-sectional area. The greater the distance of flow,

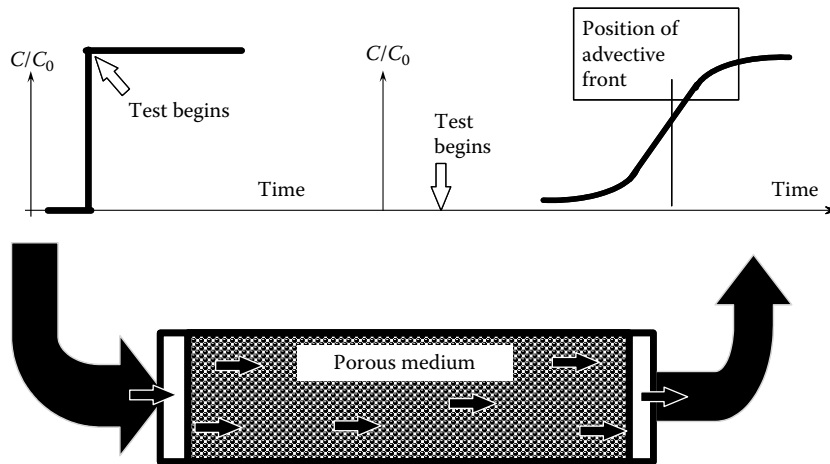


FIGURE 2.4 Experimental apparatus to illustrate dispersion in a column. The test begins with a concentration input of tracer $C/C_0 = 1$ at the inflow end. The relative concentration versus time function at the outflow characterizes dispersion in the column.

the greater the spread of the contaminant. At low velocities diffusion is dominant, and at high velocities dispersion is dominant.

As seen in Figure 2.6, diffusion of contaminants can translate to movement of great distances even through low-permeable rock, and can be considered an important factor in the movement of inorganic toxic contaminants. The overall spread of the species will depend on whether the source of contamination is continuous or instantaneous, as depicted in Figure 2.7. Despite the fact that the medium is isotropic, dispersion is anisotropic. It is stronger in the direction of flow than normal to it. The continuous contaminant spreads more from the source as time passes. The point source

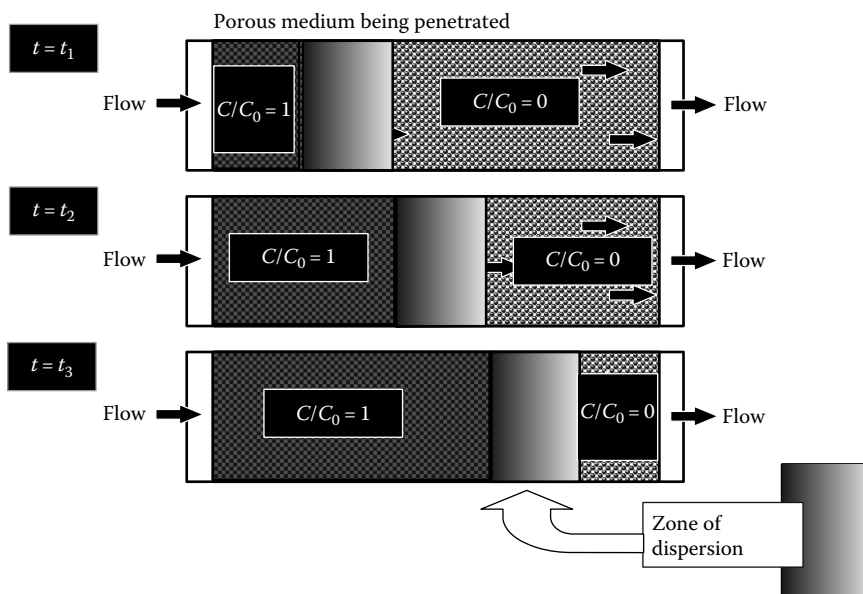


FIGURE 2.5 Schematic representation of dispersion within the porous medium at three different times. A progressively larger zone of mixing forms between the two fluids ($C/C_0 = 1$ and $C/C_0 = 0$) displacing one another.

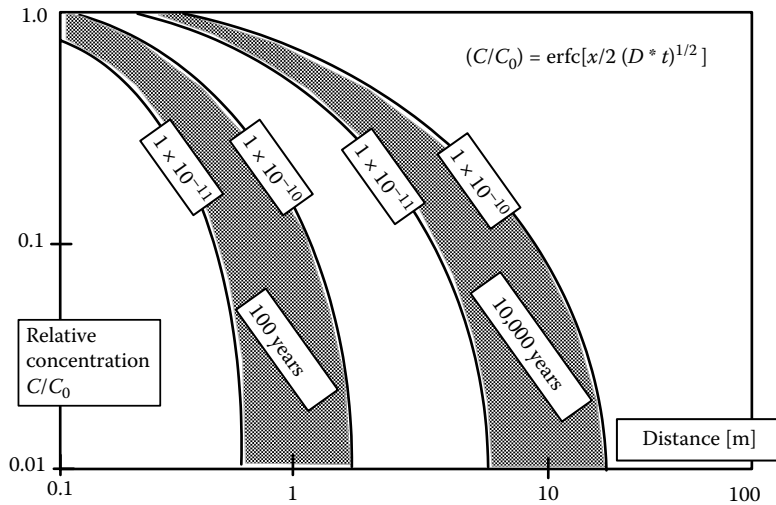


FIGURE 2.6 Positions of the contaminant front migrating by molecular diffusion away from a source where $C = C_0$ at $t > 0$. Migration times are 100 and 10,000 years.

contaminant contains a fixed mass, yet it is spread over a larger volume with time. Equations dictating this movement are used as a preliminary estimate. The contaminant concentration at a given point at a given time is

$$C(x, y, z, t) = \frac{M}{8(\pi t)^{3/2} D_x D_y D_z} \frac{\exp - X^2 - Y^2 - Z^2}{4D_x t 4D_y t 4D_z t}, \quad (2.3)$$

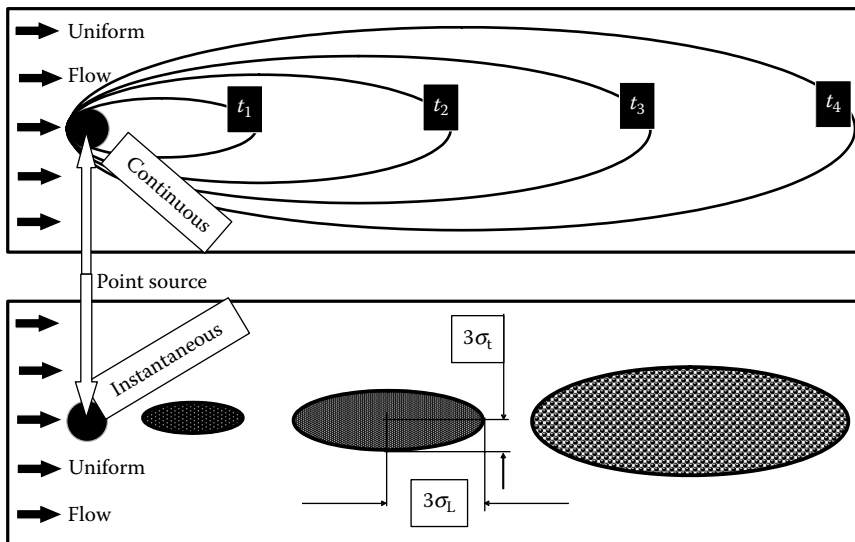


FIGURE 2.7 Spreading a tracer in a two-dimensional uniform flow field in an isotropic sand. (a) Continuous tracer feed with step-function initial condition; (b) instantaneous point source. (From Domenico, P.A., *Physical and Chemical Hydrogeology*, Wiley, Canada, 1990.)

where M is the mass of the contaminant, D is the coefficient of dispersion in the x , y , or z direction, and $X = (x - vt)$, $Y = y$, $Z = z$ [49].

Density plays a key role in the downward movement of the contaminant. As density increases, relative to water, the contaminant plume which was shallow and close to the water table will sink into the groundwater. The assumption of homogeneous media is not true to reality; most geological media contain much heterogeneity. Figure 2.8 shows variations in the heterogeneous media. K_1 represents coarse grained sand and K_2 smaller grained sand in (c). A thin horizontal layer of higher conductivity extends through the original domain, most of the flow occurs in this layer, and overall travel time is one-fifth that in (d). Diagram (d) represents a discontinuous layer of flow conductivity, contamination moves the first and under the second lens, (e) indicates the discontinuity of a thin and high conductivity layer. The stratigraphic differences are important to understand the movement of water in the aquifer.

Heterogeneities are usually determined by careful drilling and mapping. This is more applicable to large-scale heterogeneities. Changes in hydraulic conductivity can be attributed to small-scale heterogeneities such as changes in granular aquifers (changes in silt or clay content). Such heterogeneities cannot be determined from drillings from borehole to borehole. This fact leads to errors in dispersivity by up to an order of magnitude from those determined experimentally; hence dispersion plays a great role in contamination transport. Added complexity occurs when reactions within groundwater during transport of the contaminants occur, varying the concentrations substantially. These include adsorption/desorption reactions, solution precipitation reactions, oxidation/reduction reactions, ion-pairing or complexation reactions, and microbial cell synthesis. With the influence of reactions, specifically adsorption/desorption, the one-dimensional advection–dispersion equation becomes

$$D_1 \frac{d^2 C}{dl^2} - \bar{v}_1 \frac{dC}{dl} + \frac{p_b}{n} \frac{dS}{dt} = \frac{dC}{dt}, \quad (2.4)$$

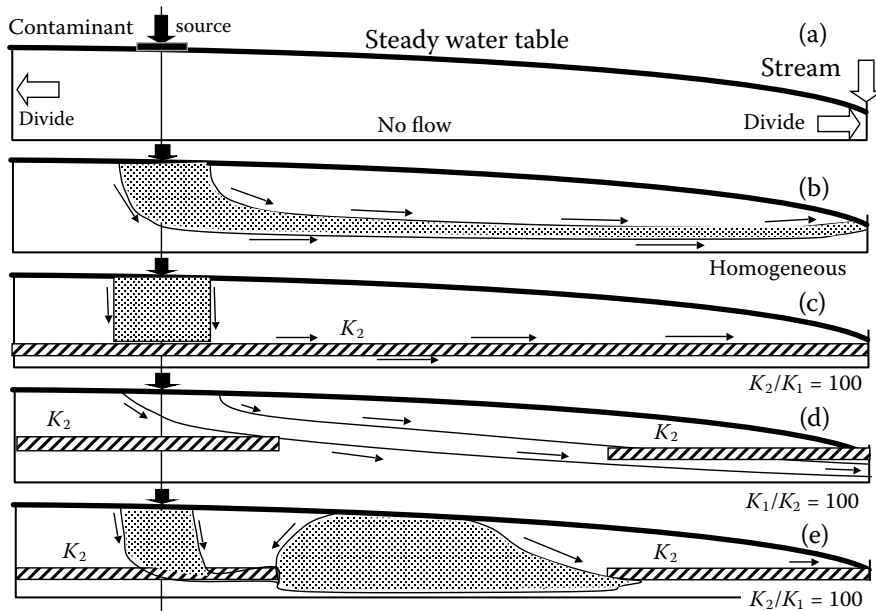


FIGURE 2.8 Effect of layers and lenses on flow paths in shallow steady-state groundwater flow systems. (a) Boundary conditions; (b) homogeneous case; (c) single higher-conductivity layer; (d) two lower-conductivity lenses; (e) two higher-conductivity lenses. (Adapted from Freeze, A.R. and Cherry, J.A., *Groundwater*, Prentice-Hall, New Jersey, 1979.)

where p is the bulk mass density of the porous medium, n is the porosity, S is the mass of the chemical adsorbed on the porous medium, and p/n (dS/dC) is the change in concentration due to adsorption/desorption following:

$$-\frac{dS}{dt} = -\frac{dS}{dC} \frac{dC}{dt} \quad \text{and} \quad -\frac{p_b dS}{n dt} = -\frac{p_b}{n} \frac{dS}{dC} \frac{dC}{dt}. \quad (2.5)$$

The term dS/dC represents partitioning of the contaminant between solution and solids. In the lab, the mass adsorbed per unit mass of dry solids is plotted against the concentration of the constituent in solution in a log/log graph. The resulting expression follows Equation 2.6:

$$\log S = b \log C + \log K \quad \text{or} \quad S = K_d C^b \text{ (Freundlich equation)}, \quad (2.6)$$

which represents the relation between the mass of the solute species adsorbed (S) and the solute concentration (C) where K and b are constants that depend on solute species, type of porous media, and other conditions.

Reactions generally slow the rate with which the front of contaminants moves. The retardation equation for reactions is given by

$$\frac{\bar{v}}{\bar{v}_0} = 1 + p_b \frac{K_d}{n}, \quad (2.7)$$

where $\bar{v}$ is the average linear velocity and $\bar{v}_0$ is the velocity of the $C/C_0 = 0.5$ point.

For example, for unconsolidated granular deposits, porosity typically is between 0.2 and 0.4 and average mass density is 2.65 for unconsolidated deposits. For the porosity, given the bulk mass densities (p) are 1.6–2.1 g cm⁻³, p_b/n values from 4 to 10 g cm⁻³ are to be used. If $K_d = 1$ mL g⁻¹ then the flow of groundwater would be slowed by a factor of 5–11 times. If $K_d = 10$ mL g⁻¹ then the contaminating species would not move far from its point of input. A mixture of contaminants will separate into zones after time, given by $\bar{v}/\bar{v}_0$ for each species. These zones will travel at their own velocities. Later, when the contaminant discharge is discontinued, lower concentration water will pass through and adsorbed contaminant will be transferred into the liquid phase. If reactions are reversible, then in time, all evidence of contamination will be negligible; although this may be irreversible in a realistic time period when contaminants react slower than the actual movement of water, the retardation time will be even slower than that for the case of a fast reaction. Information on the movement of contaminants in the porous media is hard to come by and the use of the general retardation equation will yield errors in the prediction of the rates of migration of contaminants.

Heavy metals in contaminated water rarely occur at concentrations above 1 mg L⁻¹. Concentrations are low due to solubility, taking into account that other minerals are dissolved in this same water as well as the possibility of adsorption onto clay minerals or on hydrous oxides of iron and manganese or organic material. Isomorphous substitution of coprecipitation with minerals or amorphous solids can also be of some interest. Most heavy metals form hydrolyzed species and form complex species by combining with inorganic anions, such as HCO₃⁻, CO₃²⁻, SO₄²⁻, Cl⁻, F⁻, and NO₃⁻. Complexing with organic compounds may be important where present.

An equation that sums all amounts of the particular heavy metal complexed with various anions will give the total amount of metals present in all forms. If the total is known, then the amount of each species can be calculated using mass action equations. The hydrolyzed and inorganic species with mercury, for example, include HgOH⁺, Hg(OH)₂, HgCl₂, HgS, HgO, and Hg(HS)₂. In assessing the mobility of mercury and any other heavy metal, a knowledge of these and other species must be

looked at. As mentioned before, the increasing pH of groundwater leads to increased hydrolysis of the heavy metals. As their concentration in aquifers increases, so does their probability of complexing with anions present such as CN^- and HS^- . Heavy metal concentration can be calculated using concentration data obtained from laboratory analysis. Being able to predict the mobility of heavy metals in groundwater depends on the ease with which the concentration of the most dominant complexes formed can be predicted.

A generalized table of the mobilities of heavy metals in soil is shown in Table 2.2. This directly applies to aquifers since it is comparative and no numbers have been given.

Almost all the trace metals found in groundwater are influenced redox conditions, due to changes in the oxidation state of the metal complex. Redox conditions, in a way, may influence the concentration of trace metals in the solid phase of the porous medium that cause adsorption of the trace metal. The diagram of Eh versus pH for heavy metals in water shows the main stability regions of the particular heavy metal complexes.

In anaerobic groundwaters, insolubility of sulfide minerals can limit trace metals to very low concentrations. In groundwater, which is nonacidic and has a high concentration of dissolved inorganic carbon, the solubility of certain carbonate materials will, if equilibrium is achieved, limit the levels of trace metals at low concentrations, that is, Cd and Pb. This is true if excessive amounts of inorganic or organic substances, which tend to complex with heavy metals in water, are not present. Adsorption is the key mechanism that tends to keep concentrations far below those dictated merely by solubility. It occurs due to the presence of clay minerals, organic matter, crystalline solids, and other amorphous solids in the porous material. Certain oxides, for instance Fe and Mn, not only control but also enhance adsorption onto the medium for which they form a coat.

2.2.2 CASES AND REMEDIATION

In 1947, the city of Babylon in New York saw the beginning of land filling. Disposal included urban refuse, incinerated garbage, cesspool waste, and industrial refuse. The refuse was placed below the water table and the cesspool was treated and placed in lagoons. The surface sand aquifer was about 27.5 m thick and had a hydraulic conductivity of $1.7 \times 10^{-3} \text{ m s}^{-1}$. Contaminants in the aquifer included the major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , and NO_3^- , heavy metals (particularly iron and manganese), and organic compounds. The Cl^- plume began 9.1 m below the water table and continued 12.1 m below. It did not react, so the mass transfer continued. The advection

TABLE 2.2
Relative Mobilities of Heavy Metals

Relative Mobility	Conditions			
	Oxidizing	Acid	Neutral (Alkaline)	Reducing
Very high			Se	
High	Se	Se, Hg		
Medium	Hg, As, Cd	As, Cd	As, Cd	Tl
Low	Pb, As, Sb, Tl	Pb, Bi, Sb, Tl	Pb, Bi, Sb, Tl, In	
Very low to immobile	Te	Te	Te, Hg	Te, Se, Hg, As, Cd, Pb, Bi, Tl

Source: Ferguson, J.E., *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, New York, 1990.

velocity was determined at $2.9 \times 10^{-4} \text{ cm s}^{-1}$, which is the range expected for a sand aquifer. Dispersivities in the x , y , and z directions were 18.6, 3.1, and 0.6 m, respectively. Tracer tests estimated that the value in the x -direction would be 6 times those in the y -direction and the distance in the z -direction would be considerably smaller. The amount of Cl^- away from the source declined constantly, suggesting that the point source was continuous as indicated in Figure 2.7. Most of the nitrogen was present as NH_4^+ , indicating reducing conditions near the source. Mixing brought oxygen to the plume, producing $\text{NO}_3^- - \text{N}$ as the distance from the source increased. Tracking the nitrogen species allowed one to assess the redox conditions.

The area that was reduced is an explanation for the mobility of the heavy metals, iron and manganese. The Eh–pH diagram shows that Fe^{2+} was the stable form of iron at moderate reducing conditions and at a pH of 6; this was true for Mn^{2+} as well. The gradual increase in oxidizing conditions down the plume decreased mobility with the formation of solids [i.e., $\text{Fe}(\text{OH})_3$ and $\text{MnO}(\text{OH})$] [47]. It is a common practice to apply similar cases to areas that have minimum information: for instance, in the area around the Saint-Laurent Basin (Quebec, Canada), where four types of aquifers exist and one is similar to that mentioned in the Babylon case study. This is the one of unconsolidated sand and gravel deposits. Methods of remediation are available for removing inorganics from groundwater; they include chemical addition, removal of suspended solids, ion exchange, and polymeric binding with microfiltration. Changing the pH of water with chemical addition will cause the precipitation of heavy metals. To adjust acidic water, pass through a limestone bed mixed with lime slurries, add caustic soda (NaOH), or add soda ash (Na_2CO_3). To adjust alkaline water, bubble carbon dioxide in the water or add a strong acid. It is rare to have water that is too alkaline. Acids are added to adjust the pH back to normal after a high pH resulted in precipitation. Some metals do not precipitate out of solution at high pH and may need to be precipitated as a sulfide rather than a hydroxide, since they are soluble.

Heavy metals, such as hexavalent chromium, are soluble in water at high pH. This heavy metal is used in industrial operations and is not naturally found in groundwater. Its anthropogenic spread through natural aquifers could have serious health consequences in the affected population (as depicted in the feature film, *Erin Brockovich* [51]). Hexavalent chromium is best reduced to its less soluble trivalent form for removal. The pH is reduced to pH 2, a chemical reducing agent such as sulfur dioxide is added, the pH is raised, and trivalent chromium is precipitated. Mercury is precipitated with sulfide addition. The lower treatability limit for mercury is $10\text{--}20 \text{ mg L}^{-1}$ by sulfide precipitation, $1\text{--}5 \text{ mg L}^{-1}$ with ion exchange, $1\text{--}10 \text{ mg L}^{-1}$ with alum coagulation, $0.5\text{--}5 \text{ mg L}^{-1}$ with iron coagulation, and 0.25 mg L^{-1} with activated carbon. Arsenic in groundwater may be present in arsenite (AsO_3^{2-}) or arsenate (AsO_4^{3-}). Oxygen will oxidize the arsenite to arsenate and most surface water contamination will be in the arsenate form. If contamination occurs in the deep and likely anaerobic aquifer, the arsenite or arsenic form should be somehow oxidized since arsenate is easier to remove. To remove arsenic, a floc must be formed. A polyvalent metallic coagulant must be added to produce a hydroxide floc. A relatively new method of precipitation is the addition of iron to water by electrochemical methods to enhance the precipitation of other inorganics. The system uses sacrificial electrodes to produce an insoluble ferrous ion, which absorbs and precipitates heavy metals.

Suspended solids can be removed by flocculation, chemical addition, and pH adjustment, which convert inorganic contaminants to no soluble forms. This together with one of several types of settlers can be employed in the removal of suspended solids. Ion exchange is the exchange of an ion with high affinity to the sorbent for an ion with lower affinity. All of the heavy metals, in an aqueous environment, are in the divalent or trivalent state, with the exception of hexavalent chromium. A home sodium-ion-exchange unit will remove all these compounds. Ion exchange is not cheap and the brine with heavy metals will have to be disposed of. The ionex process is put to the best use in low concentrations as the final treatment before potable use. Polymeric binding and microfiltration is a two-step method that selectively removes metals from groundwater. First the addition of a water-soluble polymer binds the metal sand, which is then followed by microfiltration. The favored polymer for heavy metals is polyethylene-imine at low pH.

2.3 HEAVY METAL POLLUTION SOURCES

Due to man's industrial activity the concentrations of some heavy metals have reached high levels, posing a danger to public health. Whereas the nature of domestic wastewater is relatively constant, the extreme diversity of industrial effluents calls for an individual approach to handling each type of industry and often entails the use of specific treatment processes. Therefore, a thorough understanding of the metal handling upstream production processes and of the overall production system organization is fundamental.

2.3.1 ACID MINE DRAINAGE

The major source of liquid waste in the mining industry is acid mine drainage (AMD). AMD is by far the most extensive and most severe environmental problem associated with mining activities, both current as well as past.

Precious metal and uranium mines contain sulfide minerals, either in the ore or in the surrounding waste rock. AMD is common in areas where mining openings intersect the water table and where rocks contain pyrite and/or other sulfides. When these sulfide minerals, particularly pyrite and pyrrhotite, are exposed to oxygen and water, a process of conversion of sulfide to sulfate takes place. Water in contact with these oxidizing minerals is made acidic and water carries with it toxic metals and elevated levels of dissolved salts. As the reactions proceed, temperature and acidity increase, resulting in an increased rate of reaction. Between pH levels of 2 and 4, bacteria and ferric iron catalyze the reaction rate. Rainfall and snowmelt flush the toxic solutions from the waste sites into the downstream environment. If acidic drainage is left uncollected and untreated, it could contaminate groundwater and local water courses, damaging the health of plants, wildlife, and fish and eventually posing a threat to human health, particularly through the toxicity of the heavy metals that it carries.

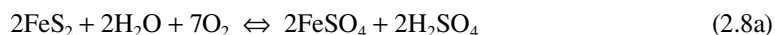
At active mine sites (and some inactive mine sites), mining companies operate comprehensive systems to collect and treat effluents and seepage from all sources. These facilities, when well operated and maintained, are sufficient to prevent downstream environmental impact. However, acid generation may persist for hundreds of years following mine closure. The problems are compounded by the demise and disappearance of the original mine operators.

The operation of treatment plants for very long periods of time is clearly not desirable and counter to the principles and goals of sustainable development. In addition, the conventional lime treatment process produces sludges that contain a very low percentage by weight of solids. In some severe cases, in a few decades the volume of lime sludge will exceed the volume of tailings or waste rock producing the acidic drainage.

2.3.1.1 Chemistry of Acid Mine Water

The principles of AMD generation are nowadays fairly well understood. Pyrite and other sulfide minerals on exposure to oxygen and water, and in the presence of oxidizing bacteria such as *Thiobacillus ferrooxidans*, oxidize to produce dissolved metals and acidity (sulfuric acid) according to the following steps [52].

The first of these reactions is the oxidation of pyrite:



The next step is the oxidation of ferrous ion to ferric ion:



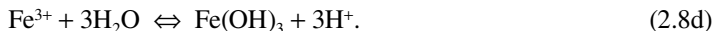
This process occurs very slowly at the low pH values found in acidic mine water. Below pH 3.5, the iron oxidation is catalyzed by the iron-oxidizing bacterium *T. ferrooxidans*, and in the pH range

of 3.5–4.5, it may be catalyzed by a variety of *Metallogenium*, a filamentous iron-oxidizing bacteria. Other bacteria that may be involved in acid mine water formation are *T. thiooxidans* and *Ferrobacillus ferrooxidans*.

The ferric ion further dissolves pyrite:



which in conjunction with reaction 2.8b constitutes a cycle for the dissolution of pyrite. At pH values much above 3, iron(III) precipitates as the hydrated iron(III) oxide:



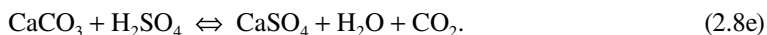
The beds of streams afflicted with AMD are often covered with “yellowboy,” an unsightly deposit of amorphous, semigelatinous $\text{Fe}(\text{OH})_3$. The most damaging component of acid mine water, however, is sulfuric acid. It is directly toxic and has other undesirable effects. While the devastation potential of AMD is very high, its dispersed nature and large areas involved in its generation represent a formidable problem in devising a suitably effective control of it. This is the reason why different techniques devised to treat AMD met with only little success. The techniques are based on the following methodologies:

Chemical: limestone/lime application to enhance alkalinity; sulfide precipitation or removal; application of bactericides.

Physicochemical: ion exchange barrier and application of a vegetative and/or geological membrane (cover) to prevent oxygen diffusion.

Biological: other than wetlands, not many biological treatments are known so far.

One approach to eliminating excess acidity involves the use of carbonate rocks. When acid mine water is treated with limestone, the following reaction occurs:



Unfortunately, because iron(III) is generally present, reaction 2.8d occurs as the pH is raised. The hydrated iron(III) oxide that forms as a result of elevated pH soon covers the particles of carbonate rock with a relatively impermeable layer. This armoring effect prevents further neutralization of the acid.

2.3.1.2 Extent of the Damage

The acidic water eventually interacts with other minerals and solubilizes heavy metals such as lead, copper, zinc, cadmium, and nickel that may even be present in minute quantities. Table 2.3 lists the amounts of major cations and anions contained in the mining water and solids of a typical AMD.

AMD is generated not only in and around abandoned mine sites but also at currently active operations. The principal sources of AMD at active mine sites are piles of waste rock containing pyrite, which is exposed to the atmosphere, to precipitation, and to springwater runoff. According to Kalin [53], 113 million cubic meters of contaminated water are produced annually from mining waste management areas in Canada. The flowrates of wastewater vary from 4 to 12,000 $\text{m}^3 \text{ day}^{-1}$ and the level of contamination varies from parts per million (mg L^{-1}) levels to grams per liter levels [54]. Filion et al. [55] have estimated the cost of remedial action at operating and abandoned mine sites across Canada in the order of 4 billion Can\$ over the next 20 years. The rate of generation of heavy metal pollution is likely to further increase since the large-scale mining of low-grade ores uses the method of open pits, which often cut into the groundwater streams. During mining, the water is pumped out of the mine; however, once a mine is closed, water flows into the pit (filling it)

TABLE 2.3**Quantitative Analysis by ICP-AES and Ionic Chromatography of the Major Cations and Anions in Mining Water and Solids**

Element	Inflow ($\mu\text{g L}^{-1}$)	Outflow ($\mu\text{g L}^{-1}$)	P-deposit (Inflow) (mg kg^{-1})	P'-deposit (Outflow) (mg kg^{-1})
Fe (mg L^{-1})	98.57	34.10	600×10^3	610×10^3
Fe ²⁺ /Fe ³⁺	88.00	22.00	—	—
Cr	2.79	1.98	25.80	82.00
As	47.42	10.61	438.00	460.00
Ba	5.55	12.99	39.00	456.00
Nd	9.14	9.29	18.70	41.23
Ce	32.07	33.85	32.43	95.63
La	13.83	14.33	12.25	38.39
U	561.80	634.00	91.55	213.70
Cu	4.38	7.40	8.80	27.60
Pb	1.23	4.39	12.00	21.40
Zn	107.63	142.00	15.20	88.90
Ni	62.87	75.22	13.70	31.90
Co	44.87	56.51	4.27	17.50
SO ₄ ⁻ (mg L^{-1})	1938.00	1888.0	nd	nd
Cl ⁻ (mg L^{-1})	177.00	157.00	nd	nd
F ⁻ (mg L^{-1})	25.00	24.20	nd	nd

and forms a lake. The seriousness of this problem is demonstrated by the example of Berkeley Pit in Montana (<http://formontana.net/pit.html>), which extends over an area of 77 ha, is 542 m deep, and is filling at a rate of 23 million liters per day [56]. Currently, the water contains approximately 180 mg L^{-1} of Cu and 500 mg L^{-1} of Zn in combination with 1000 mg L^{-1} of Fe, and has an acidic pH of 2.8. This site has also been designated as the experimental site of the U.S. “environmental superfund” for testing metal removal/recovery techniques.

The movement of tailings-derived water away from mining sites and into adjoining surface and groundwater flow system constitutes an ever-increasing environmental problem of truly monumental dimensions. The major problem is that it is difficult, in many instances almost impossible, to contain or curtail AMD. It is the most persistent and, unfortunately in many instances, NONPOINT source pollution problem of mining regions. There is no typical acid mine water, the ferric to ferrous ion ratio may vary, and several other ions such as silica, aluminum, calcium, or magnesium may be present in significant quantities in addition to the dissolved other toxic heavy metals. Untreated AMD pollutes receiving streams and aquifers. The impact on the environment can be severe, leading to a virtual disappearance of aquatic life, a low pH of the water, and a coating of river bottoms with a layer of rust-like particles. Milling operations include the comminution and concentration of the ore. Waste rock and the process water from these operations are usually discharged into large basins called “tailing ponds.” Although most of the heavy metals are present in the form of suspended solids that settle to the bottom of the basins, the overflow from these ponds still contains low but significant concentrations of toxic metals [52]. Furthermore, the dams of these ponds are often constructed from waste rock; thus seepage from the tailings contributes to AMD [53].

2.3.1.3 Radioactive AMD

The uranium mining industry produces a large volume of low-level radioactive waste material, which, following milling, extraction, and neutralization processes, is deposited in extensive tailings

impoundments. As mentioned, in many cases the ore bodies are associated with metal sulfides such as pyrite, marcasite, and pyrrhotite, which are not desired products and are released to the tailings as part of the mill wastes. Upon weathering, these metal sulfides are readily oxidized, producing AMD conditions from these tailings piles, with subsequent leaching of the tailings material resulting in highly acidic pore water containing significant concentrations of iron, sulfate, heavy metals, and trace radionuclides. The migration of such poor-quality tailings water by either surface runoff or subsurface groundwater can lead to serious deterioration in the quality of adjacent natural water systems.

The mining industry is thus faced with the difficult task of devising long-term abandonment schemes that minimize pyrite oxidation and prevent the release of contaminants to the environment. These schemes should be cost effective and should require very little future maintenance or monitoring. Some radionuclides found in water, particularly uranium, thorium, and radium, originate from natural sources, particularly leaching from minerals. The levels of radionuclides found in water typically are measured in units of picoCuries per liter (one picoCurie is equal to 2.2 disintegrations per minute). The U.S. Public Health Service specifications stipulate that water supplies should not contain more than 3 picoCuries per liter of naturally occurring radium-226. The uranium tailings will require proper management technology, without much human involvement in the form of continuous treatment and monitoring, in limiting the release of contaminants to the environment. The mining and milling of uranium-bearing ores results in four types of waste: waste rock, mine water, process effluents, and solid wastes (tailings). Liquid effluents appear to be the most serious waste disposal problem from operating mines and mills, and the chemicals added in the milling process are of particular concern. The solid wastes represent a problem on account of both their magnitude and their radioactivity. On abandonment, the containment of the radioactivity is of utmost concern because of the hazards of long-lived radioisotopes in liquid effluents. A brief list of radioactive elements and their respective half-lives is presented in Table 2.4.

2.3.1.4 Treatment of AMD

The control and prevention of radionuclides and heavy metals contamination of surface and groundwater is best made during the ore treatment procedure and prior to waste and effluent disposal to tailings impoundments. Ideally, due to their persistent nature in the environment and toxicity, the ultimate treatment of heavy metals in effluents would be either their very stable mineralization and deposition, or a complete recovery (and recycle) [57]. However, as these alternatives could hardly be cost feasible and reasonably expected, carefully crafted regulatory limits on the discharge of metals into the environment need to be crafted and adhered to with strict enforcement.

2.3.1.4.1 Lime Addition

Upon disposal of effluent waste to tailings impoundments, lime and barium chloride are added to reduce the acidity and promote the chemical precipitation of heavy metals and radionuclides. However, this treatment mode is a nonpermanent solution because tailings are subject to continuous infiltration by rainfall and an oxygen supply that increases the acidity of water due to sulfide oxidation and promotes the formation of heavy metal and radionuclide leachates. Lime therefore has to be added continuously; thus increasing sludge volumes with time, sludge volumes produced by lime addition will be greater than the tailing waste volumes! This is clearly not the best long-term treatment method to abate AMD.

2.3.1.4.2 Vegetation Cover

The most promising long-term compromise solution has been establishing a vegetation cover directly on the tailings material [58]. The vegetative cover on tailings has provided greater surface stability by controlling erosion and has improved the general aesthetics of the area. Its overall effect on acid generation and tailings area water quality, however, cannot be established to date. There has been no evidence of improvement in the quality of water that leaves a tailings area even though a site may have been vegetated for the last 10 years.

TABLE 2.4
Persistent Radionuclides in Water

Radionuclide half-life reaction, source, comment from reactor, and weapons fission:

Strontium-90 28 years Fission products radioisotopes of highest significance

Cesium-131 30 years because of their high yields

Iodine-131 8 days and biological activity

Cobalt-60 5.25 years from nonfission neutron reactions in reactors

Iron-55 2.7 years $^{56}\text{Fe}(n,2n)^{55}\text{Fe}$, from high-energy neutrons acting on iron in hardware

Manganese-54 310 days from nonfission neutron reactions in reactors

Plutonium-239 24,300 years $^{238}\text{U}(n,\gamma)^{239}\text{Pu}$, neutron capture by uranium

Barium-140 13 days these fission products

Zirconium-90 65 days are listed here

Cerium-141 33 days in generally decreasing

Strontium-89 51 days order of

Ruthenium-103 40 days fission yield

Naturally occurring from ^{238}U series:

Radium-40 1620 years diffusion from sediments, atmosphere

Lead-210 21 years ^{226}Ra —6 steps— ^{210}Pb

Thorium-230 75,200 years ^{238}U —3 steps— ^{230}Th produced *in situ*

Thorium-234 24 days ^{238}U — ^{234}Th produced *in situ*

Naturally occurring and from cosmic radiation:

Carbon-14 5730 years $^{14}\text{N}(n,p)^{14}\text{C}$,* thermal neutrons from cosmic or nuclear weapon sources reacting with N_2

Silicon-32 300 years $^{40}\text{Ar}(p,n)^{32}\text{Si}$, nuclear splitting of the nucleus of atmospheric argon by cosmic-ray protons

Potassium-40 1.4×10^9 years 0.0119% of natural potassium

2.3.1.4.3 Wet Barriers and Wetlands

Wet barriers, such as water and/or wetland cover on tailings, are believed to be effective in preventing acid generation by cutting off the oxygen supply to the tailings. The anoxic conditions so produced further support the growth of anaerobic heterotrophes such as sulfate reducers, which, with the breakdown of sulfates, produces hydrogen sulfide, thereby precipitating dissolved metals as sulfides [59]. Wet barriers are therefore artificial whereas wetlands are natural. Analysis of algae from a wetland that was removing manganese from mine water demonstrated phenomenal plant uptake, and Mn concentrations as high as 56,000 ppm (dry weight) were recorded. Iron and manganese oxidizing bacteria are also very active in these acidic wetlands; so much so that some researchers believe they are the most critical aspect of metal removal in cattail marshes [60]. In the organic-rich substrate, other bacteria are active. *Desulfovibrio desulfuricans*, for example, converts the sulfate component of mine water into hydrogen sulfide. This, in turn, reacts with dissolved metals, adsorbed metals, and precipitated metals to form insoluble metal sulfides. This is the eventual fate of all the metals removed from acid water, as dead vegetation sinks to the bottom and is replaced by new vegetation. Absorption by the organic substrate (especially peat) can also be very high. Finally, there are geochemical removal mechanisms occurring in the wetland that may be significant. For example, the cattail marshes that are most successful in removing manganese all have an incorporated layer of limestone beneath the organic substrate. This produces an environment of near-neutral pH and high carbon dioxide concentrations (due to neutralization reactions) and may result in the precipitation of manganese carbonate. Artificial wetlands constructed for the treatment of wastewater or AMD have different design considerations than those for the control of flood, storm, or wildlife habitat management.

2.3.2 METAL FINISHING AND SURFACE TREATMENT OPERATIONS

Surface finishing consists of various chemical and physical processes, including electroplating, that change the surface of a product or enhance its appearance, increase its corrosion resistance, or produce surface characteristics essential for subsequent operations. The major surface finishing operations consist of pretreatment, electroplating, electroless plating, anodizing, chromating (conversion coating), cyanide hardening, and quenching. The most prevalent surface finishing operations are electroplating, anodizing, and hot dip galvanizing. Table 2.5 gives a breakdown of metal finishing by specific industry.

Surface treatment is applied mainly to metal parts, but also to certain synthetic materials. It involves the following:

- a preliminary preparation of the surface (degreasing and pickling),
- a coating by means of electroplating,
- a coating by chemical means.

Automobile Parts: In recent years the use of electroplated metals for decoration in the automobile industry has fallen drastically. The reasons for this change are a trend toward smaller cars and a designer preference for materials other than nickel and chrome. Bumper manufacturers are the major clients for decorative surface finishing services. Although the trend to soft plastic coatings and paint finishing on bumpers has reduced this market, the demand in the United States for this plating service is larger than the present capacity. Consequently, increased nickel and chrome plating in Canada is expected for the next few years. Demand for functional finishes has increased with pressure to reduce corrosion and extend the life of vehicles. As a result, zinc plating will continue to grow at about 10–20% per year as usage extends to more automobile parts.

Steel Strip Mills: Cold rolled steel in strip form is plated with either zinc or tin. The zinc-plated strip is used in the fabrication of parts that require added corrosion protection on interior surfaces. Tin-plated strips are used primarily in can manufacturing; however, aluminum is replacing tin-plated cans in more and more areas.

Hardware: The demand for hardware products comes directly from the housing and construction industry and the quantity of surface finishing required fluctuates accordingly. The types of surface finishes required are nickel–chrome, zinc, brass, and bronze.

TABLE 2.5
Surface Finishing Market Breakdown

Industry	% of Market (Canada, 1983)
Automobile parts	26.0
Steel strip mills	14.0
Hardware	12.0
Electrical appliances	10.0
Wire goods	10.0
Plumbing fixtures electrical	6.0
Electrical equipment	5.0
Furniture	5.0
Pole hardware and heavy steel	5.0
Electronics	4.0
Engine and worn parts	2.0
Hollowware and flatware	0.5
Jewelry	0.5

Electrical Appliances: The major appliance industry, including manufacturers of stoves and refrigerators, has a constant requirement for surface finishing, primarily for decorative nickel–chrome plating on handles and trim. No increase in the surface finishing demand is expected from this industry.

Wire Goods: These products include display racks, shelving, and shopping carts. The typical surface finish is electroplated nickel, chrome, and brass. Applications for wire goods are numerous and growth potential is in the order of 5–8% per year.

Plumbing Fixtures: These products include taps and bathroom and kitchen fixtures. Base metals are either zinc or chrome plated. Demand is related to the housing and construction industries.

Electrical Equipment: Products included in this group are service boxes, conduit pipes, and transformer parts. Zinc and tin electroplating is used. Surface finishing production rates for these goods fluctuate with the housing and construction industries.

Furniture: Steel furniture is usually plated with nickel and chrome, nickel and brass, or brass only. Growth in this area is highly variable and difficult to predict as it depends on regional trends and designer preference.

Pole Hardware and Heavy Steel: Products such as highway guard rails, transmission towers, and some heavy steel structures used in construction are included here. Hot dip galvanizing is used since the parts are too big to electroplate.

Electronics: The production of printed circuit boards requires primarily copper plating but nickel, gold, tin, and tin–lead processes are also used. While production rates for printed circuit boards are expected to increase over the next few years, the reduction in the surface areas actually plated and the trend to reduced water usage and metal recovery suggest that pollutant generation rates from this industry will not increase.

Engine and Worn Parts: Parts requiring surface finishing come from pumps, diesel engines, gasoline engines, paper mill rolls, etc. The parts vary in size and require heavy deposits of chromium to restore the original dimensions and to provide a durable surface coating.

Hollowware and Flatware: Hollowware products include coffee pots, tea pots, ice bowls, cream and sugar pots, gravy boats, and flower holders. These products are often plated with silver using a silver cyanide bath. There is little growth expected in this market. Flatware includes tableware such as knives, forks, and spoons. These products are made either from stainless steel or from cold-rolled steel, which is plated in a silver cyanide solution. Demand for the product is primarily dependent on the population growth and on the formation of new households; consequently little growth is expected in the future.

Jewelry: All costume jewelry falls under this heading. The typical surface finish is a flash-coating of precious metals such as gold or rhodium on a nickel base. Annual growth is expected to be about 1–3%.

Effluents from a finishing industry must be separated into three categories:

- concentrated spent baths,
- wash waters containing an average concentration of substances likely to precipitate (soaps, greases, and metallic salts),
- dilute rinse water that may be recyclable after treatment.

To secure and facilitate treatment, acidic and chromate-laden effluents must be separated from alkaline and cyanide effluents. The average composition of wastewaters from a surface finishing plant is presented in [Table 2.6](#).

TABLE 2.6
Principal Constituents of Untreated Effluents from Major Metal Finishing Processes.
Composition of Wastewater from Surface Finishing Industries

Species	Plating on Steel	Plating on Zinc	Plating on Brass	Plating on Plastic	Anodizing	Concentration (mg L ⁻¹)
Fe ²⁺	x					1–10
Cu ²⁺	x	x	x	x		5–50
Ni ²⁺	x	x	x	x	x	2–15
Cr ⁶⁺	x	x	x	x	x	10–120
Cr ³⁺	x	x	x	x	x	0.1–1
Zn ²⁺	x	x				10–50
Cd ²⁺	x					10–50
Sn ²⁺	x			x		0.1–20
CN ⁻	x	x	x			1–50
SO ₄ ²⁻	x	x	x	x	x	15–25
Cl ⁻	x	x	x			1–250
CO ₃ ²⁻	x	x	x	x		10–50
Si ₃ ²⁻	x	x	x	x		30–50
PO ₄ ³⁻	x	x	x		x	20–50
Organics	x	x	x	x		0.1–1

Source: Environment Canada, Environmental Protection Service. Overview of the Surface Finishing Industry: Status of the Industry and Measures for Pollution Control. EPS 2/SF/1, Ottawa, Canada, p. 43, 1987.

Note: The cross x is stated whenever the species was detected in the water effluent.

The pollutants may be divided into several families:

- toxic pollutants such as CN⁻, Cr(VI), and F⁻,
- pollutants that change the pH, that is, acidic or basic substances,
- pollutants that raise the SS level such as hydroxides, carbonates, and phosphates,
- pollutants covered by a particular regulation, S²⁻ and Fe²⁺,
- organic pollutants (EDTA, etc.), especially from degreasing.

All the constituents of baths are found in the rinse water, which may also contain metallic ions (Ni, Cr, Cu, Zn, Sn, Cd, Au, Ag, Pb, Fe, and some others) dissolved from the parts treated. The discharge conditions standards vary greatly, depending on the country, and are rapidly becoming increasingly strict as to pollution concentration as well as the flows of rinse water. A large portion of these effluents is received by municipal sanitary sewers (78%). The heavy metals are generally removed by the activated sludge process and become a part of the resulting biological sludge. The beneficial properties of the sludge, which is often used as a fertilizer in agriculture, are then limited because of the heavy metal content [61].

The general guidelines to limit pollutant discharges from surface finishers depend on the laws of each country. In France, for example (decree of November 8, 1985), the metal concentration of (Zn + Cu + Ni + Al + Fe + Cr + Cd + Pb + Sn) combined should be less than 15 mg L⁻¹. In particular, the thresholds summarized in Table 2.7 should not be exceeded (mg L⁻¹).

The Canadian federal guidelines [62] for metal finishing liquid effluents presented in Table 2.8 provide a baseline standard for water discharges.

A quick comparison of Tables 2.6 through 2.8 shows that the metal concentrations in untreated plating shop effluents may be as much as 120 times higher than those permissible by law. Clearly,

TABLE 2.7
France Guidelines for Metal Finishing Liquid Effluents

Cr VI	0.1	Zn	5.0
Cr III	3.0	Fe	5.0
Cd	0.2	Al	5.0
Ni	5.0	Pb	1.0
Cu	2.0	Sn	2.0

untreated metal plating effluent streams may contribute a large amount of metal pollutants to the environment. For example, chromium is most likely to be found at high concentrations in the effluent streams.

2.3.2.1 A Typical Electroplating Process

Electroplating is the electro-deposition of an adherent metallic coating upon an electrode, which is the workpiece, for the purpose of obtaining a surface with properties or dimensions different from those of the basic metal. These properties may include improvement of appearance, corrosion protection, wear resistance, and so on. The operation takes place in aqueous solutions containing the metal ion to be plated. The workpiece is cathodic, and in most instances the metal ion is constantly replenished from an anode containing the metal. A notable exception is chromium where the anode is insoluble and metal ions are replenished by the addition of chromic acid. Electroplating must be preceded by cleaning and activating operations, and a typical sequence of operations involved would be the following:

1. Vapor degrease or soak clean in an emulsion or detergent cleaner.
2. Spray clean in a detergent cleaner.
3. Electroclean in an alkaline cleaner. (The function of electrocleaning is to remove remaining soil and to make the surface chemically active. The operation takes place in an alkaline solution and the work may be anodic or cathodic.)
4. Sulfuric acid dip.
5. Electroplate.
6. Electroclean.
7. Sulfuric acid dip.
8. Second electroplate. Rinsing would follow each process step except 1.

Surface finishers produce and discharge a variety of waste streams, including process wastewaters, spent process solutions, sludges, and air emissions. For proper plating to occur, the parts must

TABLE 2.8
Federal Guidelines for Metal Finishing Liquid Effluents

Metal	Cu	Zn	Cd	Cr	Ni	TSS
Maximum total concentration (mg L ⁻¹)	1.0	2.0	1.5	1.0	2.0	30.0

Source: Environment Canada, Environmental Protection Service. Overview of the Surface Finishing Industry: Status of the Industry and Measures for Pollution Control. EPS 2/SF/1, Ottawa, Canada, p. 43, 1987.

be clean and free of contamination from previous processes. Considerable quantities of raw water are thus used to rinse the parts. Depending on the process for which the rinsing takes place, the wastewater produced may be acidic or alkaline and may contain particular metals or combinations, solvents or cleaning solutions, and/or particulates. Another source of wastewater contamination comes from floor drains. Often, through poor housekeeping, plating solution is allowed to drip as the rack or barrel is passed from tank to tank, and this solution subsequently finds its way into the plant sewer system. Several waste streams, including spent process solutions and sludges, are considered hazardous. Any substance or mixture being discarded is considered hazardous if it is flammable, carcinogenic, toxic, corrosive, and explosive or meets other criteria developed by a (Canadian) federal-provincial working group. Spent process solutions include the following:

- a. Acidic waste from pickling, etching, bright dipping, and electropolishing.
- b. Alkaline cleaning baths and electrocleaning baths.
- c. Solvent degreasing waste.
- d. Salt bath descaling solution.
- e. Spent baths themselves when they can no longer be rehabilitated.

The acidic waste contains a high level of dissolved metals, oils, and suspended particles. The large number of different compounds and additives in cleaning solutions often make recovery of metals or chemicals from the spent solutions impractical. Solvent waste contains soil and oily buildup. Spent plating and coating solutions are generated during electroplating, electroless plating, hot dip coating, anodizing, and chemical conversion coating operations. These wastes, and the relating rinse waters, may be acidic or alkaline and may contain hexavalent and trivalent chrome, cyanide, and other toxic compounds.

A number of metal finishing operations leave sludges on the bottoms of plating bath tanks. Large amounts of sludge are also formed during cleaning, painting, and effluent treatment. Sludge from effluent treatment is only 1–5% solids and can be dewatered to reduce its volume. Sludges usually contain hazardous materials, which could upset the municipal treatment plant if discharged to sewer. Figure 2.9 shows a schematic flow sheet of a copper–nickel–chrome plating system without waste treatment. One should note the numerous opportunities that the wastewater has to pick up pollutants.

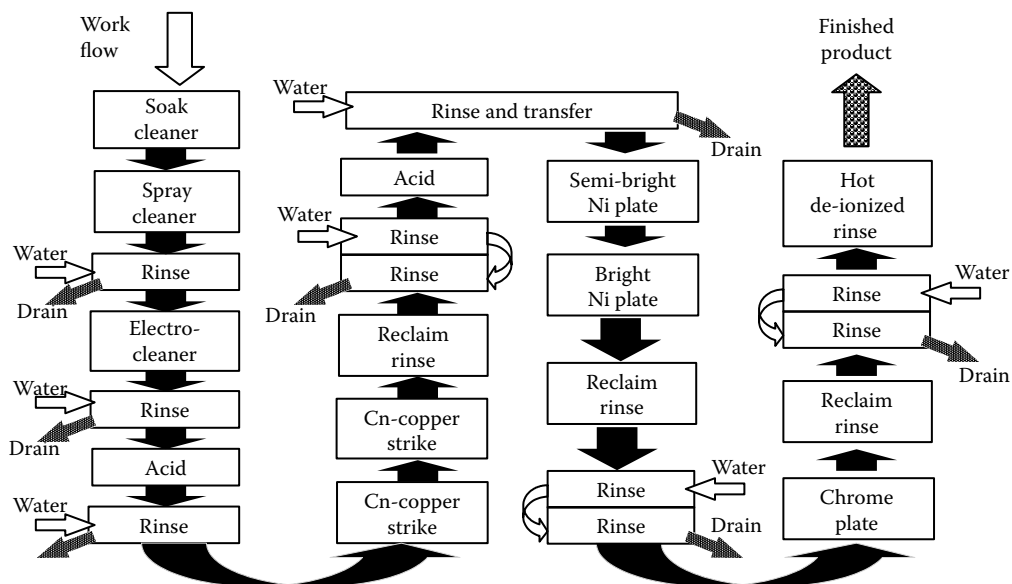


FIGURE 2.9 A schematic flow sheet of a copper–nickel–chrome plating system without waste treatment.

2.3.2.2 Future Trends in Electroplating

Since pressures to reduce impact and liability will continue, if not increase, for the foreseeable future, prudent firms that expect to be using conventional processes are working toward optimizing them. Two popular trends include:

- Approaching zero exposure—isolating employees from contact with materials or effluents in process operations, thus approaching zero risk conditions.
- Approaching zero discharge—maximizing material utilization and recovery, thus minimizing the impact on the environment from wastewater, air emissions, and concentrated waste streams (spent process solutions and treatment sludges and solids).

The techniques that firms employ to achieve near-zero exposure and discharge from wet processes depend on the specific process and production situation, but can involve:

- Enclosing process lines (a common practice in the printed wiring board and semiconductor industries).
- Reducing and recovering dragout.
- Using process solution and rinse purification and recycle technologies.
- Using racking and fixturing off-line to reduce operator exposure and using configurations that optimize process efficiency and yield and minimize waste.
- Using process automation and control systems to optimize material usage and yield.
- Modeling processes for optimization.

Examples of processes using metals with environmental health and safety (EH&S) concerns that can approach near-zero discharge include:

- Chromium plating.
- Chromic anodizing.
- Nickel plating.
- Electroless nickel plating.
- Cadmium plating.
- Lead plating.
- Tin–lead plating.

Hundreds of surface finishing facilities have already implemented process optimization projects that have resulted in near-zero discharge. The improvements have typically yielded cost savings, since the optimized processes exhibit better performance, along with lower material usage and reduced waste generation. In addition, a small fraction of existing surface finishing facilities have enclosed automated process lines with ventilation and air emissions control systems that provide near-zero exposure risk. Industries such as printed wiring board manufacture provide examples where such systems have been successfully implemented.

2.3.3 LEATHER TANNING PROCESS

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans

(man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents. The process of leather tanning generates wastewater effluents containing chromium, which, when emitted at high concentrations, can be toxic to the environment. The public's awareness of the dangers of harmful effluents has grown during the past decade and the need for stricter environmental regulations has forced many process-related industries to dramatically refine their dangerous polluting effluents. The industry's growth in the Western world has stagnated since the 1980s due to the influence of more affordable synthetic leather substitutes. Western regulations regarding wastewater controls are more stringent than those of developing countries and this translates into higher relative production costs for the tanners in developed countries.

2.3.3.1 Description of the Chromium Tanning Process

The modern process of chrome tanning dates back to its discovery by Frederick Knapp in 1958. The purpose of chrome tanning is to transform a hide or skin into a finished leather product that is insusceptible to putrefaction. By varying the specifics of a process, it is possible to obtain leather with the required grain, temper, break, and strength. Specifically, tanning is the reaction of the collagen protein fibers of the hide with chromium. The most widely believed mechanism is that of a coordination of the protein carboxyl groups with a chromium complex [63]. The tanning process can be divided into two divisions:

1. **Beamhouse:** Hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. After soaking, the hides are fleshed to remove excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to vegetable tanning, which is a long-drawn process (~3 weeks) starting with low chemicals concentration that is gradually increased as tannage proceeds.
2. **Tanyard:** Chrome-tanned leather tends to be softer and more pliable, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather that is made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fat liquoring are usually performed to produce usable leathers, and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin.

Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulfate. In the typical one-bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome-tanned leather is piled down, wrung, and graded for thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. Grain leathers from the shaving machine are then separated for retanning, dyeing, and fat liquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i.e., shoe leather), the dye must penetrate further into the leather. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound.

Fat liquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beamhouse and tanyard processes. Fat liquoring is usually performed in a

drum using an oil emulsion at temperatures of about 60–66°C (140–150°F) for 30–40 min. After fat liquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying. Chromium (trivalent) tanning agents are added in the tanning step. Any unfixed tanning agents are removed from the leather in the wringer. The products at this point are referred to as blue hides. Tanneries often perform only the beamhouse and tanyard processes and sell their “blue” hides to retanners.

2.3.3.1.1 Beamhouse Operations

Cured hides received from market must undergo pretreatment before they can be processed into leather. The objective of beamhouse operations is to prepare the hides. Figure 2.10 shows a schematic for the process. In the side-and-trim step the hides are cut into two sides and any unwanted sections of the hide are trimmed off. The wash-and-soak step involves soaking of the hide in water for 8–20 h. The hides absorb water to make up for the moisture lost in the curing process. Washing removes nonfibrous proteins, dirt, salt, blood, and manure from the hide. Fleshing is the mechanical removal of excess flesh, fat, and muscle from the hide. This is done in cold water so as to ensure that the fat remains congealed. Alkaline chemicals (Na_2S and NaOH) are then added to dissolve any hair and to destroy hair roots.

2.3.3.1.2 Tanyard Process

A schematic for the tanyard process is shown in Figure 2.11. Sulfated/chlorinated ammonium salts are added in the bating step to solubilize any alkaline material present from the beamhouse process. Bates (enzymes) are added to further destroy hair roots and pigments and to prepare the collagen fibers for their reaction with the tanning agents. An acidic medium is required for chrome tanning; hence the addition of H_2SO_4 in the pickling step ensures that all alkaline material has been washed away. Salt is also added in the pickling step as it prevents “acid swelling” by reducing excess moisture. Chromium (trivalent) tanning agents are added in the tanning step. Any unfixed

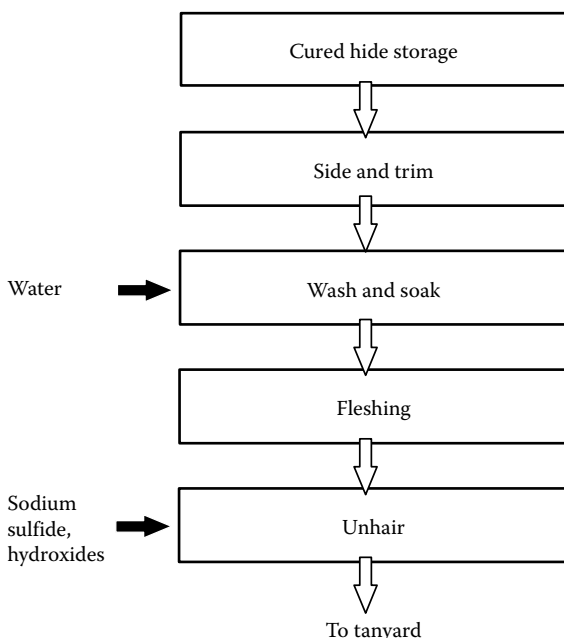


FIGURE 2.10 Leather tanning—a box schematic diagram for the beamhouse process.

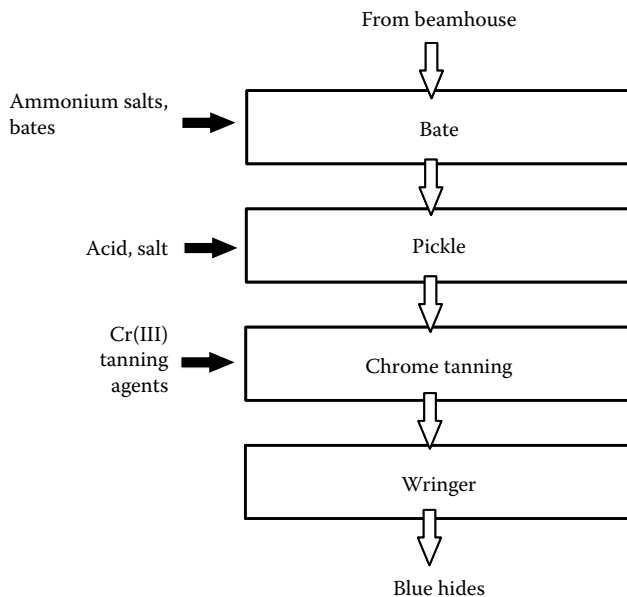


FIGURE 2.11 Leather tanning—a box schematic diagram for the tanyard process.

tanning agents are removed from the leather in the wringer. The products at this point are referred to as blue hides.

2.3.3.1.3 Retanning

Retanning is necessary to convert the blue hides to leathers suited for a specific use. A schematic for the process is shown in Figure 2.12. Chromium is usually used as the retanning agent. The leather quality is often upgraded by the introduction of phenols and other complementary tanning agents. The leather is then bleached and dyed as desired. The addition of fat liquor replaces any natural oils lost in the beamhouse and tanyard processes. Final finishing includes drying, conditioning, buffing, and plating.

2.3.3.2 Wastes Generated in the Chromium Tanning Process

The beamhouse process normally accounts for about 40% of wastewater volume in a tannery [64]. Beamhouse wastes have a high pH of 10–12 and contain high amounts of proteins and sulfides. Nitrogen, BOD, and TSS are also very prevalent in beamhouse wastes. Wastes from the bating step have high ammonia concentrations and also contain proteins and dissolved hair. The pickling step generates a highly acidic waste (pH 2.5–3.5) containing salts. Toxic levels of trivalent chromium at elevated temperatures characterize the acidic waste from the tanning and retaining steps. The retanning process also yields wastes containing dyes and sulfonated oils at elevated temperatures. Tanyard and retanning effluents have considerably high levels of COD. These elevated COD levels are caused by high ammonia concentrations from the bating step. In addition to nitrogenous COD demand, if a phenol retanning step is used in the process it may account for up to 30% of the total COD [65]. The retanning finishing step also contributes to higher levels of COD. This is due to the introduction of organic dyes, sulfonated oils, pigments, and coatings.

2.3.3.2.1 A Leather Tannery Wastewater Case

Production levels, seasonal variations, process variations, and the batch nature of tannery operations result in large variations in the wastewater sampled parameters. A medium-sized tannery

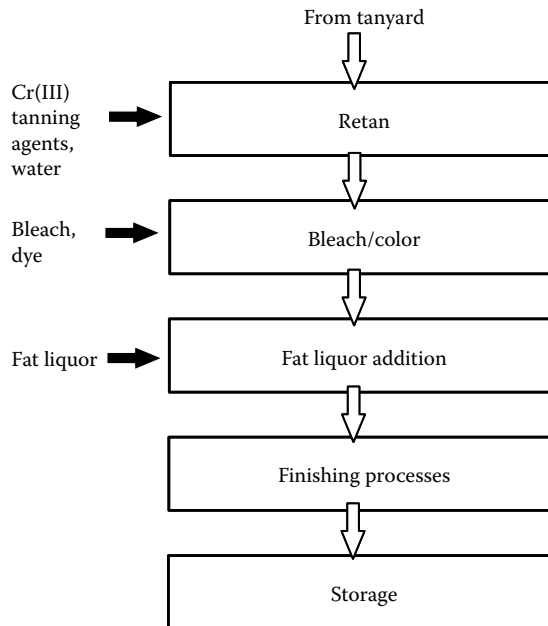


FIGURE 2.12 Leather tanning—a box schematic diagram for the retanning process.

may typically process 500–1000 kg of hides in one batch. About 50,000–150,000 L of water are used for each batch, thus requiring approximately 200,000–500,000 L of water per day. Table 2.9 shows a typical case raw effluent composition.

It is evident from the above table that extremely high chromium concentrations are present. This is due to the washing of the chromium from the original tanning step. It can be seen that high concentrations of undesirables are present. Table 2.10 shows the parameters for river outfall. High levels of chromium, phenols, COD, BOD, and oil and greases are present following a simple settling pretreatment. The highly acidic nature of the effluent (pH 3.3) should be raised to a more moderate level. High levels of COD exert a heavy load on the receiving water body and require a special treatment to reduce them. The case is similar for chromium content.

TABLE 2.9
Original Wash Sampling Results^a (pH 5.0)

Parameters	#1	#2	#3
Total solids	5444	—	2520
TFS	1480	140	127
Oil and grease	0.42	88.5	94.7
BOD	536	120	410
COD	3047	1445	1032
Pb	1.1	7.5	7.5
Cr	122	140	120
Phenols	0.14	2.5	1.95

^a All results are in mg L⁻¹ (ppm).

TABLE 2.10
River Outfall Sampling Results^a (pH 3.3)

Parameters	#1	#2	#3
Total solids	1540	—	1300
TFS	—	88	165
Oil and grease	0.01	44	98.7
BOD	454	238	904
COD	2500	1875	3016
Phosphates	0.25	3.7	—
Pb	0.25	7.75	7.5
Cr	91	40	130
Phenols	0.52	1.55	0.40
NH ₄	—	0.91	1.61

^a All results are in mg L⁻¹ (ppm).

2.3.3.3 Effluent Treatment

There are various options for reducing chromium effluent concentration in a leather tanning process. Chrome recycling within the process can account for large economic savings with respect to the amount of chemicals required and will allow for a lesser concentrated chromium effluent. Ideally, direct recycling could account for reductions of 40% in “suspended” solids, of 50% in BOD, and of 80% in toxicity [65].

2.3.3.3.1 Changing Process Chemicals

The following are three forms of chemical changes capable of improving effluent quality: organic acid pickling, “low-use” chrome compounds, and synthetic tanning agents. As mentioned in the above description of the chromium tanning process, the pickling step usually employs sulfuric acid to prepare the hides for chrome tanning. Substitution of H₂SO₄ for organic acids can substantially reduce (approximately 20%) the chrome required in the tanning process. Organic acids show a reduced affinity for collagen fibers, thus enabling acid penetration and chrome fixation to occur more rapidly [65]. Employing low-chrome compounds is the most widely used method for chromium effluent reduction. These low-chrome compounds are commercial tanning agents (e.g., Chromotan, Blancoral, and Baychrome 2403) capable of producing quality tanned leather at lower chrome concentrations. Low-chrome compounds combined with low float (liquor to hide ratio) techniques are capable of lowering chrome and water consumption [65]. Substitution of chromium tanning complexes for synthetic tannins would totally eliminate chromium from the process. However, this is not possible because product quality would suffer. The most common of the new synthetic tannins are those of complex aluminum salts. Research is presently being done to find new chrome-free tanning agents consistent with a fine quality of leather [65].

For example, a leather tanning process has been developed in which animal skins are treated with a tanning agent comprising a mixed complex of aluminum(III) ions and titanium(IV) ions, and as a masking compound a salt of a polyhydroxymonocarboxylic acid. Titanyl sulfate solution, prepared by the dissolution of hydrous titanium oxide in sulfuric acid, can be mixed with aluminum sulfate in the desired proportions, treated with masking agent and basified to the appropriate acidity, and then used in the “cleaner” tanning process.

2.3.3.3.2 Treatment Improvements

Process effluent streams containing alkaline materials are segregated from acid streams (containing chromium). High sulfide concentrations in the alkaline streams are first targeted by screening and

then by sulfide oxidation. The oxidation takes place in an aerated tank and uses manganese sulfate as a catalyst. Oxidation may also be forced using peroxide addition. The effluent from the oxidation step is mixed with the segregated acid effluent in an equalization tank. Chromium precipitation and subsequent recycling is another means of reducing chromium in the effluent. This is done by raising the pH to an optimum level (8.5) using a hydroxide. The chromium precipitates as chromium hydroxide ($\text{Cr}(\text{OH})_3$). Coagulants and flocculants are also added to aid in substrate removal. The hydroxide precipitate is then filtered and redissolved in sulfuric acid to form chrome sulfate, which is subsequently recycled [65]. Application of ion exchange resins to remove undesirable ions from wastewater (i.e., chromium) has to be carefully considered in combination with appropriate pretreatment since the organic components in wastewater can seriously affect resin performance. Metal biosorption metal removal/recovery effluent treatment alternative deserves special attention because of the low cost of biosorbent materials. The introduction of newer technologies in both leather tanning processes and the treatment of wastewater can greatly lower the pollution load normally posed by conventional tannery effluent disposal.

2.3.4 FERROUS METAL INDUSTRIES

The production of metals via extraction from metal ores is one of the oldest metallurgical processes. In the Roman Empire, metal production was used to make dishes, tools, and weapons. During the following centuries, more metal was required as a result of industrialization, and the metallurgical industry was born. The modern metallurgical industry can be separated into two main categories: ferrous and nonferrous. Ferrous metallurgy deals with the production of iron and its alloys, whereas nonferrous metallurgy deals with the production of other metals such as copper, nickel, lead, and zinc. Previously, there has been little concern about heavy metal emissions from the industry, owing to ignorance of the impact of heavy metals on the environment. Today, the toxicity of heavy metals is relatively well established and key pollution regulations have been legislated for the mining and metal production industries. Studies have demonstrated that the heavy metal pollution arising from metal production usually becomes water pollution. For example, heavy metals in air emissions are brought down into water during rainfall, they are leached from solids into surface streams and rivers, and effluents from industries are often discharged directly into rivers or other receiving surface water bodies (Figure 2.13).

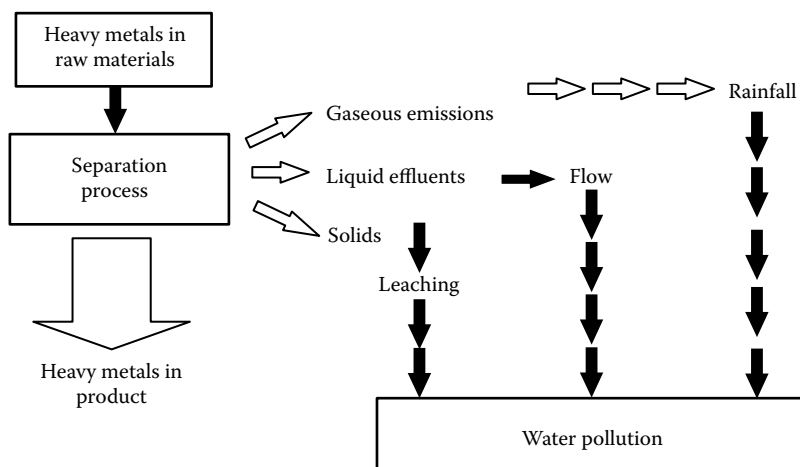


FIGURE 2.13 Heavy metal sources from metal production.

2.3.4.1 Ferrous Metal Processing

Ferrous metal processing can be divided into three categories:

1. Primary iron and steel production.
2. Ferroalloy production.
3. Ferrous foundry production.

The process used in the production of ferrous metals is similar for all three types of production categories and can be summarized in general as illustrated by the flow sheet in Figure 2.14.

Depending on the category of industry, the furnace and the reactants involve change. Air emissions arise from the recuperation of heavy metals that are in exhaust gas. The recovery is not 100% effective; hence heavy metals are discharged into the atmosphere. The air pollution control equipment used will be different, depending on the type of furnace used. Solid wastes from ferrous processing industries are present in the form of slags and dusts. Dusts that cannot be recycled back into the process are disposed of continuously. Slag comprises waste oxides and is usually dumped in a slag dump. Generally, water pollution comes from process water, contact cooling water, and wash-down water. A sludge plant is commonly used to treat process wastewater. [Table 2.11](#) shows the most common heavy metals that can be found in wastewaters from the three different ferrous industries.

2.3.4.1.1 Primary Iron and Steel Production

Iron is produced by a blast furnace process. Steel is produced from pig iron originating from the blast furnace [66]. In 1976, the Canadian production of steel amounted to 10,916,929 tons from basic oxygen and open hearth furnaces and 1,665,880 tons from electric arc furnaces [66]. Usually, iron and steel production is integrated in the same plant. Total emissions from primary iron and steel production are estimated at 83 tons per year of copper and 51 tons per year of nickel [66]. Heavy metals pollution results from three kinds of emission: water, air, and solids. [Table 2.12](#) gives a comparison between water pollution, air emissions, and solid disposals from an iron and steel

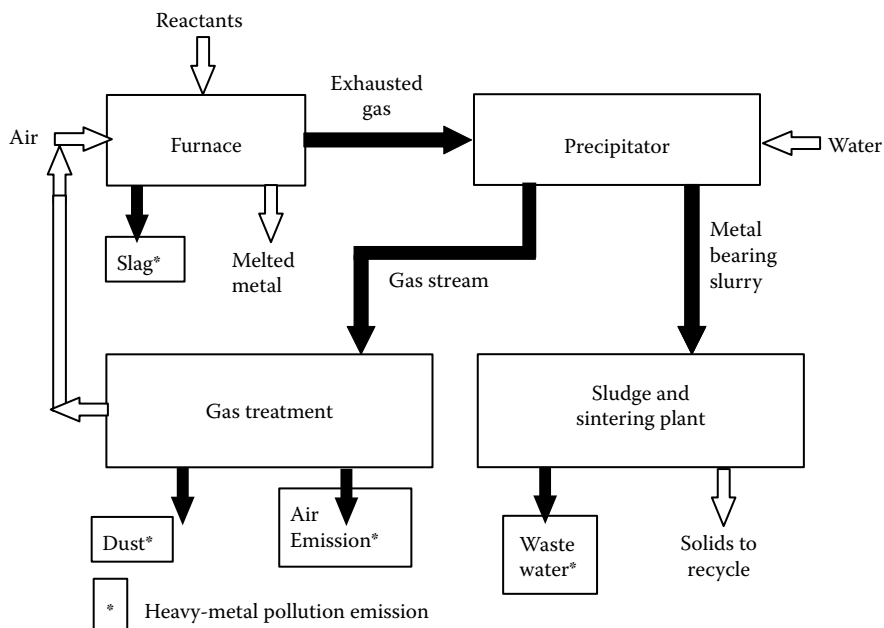


FIGURE 2.14 Flow sheet of a typical ferrous metal production plant.

TABLE 2.11**Heavy Metals in Wastewater from Ferrous Industries**

	Sb	Bi	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Mo	Ni	Se	Zn
Primary Iron	—	—	x	x	x	x	x	x	—	x	—	x	—	x
Ferro-alloy	—	—	x	x	—	x	x	x	—	x	—	x	—	x
Foundries	x	x	x	x	x	x	x	x	x	x	x	x	x	—

making plant. From this table it can be seen that solid disposals are more polluting than water discharges.

2.3.4.1.2 Ferroalloy and Ferrous Foundry Production

A ferroalloy is an alloy consisting of iron and one or more other metals. Various kinds are produced in the world, mainly ferrosilicon, ferromanganese, silicomanganese, and ferrochromium. [Table 2.13](#) shows the composition of the effluent of a ferrochrome production plant.

Foundries range in size from small operations to the large production type, which turn out tonnage casting. Some plants produce special wear- and heat-resistant castings, which are usually high alloy. Other plants produce the normal gray iron and ductile iron castings, which may weigh from a few ounces to several tons. Because of the various operation conditions (capacity and charge), no typical data have been found that could be considered as representative of the industry branch.

In conclusion, in ferrous metal production, solid wastes contain the highest amounts of heavy metals followed by air emissions and liquid effluents. Solid wastes are considered as relatively inert. The air emission and liquid effluents containing heavy metals are the most damaging to the environment, since these heavy metal concentrations and discharge rates are very high and can be easily brought into the water table or accumulate directly in the aquatic environment and biota.

2.3.5 COAL-FIRED POWER GENERATION

The whole thermal-power industrial sector, including both conventional and nuclear power-generating plants, withdrew 64% of the total water intake in 1996. Next to fuels, water is the most important resource used in large-scale thermal power production. The production of 1 kW h of electricity requires 140 L of water for fossil fuel plants and 205 L for nuclear power plants. Some of the water is

TABLE 2.12**Amount of Wastewater, Air Emissions, and Solid Disposals for an Example of an Iron Making Plant**

Pollutant	Wastewater Effluents (kg h ⁻¹)	Air Emissions (kg h ⁻¹)	Solid Disposals (kg h ⁻¹)
Cd	<0.023	—	—
Cr	<0.023	—	3
Cu	<0.023	1	7
Fe	0.517	—	422
Pb	<0.025	7.23	62
Mn	—	2.71	36
Ni	<0.023	0.41	—
Zn	<0.025	—	160

TABLE 2.13
Concentrations of Metals in Effluents from a Ferrochrome Production Plant

Pollutant	Stream #1 (mg L ⁻¹)	Stream #2 (mg L ⁻¹)	Stream #3 (mg L ⁻¹)
Fe	<0.1	<0.1	0.3
Cr	<0.1	<0.1	<0.1
Cu	<0.01	0.02	<0.01
Pb	<0.11	<0.1	<0.1
Mg	24	59	1.5
Hg	<0.0005	<0.0005	<0.0005
Cd	0.019	<0.005	<0.005
Zn	61	0.3	0.02
Ni	0.06	0.01	<0.05

converted to steam, which drives the generator producing the electricity. Most of the water, however, is used for condenser cooling because today's processes can only convert 40% of the fuel's energy into usable electricity. The rest is wasted. This shows the double cost of inefficient energy use: first, in the wasted energy, and then in the water required to cool the wasted heat to the temperature where it can be released safely into the environment. This requires a continuous flow of cooling water circulating through the condenser. All the cooling water is therefore returned to the environment much warmer. However, the temperature can be reduced using cooling towers and other such devices.

Nonnuclear thermal electric power generating stations are a somewhat less known source of a large amount of metal emissions yearly. This is due to the large flowrates of water involved in operation of the plants. On the other hand, their consumption of coal that brings in trace metal impurities is truly gigantic. A large coal train called a "unit train" may be 2 km (over a mile) long, containing 100 cars with 100 tons of coal in each one, for a total load of 10,000 tons. A large plant under full load requires at least one coal delivery this size every day. Plants may receive as many as three to five trains a day, especially in "peak season," during the summer months when power consumption is high. A large thermal power plant (e.g., Nanticoke, Ontario, Canada) could store several million tons of coal for winter use when the supply faces interruptions.

Metals from coal, as they do not combust, end up in their gaseous, aqueous, and solid waste streams. Coal also contains low levels of uranium, thorium, and other naturally occurring radioactive isotopes whose release into the environment leads to radioactive contamination. While these substances are present as very small trace impurities, enough coal is burned that significant amounts of these substances are released. A 1000 MW coal-burning power plant could release as much as 5.2 tons per year of uranium (containing 74 pounds of uranium-235) and 12.8 tons per year of thorium. The radioactive emission from this coal power plant is 100 times greater than a comparable nuclear power plant with the same electrical output; including processing output, the coal power plant radiation output is over 3 times greater [67].

Trace amounts of mercury exist in coal and other fossil fuels [68]. When these fuels burn, toxic mercury is released, which accumulates in the food chain and is especially harmful to aquatic ecosystems. Worldwide emissions of mercury from both natural and human sources were estimated at 5500 tons in 1995 [68]. U.S. coal-fired plants emit an estimated 48 tons annually, which is approximately one-third of all mercury emitted into the air by human activity in the United States [68]. In contrast, China's coal-fired power plants emitted an estimated 68 tons of mercury in 1999, which was about one-eighth of Chinese human-generated mercury emissions [69].

Of the three types of plants (coal fuelled, oil fuelled, and mixed), coal-fuelled plants are the worst polluters due to the high-sulfur coal burned and their high water consumption rates. It is possible to significantly reduce metal emissions if appropriate and currently available technologies are incorporated

into the power generation operation schemes. Unfortunately, too few plants have made any efforts to address this particular problem, which remains as overwhelming as ever.

2.3.5.1 Coal-Fired Station Types

There are two types of generic station types. The waste stream compositions of each model depend on coal composition, scrubber design, and system operation. For instance, the “Eastern” type of power plant uses high-sulfur bituminous coal fuel, while the “Western” type uses low-sulfur lignite coal fuel. Unfortunately, available sources list only the emission of iron from streams, specifically, grouping all other metals present into one category. The other metals that may be present are aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, thorium, titanium, vanadium, zinc, and zirconium. However, the metals usually present in the largest concentrations are aluminum, manganese, iron, nickel, copper, zinc, and vanadium [70].

First Model (Eastern) – Typical Characteristics:

- 400 MW generating capacity,
- high-sulfur bituminous coal fuel,
- dry fly ash handling system,
- recirculating bottom ash handling system,
- once-through seawater cooling,
- limestone-based flue gas desulfurization,
- combined fly and bottom ash disposal area,
- separate flue gas desulfurization (FGD) sludge disposal area.

Periodic wastewater streams contain metals from the substances removed during the annual boiler and equipment cleaning. These streams are high in metal concentrations (Table 2.14). Some

TABLE 2.14
First Model (Eastern) of a Power Generating Station—Stream Data

Source	Flow (L y ⁻¹)	Iron (mg L ⁻¹)	Other Metals (mg L ⁻¹)
Periodic:			
Air preheater wash	500,000	7560	1320
Boiler fireside wash	1,000,000	1060	935
Boiler steamside wash	600,000	6900	1000
Continuous:			
	L s ⁻¹		
Coal pile runoff	0.6	5320	610
Filter backwash	0.9	0.7	5.2
Ionex regeneration	1.3		
Cation		0.3	7.1
Anion		6.2	0.5
Fly/bottom ash disposal	1.5	0.7	17
Bottom ash blowdown	23	23	20
Boiler room sump	20	13	60
Condensate polisher	0.4	0.2	<0.1
Cooling water	17,000	1.1	7.5
FGD sludge disposal	1.5	0.4	20
FGD system blowdown	11	1.0	14

Source: Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, Ontario, Canada, 1985.

continuous wastewater streams contain high metal concentrations. These are produced in the daily operation of the station from the condenser cooling blowdown, the ash transport systems, and FGD systems. While metal concentrations in other continuous streams may be relatively low, from 1–10 mg L⁻¹, some of these streams have very large flowrates [70].

Periodic wastewater streams annually emit 8980 kg of iron and 2195 kg of other metals. Continuous streams emit 715,957 kg y⁻¹ of iron and 4,091,957 kg y⁻¹ of other metals. This is an annual total of almost 5 million kilograms per year of metals emitted into the environment.

Second Model (Western) – Typical characteristics include:

- 400 MW generating capacity,
- low-sulfur lignite coal fuel,
- combined fly and bottom ash transport with lagoon disposal,
- recirculating cooling tower,
- no FGD.

The western stations tend to be more modern and to employ more advanced technology, particularly in the cleaning of streams. Unfortunately, no general composition data are readily available for periodic wastewater streams. Continuous wastewater discharge streams show a significant reduction in metal concentrations due to the use of lower-sulfur coal and the presence of cooling towers that reduce the water flows (Tables 2.15 and 2.16). With the cooling towers, less fresh water is used and greater concentrations of metals can be removed before emission. Unfortunately, there is still the blowdown water, which is taken from the recirculating water to control the buildup of suspended and dissolved solids in the system.

The annual amount of iron released into the environment from continuous streams is 22,889 kg; the amount of other metals is 94,027 kg. This is a reduction of 96.8% and 97.7%, respectively. The majority of this reduction is due to the use of cooling towers and more efficient cleaning prior to emission through the use of reverse osmosis [70].

TABLE 2.15
Second Model of a Power Generating Station—Stream Data

Source	Flow (L y ⁻¹)	Iron (mg L ⁻¹)	Other Metals (mg L ⁻¹)
Periodic:			
Air preheater wash	730,000		
Boiler fireside wash	600,000		
Boiler steamside wash	500,000		
Continuous:			
	L s⁻¹		
Coal pile runoff	0.3	530	1670
Filter backwash	0.9	0.7	5.2
Ionex regeneration	3.4		
Cation		0.3	7.1
Anion		6.2	0.5
Combined ash lagoon overflow	30	0.4	15
Boiler room sump	20	1.6	
Condensate polisher	0.4	0.2	0.1
Reverse osmosis reject brine	1.5		
Cooling tower blowdown	100	5	40

Source: Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, Ontario, Canada, 1985.

TABLE 2.16
Environment Canada Criteria for Discharge of Wastewaters
from Thermal Power Generating Stations

Parameter	Acceptable Limits
pH	6.0–9.5
Total suspended solids	25.0 mg L ⁻¹
Chromium	0.5 mg L ⁻¹
Copper	0.5 mg L ⁻¹
Iron	1.0 mg L ⁻¹
Nickel	0.5 mg L ⁻¹
Zinc (system without recycle)	0.5 mg L ⁻¹
Zinc (system with recycle)	0.2 mg L ⁻¹

2.3.5.2 Generating Station Water Use

The steam electric power-generating industry is one of the major point-source users of surface waters. Earlier, water was used on a once-through basis for each subsystem of the plant. However, with increased competition for available clean surface water, new designs had to be implemented for plants to reduce water intake. Plants were to maximize the internal reuse of service water streams through recirculation. With lower volumes of wastewater to treat, removal of contaminants could be maximized. Metals in the water streams cause corrosion and scale problems. Most water intake requirements are for major condenser cooling. Water is also used for cooling auxiliary equipment, as boiler makeup water, and for cleaning boilers and other equipment. Particularly in coal-fired plants, water is necessary for coal spray and for the removal and transportation of combustion wastes. The metals present in station effluents, many exceeding environmental guidelines, come from demineralization of water, corrosion of equipment and scaling as well as coal pile runoff—a large source of dissolved metals—and from the cleaning of flue gas through desulfurization (FGD) or the removal of fly ash solids [70]. The various major wastewater streams in the power-generating plant are given below (Table 2.17).

TABLE 2.17
Composition of Specific Metal Concentration Present in Station Waste
Stream versus in Nature

Parameter	Natural Concentration (mg L ⁻¹)	Waste Concentration (mg L ⁻¹)
Aluminum	0.08	7.4
Manganese	0.05	15.0
Iron	0.047	1300
Nickel	0.005	55
Copper	0.003	8.6
Zinc	0.001	4.3
Barium	0.10	7.9
Vanadium		20.0

Source: Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, Ontario, Canada, 1985.

Boiler blowdown: Impurities entering the steam-generating system with boiler makeup water and corrosion prevention chemicals are concentrated as steam in the boiler. To avoid excessive buildup of the impurities, the boiler side is bled as a boiler blowdown stream. The boiler blowdown water is discharged over ash dykes.

Demineralization (DM) plant neutralization effluent: Raw water from the clarifier is treated in the DM plant with the help of ion exchange resin beds. During regeneration and backwashing, effluents are generated, which are collected in a neutralization pit. Effluents during regeneration of anionic and cationic beds are mixed together along with other effluents and discharged after pH adjustment into ash ponds. The DM plant neutralization effluent may also be eventually discharged into ash ponds, where it is treated along with other effluents before its discharge into the environment (ash pond overflow).

Cooling tower blowdown: In this system, hot water from the condenser is cooled in the cooling tower and the cooled water is recirculated to the condenser by CW pumps through the water conductor system. The blowdown from the cooling water system is taken to an ash water sump to meet the requirement of the ash handling plant.

Ash pond overflow waters: The ash slurry from the generating units is dumped in the ash dyke area. This area consists of two compartments; the first one consists of 80% of the area where most of the ash is settled and water with fine ash flows into the second compartment (stilling pond). In the stilling pond, final ash is settled. The water from the stilling pond is partially recycled and partially discharged in an open lined channel for irrigation after proper treatment.

Oxidation pond outlet: The wastewater from residential colonies along with sewage generated at thermal plants is led to the oxidation plants. The treated water from the oxidation ponds may be used for irrigation and green belt development.

Collected coal-heap runoff: The mixed runoff generated in the coal-heap area originates from atmospheric deposition (rain and snowmelt), washing, and mainly from coal-heap spraying (to minimize dust and also self-ignition). Due to the action of acid-generating microorganisms, the runoff tends to be acidic (like AMD), effectively leaching trace metal content of the huge quantities of coal throughput. The combined collected runoff of low pH is usually neutralized (lime) and the resulting precipitates settled out as toxic sludge. The water effluent may be discharged or recycled, if feasible. Its residual overall amount of toxic heavy metals in this stream, however, can be quite significant.

2.3.5.3 Conclusions

Thermal stations using fossil fuels have always been linked in the public mind with heavy air pollution. The liquid effluents from these plants have never been given much attention; hence the public has been left with a false sense of security about the purity of the water around thermal power generating plants. However, it is clear that the waste streams being emitted could use much cleaning. Many plants in North America exceed the regulatory norms for concentration of heavy metals in the environment. Unfortunately, those norms are deceptive since the environmental impact of heavy metals is measured more in terms of quantities of metals in the water bodies rather than effluent concentrations. With the immense amounts of water discharged by those plants, even if they met the norms they would still have a considerable impact on nature. A better solution would be to make plants comply with a set amount of metal emissions per day rather than with a specific stream concentration.

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3 Environmental Behavior and Effects of Engineered Metal and Metal Oxide Nanoparticles

Bernd Nowack

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3.1 INTRODUCTION

Particles in the nanosized range have been present on earth for millions of years and have been used by mankind for thousands of years. Recently however, nanoparticles (NPs) have attracted a lot of attention because of our increasing ability to synthesize and manipulate such materials. Today, nanoscale materials find uses in a variety of different areas such as electronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic, and materials applications. Because of the potential of this technology, there has been a worldwide increase in investment in nanotechnology research and development (Guzman et al., 2006).

The huge increase in the manufacturing and use of NPs makes it likely that increasing human and environmental exposure to NPs will occur. As a result, NPs are beginning to come under scrutiny and the discussion about the potential adverse effects of NPs has increased steadily in recent years; in fact, it has become a top priority in governments, the private sector, and the public all over the world (Roco, 2005; Helland et al., 2006; Siegrist et al., 2007).

Most attention has thus far been devoted to the toxicology and human health implications of NPs (e.g., see reviews by Oberdörster et al., 2005; Kreyling et al., 2006; Lam et al., 2006; Nel et al., 2006; Helland et al., 2007), but recently the behavior and effects of NPs in the environment have also caught the attention of researchers (Biswas and Wu, 2005; Moore, 2006; Oberdörster et al., 2006; Wiesner et al., 2006; Helland et al., 2007; Nowack and Bucheli, 2007).

Engineered NPs may enter the environment by a variety of different processes and pathways. The most important are depicted in Figure 3.1. NPs can enter the environment either intentionally or unintentionally. When NPs are used for water treatment or remediation of groundwater or soil, they are added in large quantities directly into the environment. Unintentional releases of NPs may come from point sources such as production facilities, landfills, or wastewater treatment plants or from nonpoint sources such as wear from materials containing NPs. Accidental release during production or transport is also possible.

It is the aim of this chapter to give an overview of the occurrence, behavior, and effects of metal and metal oxide NPs in the environment.

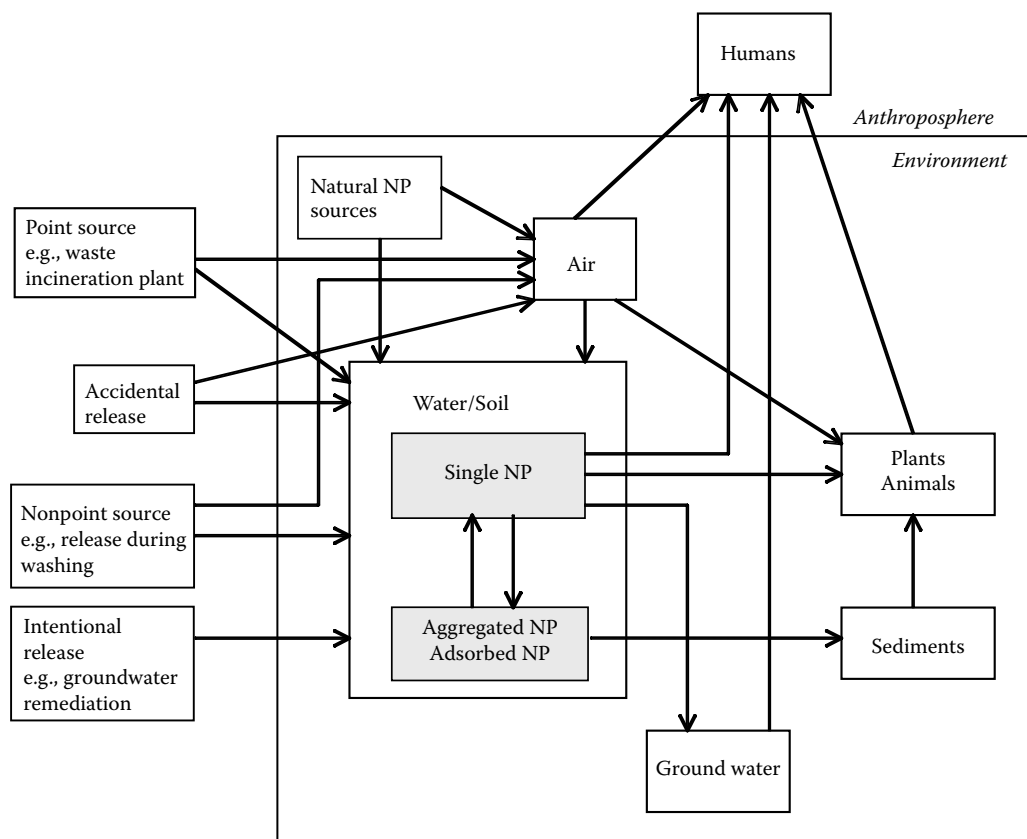


FIGURE 3.1 NP pathways from the anthroposphere into the environment, reactions in the environment and exposure of humans. (Modified from Nowack, B. and Bucheli, T.D., *Environ. Pollut.*, 150, 5–22, 2007.)

3.2 CLASSIFICATION OF NPs

NPs are usually defined as particles having dimensions of roughly 1–100 nm, a size range where unique physical properties make novel applications possible (EPA, 2007). They can be spherical, tubular, or irregularly shaped and can exist in fused, aggregated, or agglomerated forms. The fundamental properties of a material change with size and therefore also the reactivity of a particle in a chemical reaction. Minerals in the size of approximately a few to several tenths of nanometers are in the transitional range where properties are expected to be variable and to deviate from bulk behavior (Hochella and Madden, 2005). Hematite particles with a diameter of 7 nm, for example, adsorbed Cu ions at lower pH values than particles with 25 or 88 nm diameter, indicating the uniqueness of surface reactivity for iron oxide particles with decreasing diameter (Madden et al., 2006). An investigation of Pb adsorption onto TiO₂-NPs showed that the bulk material exhibited stronger adsorption and higher adsorption capacity than the nanoparticulate material (Giammar et al., 2007).

NPs can be divided into natural and anthropogenic particles (Table 3.1). The particles can be further separated based on their chemical composition into carbon-containing and inorganic NPs. Examples of natural inorganic NPs are biogenic magnetite or atmospheric aerosols such as sea salt. Anthropogenic NPs can be either inadvertently formed as a byproduct, mostly during combustion,

TABLE 3.1
Classification of NPs

		Formation		Examples
Natural	C-containing	Biogenic	Organic colloids	Humic, fulvic acids
			Organisms	Viruses
		Geogenic	Soot	Fullerenes
		Atmospheric	Aerosols	Organic acids
		Pyrogenic	Soot	CNT
	Inorganic			Fullerenes
				Nanoglobules, onion-shaped nanospheres
		Biogenic	Oxides	Magnetite
			Metals	Ag, Au
		Geogenic	Oxides	Fe oxides
Anthropogenic (manufactured, engineered)	C-containing		Clays	Allophane
		Atmospheric	Aerosols	Sea salt
		Byproduct	Combustion	CNT
			Byproducts	Nanoglobules, onion-shaped nanospheres
		Engineered	Soot	Carbon black
	Inorganic			Fullerenes
				Functionalized CNT, fullerenes
			Polymeric NPs	Polyethyleneglycol (PEG) NPs
		Byproduct	Combustion	Platinum group metals
			Byproducts	
	Engineered		Oxides	TiO ₂ , SiO ₂ , Fe ₂ O ₃
			Metals	Ag, iron
			Salts	Metal phosphates
			Aluminosilicates	Zeolites, clays, ceramics

Source: After Nowack, B. and Bucheli, T.D., *Environ. Pollut.*, 150, 5–22, 2007.

Note: The gray shaded area is covered in this chapter.

or produced intentionally due to their particular characteristics. In the latter case, they are often referred to as engineered or manufactured NPs. These engineered inorganic NPs are the topic of this chapter and are highlighted in gray in Table 3.1.

3.3 USE, PROPERTIES, AND OCCURRENCE OF INORGANIC NPS

3.3.1 NATURAL INORGANIC NPS

Natural inorganic NPs can have atmospheric, geogenic, or biogenic origin. Inorganic NPs are present everywhere in soils and geologic systems (Banfield and Zhang, 2001; Gilbert and Banfield, 2005; Waychunas et al., 2005). Chemical weathering processes of silicates, oxides, and other minerals frequently produce NPs such as amorphous silica, hydrous aluminosilicates such as allophane, clays such as halloysite, and oxides such as magnetite and hematite (Faimon, 2003; Zanker et al., 2006). In acid mine drainage, the very low pH solutions derived from the weathering of sulfide-rich rocks form a variety of different NPs when mixed with natural waters due to changes in temperature, pH, and higher oxygen concentrations. Ferrihydrite, amorphous iron oxide, and goethite (α -FeOOH) are typical examples of NPs formed during this process. Also, heavy metal NPs can be formed naturally; for example, UO_2 -NPs are formed by reaction of uranyl with green rust, an Fe(II)–Fe(III) phase (O'Loughlin et al., 2003; Figure 3.2). Polynuclear complexes and nanoclusters of aluminum, for example, Al_{13} or Al_{30} (Casey et al., 2001; Furrer et al., 2002), and of sulfides, for example, Cu_4S_6 nanoclusters (Luther and Rickard, 2005), have been found in natural waters.

Microorganisms can also generate metal NPs through the generation of metabolic energy by pathways involving inorganic ions that participate in redox reactions. Oxidation of Fe(II) results in the formation of iron oxide NPs. Different biogenic manganese oxide NPs can be formed, both inside and outside of the cell (Matsunaga and Sakaguchi, 2000). Furthermore, metal sulfide NPs can be produced

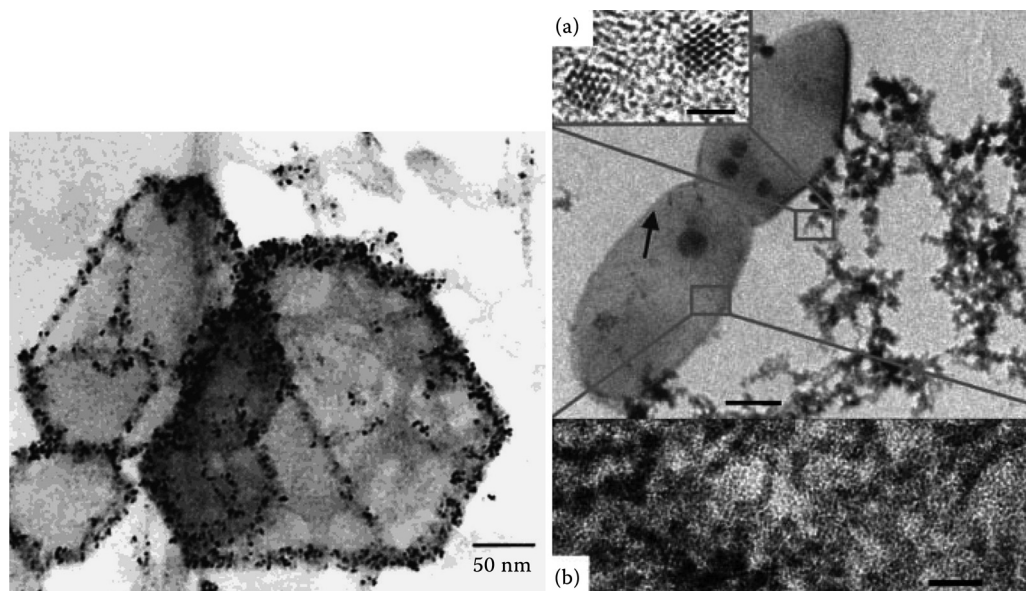


FIGURE 3.2 Natural inorganic nanoparticles: Left: UO_2 formed by reaction of U(VI) with green rust. (Reprinted with permission from O'Loughlin, E.J. et al., *Environ. Sci. Technol.*, 37, 721–727, 2003. Copyright American Chemical Society.) Right: UO_2 formed by bacterial reduction of uranium (Suzuki, Y. et al., *Nature*, 419, 134, 2002). Reprinted by permission from Macmillan Publishers Ltd.

by the action of sulfate-reducing bacteria, for example, ZnS. Biogenic UO_2 -NPs have been observed on the surface of bacteria in the presence of dissolved uranium (Suzuki et al., 2002; Figure 3.2). Some plants have been shown to transform copper into metallic copper NPs in and near roots with evidence of assistance by endomycorrhizal fungi when grown in contaminated soil in the natural environment (Manceau et al., 2008).

3.3.2 UNINTENTIONALLY PRODUCED INORGANIC NPs

Unintentionally produced NPs are formed as a byproduct of human activities. These are mostly carbon-containing particles formed during combustion processes (Kittelson, 1998; Anastasio and Martin, 2001). A small fraction of these atmospheric particles also consists of metal oxides (Cass et al., 2000). Metal NPs can also be formed by other human activities, for example, welding, where mainly metal and metal oxide particles, many of them in the NP range, are produced (Zimmer and Biswas, 2001; Lee et al., 2007). A special class of unintentionally produced NPs consists of platinum- and rhodium-containing particles produced from automotive catalytic converters. Although most of the Pt and Rh is attached to coarser particles, about 17% was found to be associated with the finest aerosol fraction ($<0.43\ \mu\text{m}$) and may therefore include NPs (Zereini et al., 2001).

3.3.3 ENGINEERED INORGANIC NPs

Engineered inorganic NPs cover a broad range of substances, including elemental metals, metal oxides, and metal salts (Aitken et al., 2006). Elemental silver is used in many products as bactericide (Morones et al., 2005), whereas elemental gold is explored for many possible applications due to its catalytic activity (Brust and Liely, 2002). Nano-Ag is one of the most promising NPs for future applications due to its antimicrobial, antifungal, and partially antiviral properties, and is mainly used in textiles and antimicrobial polymers (Blaser et al., 2008). A photograph of a nano-Ag suspension is shown in Figure 3.3. The use of nanoscale zero-valent iron (nZVI) for ground-water remediation ranks as the most widely investigated environmental nanotechnological application (Nowack, 2008) and is discussed in detail in Section 3.4. A photograph of nZVI is shown in Figure 3.3.

Nanoparticulate metal oxides are among the most used NPs (Aitken et al., 2006). Bulk materials of TiO_2 , SiO_2 , and aluminum and iron oxides have been produced for many years. However, recently they have also been manufactured in nanosized form and have already entered the consumer market. Photographs of nano-ZnO and nano- TiO_2 are shown in Figure 3.3. A recent study from Switzerland showed that in industry the most widely used metal NPs are $\text{TiO}_2 > \text{Fe oxides} > \text{SiO}_2 > \text{ZnO} \gg \text{Ag}$ (Schmid and Riediker, 2008). The distribution of NP in consumer products is $\text{Ag} \gg \text{Zn} = \text{SiO}_2 = \text{Ti} > \text{Au}$ (Project on emerging nanotechnologies, 2008). One of the most widely used NP in consumer products is TiO_2 , used for applications such as photocatalysis, pigments, and cosmetic additives (Aitken et al., 2006). The useful properties of nano- TiO_2 are its self-cleaning, antifouling, and antimicrobial activity, and its strong UV absorption. In Australia alone, there are more than 300 registered sunscreen products containing nanoscaled titanium dioxide (Australian Government, 2006). Another metal oxide NP that is used in consumer products is ZnO in sunscreens (Rittner, 2002).

TiO_2 has also been extensively studied for oxidative or reductive removal of organic pollutants (Hoffmann et al., 1995; Obare and Meyer, 2004). Illumination promotes an electron to the conduction band, leaving a hole in the valence band. This process produces a potent reducing and oxidizing agent. In water, photooxidation occurs primarily through hydroxyl radicals. Because TiO_2 requires UV light for excitation, it has been sensitized to visible light by dyes, through incorporation of transition metal ions (Obare and Meyer, 2004) or by doping with nitrogen (Liu et al., 2006). The degradation rate of several dyes by nanosized TiO_2 was found to be 1.6–20 times higher than for bulk TiO_2 particles (Nagaveni et al., 2004a). Several types of compounds such as dyes (Comparelli et al., 2004; Liu et al., 2006) and organic acids (Nagaveni et al., 2004b) have been shown to be rapidly

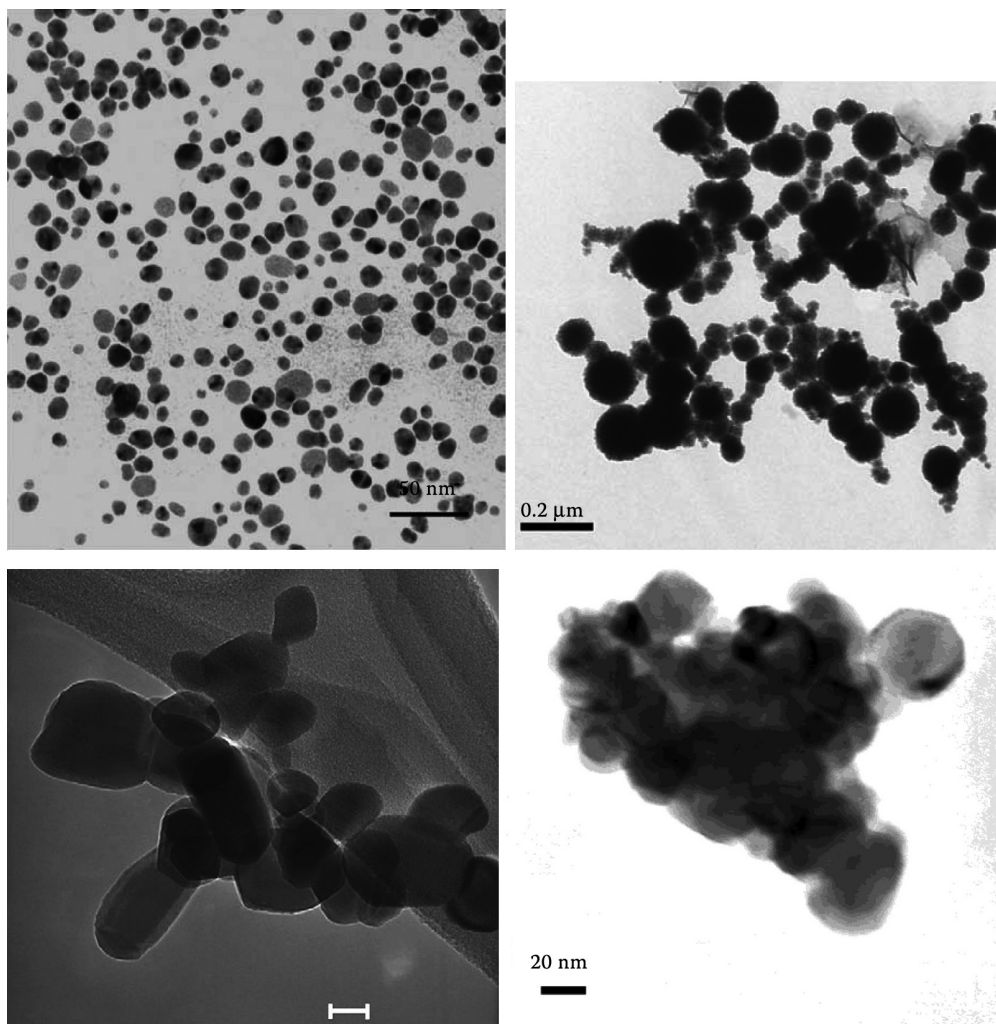


FIGURE 3.3 Examples of engineered metal and metal-oxide nanoparticles: Top left: Nano Ag (from Sondi, I. and Salopek-Sondi, B., *J. Colloid Interface Sci.*, 275, 177–182, 2004.) Top right: Nano zero-valent iron (from Sun, Y.P. et al., *Adv. Coll. Interface Sci.*, 120, 47–56, 2006.) Bottom left: Nano ZnO (from Zhang, Y. et al., *Water Res.*, 42, 2204–2212, 2008a.) All reproduced with permission from Elsevier. Bottom right: Nano-TiO₂. (Reprinted with permission from Lecoanet, H.F. and Wiesner, M.R., *Environ. Sci. Technol.*, 38, 4377–4382, 2004. Copyright American Chemical Society.)

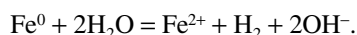
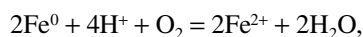
degraded. A special type of TiO₂-photocatalyst is comprised of titania nanotube materials, which were shown to have superior activity (Chen et al., 2005; Zhang et al., 2006).

Magnetic NPs offer advantages over nonmagnetic particles because they can easily be separated from water by a magnetic field. Separation using magnetic gradients, the so-called high gradient magnetic separation (HGMS), is a process widely used in medicine and ore processing (Ngomsik et al., 2005). This technique allows one to design processes where the particles not only remove compounds from water, but where they can easily be removed and then be recycled or regenerated.

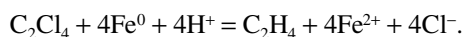
Quantum dots (QDs) made from semiconductor materials such as CdSe, CdTe, or ZnS have attracted wide interest in areas such as information technology, molecular biology, and medicine due to their exceptional photophysical properties (Gao et al., 2004; Jamieson et al., 2007). They are especially promising for medical applications (Azzazy et al., 2007).

3.4 nZVI FOR GROUNDWATER REMEDIATION

The use of nZVI is one of the most studied applications of a metallic NP in the environment (Nowack, 2008). Nanoscale metallic iron is very effective in destroying a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, and dyes (Zhang, 2003). The basis for the reactivity of ZVI is its corrosion in the environment:



Contaminants such as tetrachloroethane can readily accept the electrons from iron oxidation and be reduced to ethene:



However, nZVI can reduce not only organic contaminants but also nitrate, which is reduced to ammonia (Liou et al., 2006; Sohn et al., 2006), perchlorate (plus chlorate or chlorite), which is reduced to chloride (Cao et al., 2005), selenate (Mondal et al., 2004), arsenate (Jegadeesan et al., 2005; Kanel et al., 2006), arsenite (Kanel et al., 2005), and chromate (Ponder et al., 2000; Manning et al., 2007). ZVI is also efficient in removing dissolved metals from solution, for example, Pb and Ni (Ponder et al., 2000; Li and Zhang, 2006).

The reaction rates for nZVI can be several orders of magnitude faster on a mass basis than for granular ZVI (Tratnyek and Johnson, 2006). The reaction rates for nZVI are at least 25–30 times faster and also the sorption capacity is much higher compared with granular iron (Li et al., 2006). The metals are either reduced to zero-valent metals or lower oxidation states, for example Cr(III), or are surface complexed with the iron oxides that are formed during the reaction. Some metals can increase the dechlorination rate of organics and also lead to more benign products, whereas other metals decrease the reactivity (Lien et al., 2007).

Because the reactivity of ZVI toward lightly chlorinated and brominated compounds is low and because the formation of a passivating layer reduces the reactivity with time, many approaches are explored where the surface is doped with a catalyst (e.g., Pd, Pt, Cu, and Ni) to reduce the activation energy. The same approach has also been tested for nZVI. Surface-normalized reaction rates for such materials were found to be up to 100 times faster than for bulk ZVI (Zhang et al., 1998; Schrick et al., 2002; Lien and Zhang, 2005; Lim et al., 2007).

The nanoscale iron particles can be produced either by a bottom-down approach (e.g., milling of iron filings) or by direct chemical synthesis (Li et al., 2006). A common method for the synthesis of iron NPs is the reduction of aqueous ferric solution by reducing agents such as sodium borohydrite or sodium hypophosphite (Obare and Meyer, 2004).

The use of nZVI for groundwater remediation represents the most investigated environmental nanotechnological technique. Granular ZVI in the form of reactive barriers has been used for many years at numerous sites all over the world for the remediation of organic and inorganic contaminants in groundwater (see Figure 3.4a). With nZVI, two possible techniques are used: immobile nZVI is injected to form a zone of iron particles adsorbed to the aquifer solids (Figure 3.4b), or mobile nZVI is injected to form a plume of reactive Fe particles that destroy any organic contaminants that dissolve from a dense nonaqueous-phase liquid (DNAPL) source in the aquifer (Figure 3.4c). With this technique the formation of a pollutant plume is inhibited. Successful results of field demonstrations using nZVI have been published, with reported reductions in TCE of up to 96% after injection of 1.7 kg of NPs into the groundwater (Elliott and Zhang, 2001). A larger test was conducted where 400 kg of nZVI was injected and a significant reduction in TCE soil concentration (>80%) and

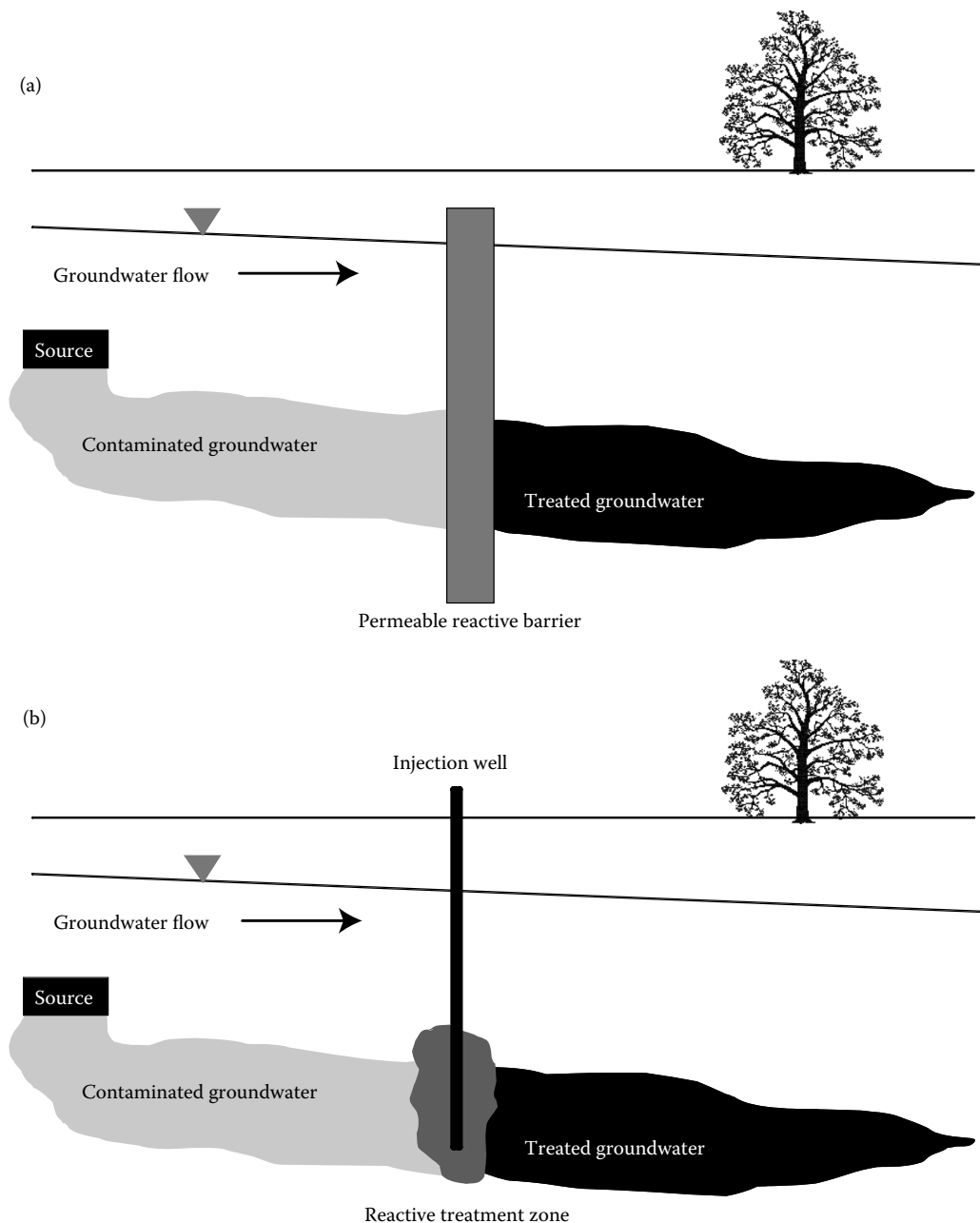


FIGURE 3.4 Three approaches to the application of ZVI for groundwater remediation. (a) conventional reactive barrier using granular ZVI; (b) injection of nZVI to form an immobile reaction zone and (c) injection of mobile nZVI. (Modified from Nowack, B. In: Krug, H.F. (Ed.), *Nanotechnology*, Vol. 2 "Environmental aspects," pp. 1–15. Springer, 2008.)

dissolved concentrations (57–100%) was observed (Quinn et al., 2005). To date, approximately 30 projects are under way where nZVI is used for actual site remediation (Li et al., 2006).

Whereas most research using ZVI has been devoted to groundwater, much less has been published about soil remediation. These studies have mostly been carried out in soil slurries and efficient

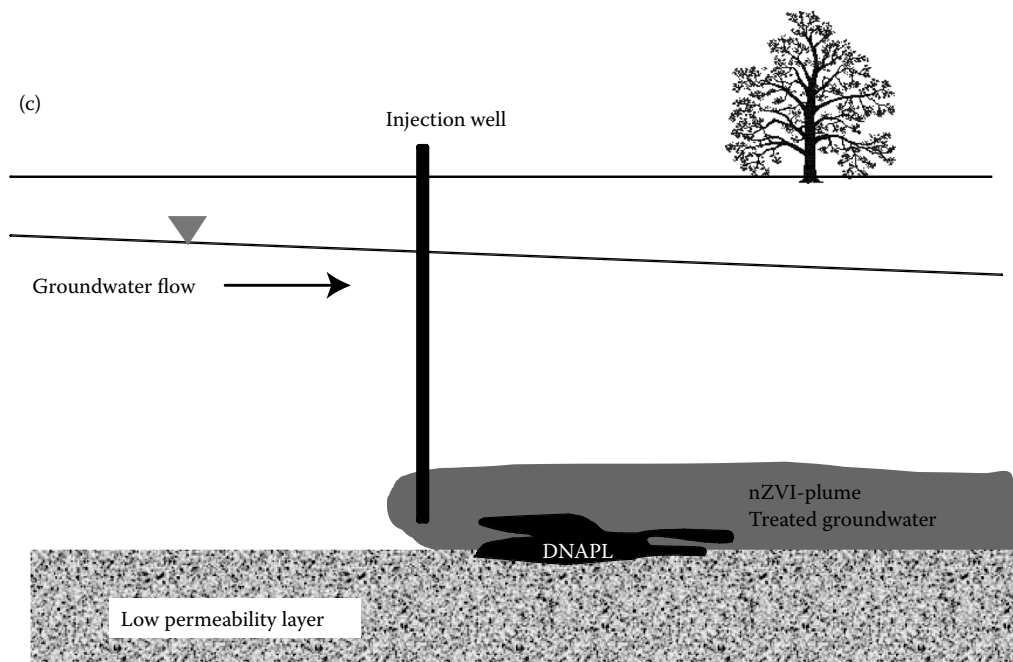


FIGURE 3.4 Continued.

removal of PAH by nZVI has been reported (Chang et al., 2005, 2007a). For PCB only a removal of about 40% was attained, caused by the very strong adsorption of PCB to the soil matrix and limited transfer to the ZVI particles (Varanasi et al., 2007). nZVI was also used to immobilize Cr(VI) in chromium ore processing residue (Cao and Zhang, 2006).

Because iron particles have a strong tendency to aggregate and adsorb to the surfaces of minerals, a great deal of effort has been directed toward methods that disperse the particles in water and render them mobile. In one approach water-soluble starch was used as a stabilizer (He and Zhao, 2005), whereas in another hydrophilic carbon or polyacrylic acid delivery vehicles were used (Schrack et al., 2004). Modified cellulose, sodium carboxymethyl cellulose (CMC), was found to form highly dispersed nZVI (He et al., 2007); also, several polymers have been tested and found to be very effective (Saleh et al., 2007). In this stabilized form the nZVI was up to 17 times more reactive in degrading trichloroethene than nonstabilized material. However, for other stabilizing agents a decrease in reactivity by a factor of 9 (Saleh et al., 2007) or 2–10 was observed (Saleh et al., 2007). To deliver the nZVI to the oil–water interface in the case of DNAPL contamination, a copolymer was used to increase colloid stability and at the same time increase phase transfer into the organic phase (Saleh et al., 2005).

3.5 RELEASE OF INORGANIC NPs INTO THE ENVIRONMENT

Whereas the magnitude and source of NPs are known for intentional release into the environment, for example, during a groundwater remediation, this is not the case for inadvertent release. Inadvertent release of NPs can occur throughout the whole life cycle (Koehler et al., 2008). The life cycle of a nanoparticle and its possible release into the environment are shown in Figure 3.5. Critical points are as follows: (i) during production and shipping of the NPs where release into air is most likely, (ii) during production of final product, (iii) during use, and (iv) finally during disposal or recycling. The amount of NPs released by the different processes depends on several factors: NP stock in the article, the article's lifetime, the way in which NPs are incorporated into the material, and the actual

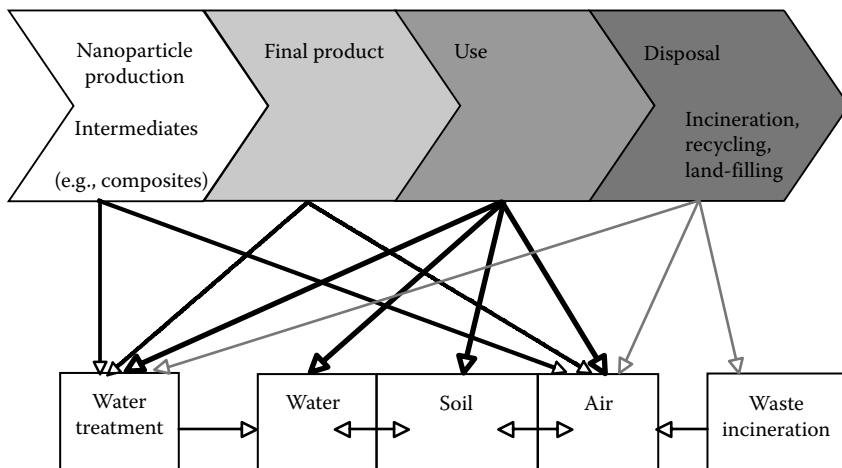


FIGURE 3.5 The life cycle of nanoproducts and the possible release of nanoparticles into technical systems and the environment. (From O'Loughlin E.J. et al., *Environ. Sci. Tech.*, 37, 721–727, 2003. With permission.)

use/usage of the article (Koehler et al., 2008). Products with a long lifetime, a loose incorporation of the NPs, and/or an intense use (e.g., through frequent cleaning) will most likely not contain NPs anymore at the time of disposal. On the other hand, factors such as a short lifetime, a low rate of usage, and a strong fixation of NPs increase the likelihood that particles will not be released until disposal (Türk et al., 2005).

Experimental data about the release of NPs during use or disposal are very scarce. The release of nano-TiO₂ from coatings on wood, polymer, and tile was the highest from coated tile, and UV light increased the release of particles (Hsu and Chein, 2007). Silver is also released in ionic form from NPs, and this was considered to be the major process of Ag release from plastics and textiles (Blaser et al., 2008).

Release of NPs into the environment can also occur at the end-of-life of nanoproducts when they are dumped in landfills or burned in waste incineration plants (WIPs). Although the particle filters of WIPs are very effective, low concentrations of NPs can leave the stack and can be distributed by air. However, the largest input of NPs into the environment is most probably from consumer products that end up in wastewater, for example, sunscreens. All NPs contained in sunscreen will be present in water, either directly washed off the skin into open waters or removed during showering or washing of textiles. This pathway is very important for nano-TiO₂ and also for nano-Ag (Mueller and Nowack, 2008).

3.6 BEHAVIOR OF INORGANIC NPs IN THE ENVIRONMENT

3.6.1 BEHAVIOR DURING WATER AND WASTE TREATMENT

As shown in Figure 3.5, the pathway of NPs from the product to the environment often leads through the sewage treatment plant (STP) or the WIP. These facilities act as filters between the product and the environment and, depending on their ability to remove NPs, can stop or at least diminish the disposal of NPs into the environment.

Most WIPs are equipped with different types of filters, but most have a multistage flue gas cleaning system consisting of electrofilters, a flue gas scrubber, a catalytic NO_x/furan/dioxin removal, and possibly a fabric filter. The concentration of particles smaller than 100 nm is lowered by such filters by around 99.9% and in the subsequent wet filter by another 95% (Burtscher et al., 2002). There is no information available about the behavior of engineered NPs during waste incineration. It is

unknown what NP fraction stays in the slag and what percentage becomes airborne. However, we can assume that even if NPs become airborne during combustion, they are efficiently removed in the filters (Mueller and Nowack, 2008).

Not much is known about the fate of NPs in wastewater treatment plants. Some information about the removal of silica NPs originating from chemical–mechanical polishing from the semiconductor industry is available (Huang et al., 2004; Chang et al., 2006; Chin et al., 2006; Den and Huang, 2006). It was shown that biological treatment was almost entirely ineffective in removing the NPs (Chang et al., 2007b). Even addition of Al-coagulant only removed about 9% of nanoparticulate silica. For QDs it was found that adding Al-coagulant removed up to 90% of the NPs by sedimentation (Zhang et al., 2008b). For a variety of metal oxide NPs (TiO_2 , Fe_2O_3 , ZnO, NiO, and silica), it was found that they were removed by 20–60% after alum addition and sedimentation (Zhang et al., 2008a). Silica was the NPs with the lowest removal from water.

The ability to immobilize particles by the processes in an STP will depend on the characteristics of the particles and the residence time in the STP. Particles $<0.1\ \mu\text{m}$ are effectively removed (97%) in packed-bed filters (Omelia, 1980). The average removal efficiency for suspended particles during treatment is 97–99% (ARA Bern, 2006; ARA Luzern, 2006). The behavior of CeO_2 NPs in a model wastewater treatment plant was determined by agglomeration and more than 95% of the particles were removed from the water (Limbach et al., 2008).

Not all wastewater is treated and even if connection to a treatment plant is 100%, there is still some wastewater discharged without any treatment during high water flow. Overflow discharge during heavy rain strongly varies between STPs, and values between 2% and 10% of the total inflow were reported (EAWAG, 1979). It can be assumed that particle concentration in the overflow discharge is equal to the concentration in the inflow, and thus significant inputs of NPs with wastewater into streams are possible even if the removal during treatment is good.

3.6.2 BEHAVIOR IN WATER

In the environment, natural colloids or NPs interact among themselves and with other natural NPs or larger particles. The formation of aggregates in natural systems can be understood by considering physical processes, that is, Brownian diffusion, fluid motion, and gravity. Aggregation is particle-size-dependent and results in efficient removal of small particles in environmental systems (Omelia, 1980). To quantify the stability of NPs in the environment, we have to predict the stability of their suspension and their tendency to aggregate or interact with other particles (Mackay et al., 2006). For example, 20-nm-sized nZVI particles aggregated within 10 min to micrometer-sized clusters (Phenrat et al., 2007). The nature of NPs is modified by adsorption processes (Fukushi and Sato, 2005) and especially surface charge plays a dominant role (Kallay and Zalac, 2001, 2002). Complexation processes between NPs and polyelectrolytes are an essential aspect to describe stabilization/destabilization and have been modeled in detail (Ulrich et al., 2004, 2005, 2006; Seijo et al., 2006).

Very often, oxide NPs received from the manufacturer cannot be dispersed again into single NPs but stay as aggregates, even under very harsh conditions of extended ultrasound (Zhang et al., 2008a). These aggregates with a size of a few hundred micrometers have a different behavior from true nanoparticulate suspensions.

Even if NPs are used as a single NP in a product, they are not necessarily released as single NP. In many applications, NPs are embedded in a matrix and release of NPs will occur through release of matrix-bound NPs (Koehler et al., 2008). As many NPs are functionalized, release of functionalized NPs is also possible. In the environment, released NPs are affected by environmental factors such as light, oxidants, or microorganisms. This can result in chemical or biological modification or degradation of the surface functionalization or the embedding matrix and may result in free NPs. The surface of pristine NPs can also be modified by environmental factors (e.g., coating by organic matter) or functionalized by chemical or biological processes. Nanoparticulate ZnO, which was

coated with the surfactant sodium dodecyl sulfate, was stable in soil suspension for 14 days without changes in particle size distribution (Gimbert et al., 2007).

QDs comprise another group of NPs that is in most cases capped with organic ligands. The capping ligands are the key factor in determining their fate in water (Zhang et al., 2008b). Whereas the coated QDs are stable in simple ionic medium, di- and trivalent metals such as Ca and Al induce aggregation and sedimentation. The metals react with the capping ligands by neutralizing their charge or forming complexes that bridge between the QDs.

3.6.3 BEHAVIOR IN POROUS MEDIA

The transport of colloids in porous media and the colloid-facilitated transport of contaminants have received much attention in the past (McGeachan and Lewis, 2002; Sen and Khilar, 2006). The movement of colloids in porous media—and therefore also of NPs that are in the same size range—is impeded by two processes: straining or physical filtration where the particle is larger than the pore and is trapped, and true filtration where the particle is removed from solution by interception, diffusion, and sedimentation. However, particles removed from solution by such processes can readily become resuspended upon changes in the chemical or physical conditions (e.g., changes in pH, ionic strength, and flow rate) (Grolimund et al., 1998; Sen and Khilar, 2006).

Several studies have investigated the transport of a wide range of engineered NPs through porous media (Lecoanet et al., 2004; Lecoanet and Wiesner, 2004; Dunphy Guzman et al., 2006). Particles smaller than 100 nm are predicted to have very high efficiencies of transport to collector surfaces due to Brownian diffusion. If all particle–collector contacts were to result in particle attachment to the collector, these small particles would be retained to a large extent by the porous medium. However, nanosized silica particles were not appreciably removed and also anatase NPs were only removed between 55% and 70%, depending on the flow velocity (Lecoanet and Wiesner, 2004). Figure 3.6 shows the breakthrough curves of several oxides of NPs in a porous medium made of glass beads. The effects of particle size and type of particle are clearly visible. The most efficient removal was observed for an iron oxide NP (Lecoanet et al., 2004). These studies show that the collector efficiency for NPs can be very different and that especially the surface-modified NPs

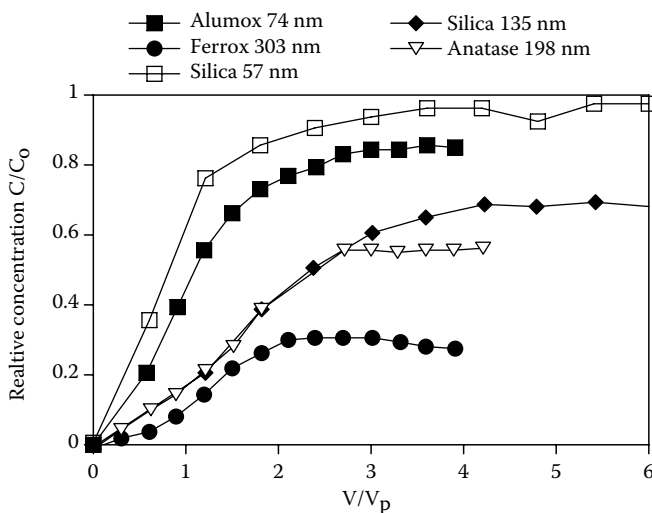


FIGURE 3.6 Breakthrough curves for metal oxide nanoparticles in a column filled with spherical glass beads. (Adapted from Lecoanet, H.F. et al., *Environ. Sci. Technol.* 38, 5164–5169, 2004.)

displayed high mobilities. Also, the environmental conditions are important and efficient removal of titania NPs was observed close to the pH at the point of zero charge (Dunphy Guzman et al., 2006). pH also played a dominant role in the transport of metallic Al NPs with much greater transport at pH 4 than at pH 7 (Doshi et al., 2008).

Because the nZVI particles used for groundwater remediation have a very strong tendency to aggregate and adsorb to surfaces of minerals, a great deal of effort has been directed toward methods to disperse the particles in water and render them mobile. In one approach, water-soluble starch was used as stabilizer (He and Zhao, 2005); in another, hydrophilic carbon or polyacrylic acid delivery vehicles were used (Schrack et al., 2004). Modified cellulose, sodium CMC, was found to form highly dispersed nZVI (He et al., 2007); several polymers have been tested and found to be very effective (Saleh et al., 2007). These modified NPs were found to be mobile under natural conditions, indicating the importance of knowing the exact surface properties of NPs for prediction of their potential mobility in the environment.

3.6.4 METAL OXIDE NPs AS ADSORBENTS

Owing to their high surface area, metal oxide NPs have a high sorption capacity for metal ions and anions such as arsenic, chromium, and lead (Waychunas et al., 2005). Contaminant sequestration is accomplished mainly by surface complexation, but aggregation of particles may encapsulate sorbed surface species. This strong interaction of metal ions and oxide NPs is very important for the behavior and cycling of metals in the environment (Hochella and Madden, 2005), but also engineered NPs have the same properties. An example is anatase (TiO_2) NP, coated with a Cu–ethylenediamine–ligand complex, that can be used to immobilize anions such as pertechnetate from groundwater (Mattigod et al., 2005). From the group of iron oxides, magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and jacobsonite (MnFe_2O_4) NPs have been proposed for Cr(VI) removal from wastewater (Hu et al., 2005a,b, 2006). These properties of engineered NPs always need to be considered when discussing their environmental significance and behavior. This will be done in [Section 3.8.3](#).

3.7 OCCURRENCE OF INORGANIC NPs IN THE ENVIRONMENT

3.7.1 MEASUREMENTS

To date, no quantitative measurements of engineered NPs in the environment have become available. This lack of studies is due to the absence of analytical methods able to quantify trace concentrations of NPs under environmental conditions. To date, most studies looking at natural NPs have used microscopic methods (Mavrocordatos et al., 2004), field-flow fractionation (FFF) (Baalousha and Lead, 2007a,b), or laser-induced breakdown spectroscopy (Wagner et al., 2003, 2004). A recent study shows the identification of natural nanosized TiO_2 particles in river water affected by mining wastes (Wigginton et al., 2007; [Figure 3.7](#)). Under laboratory conditions FFF was used to monitor the stability of nano-ZnO in soil suspension (Gimbert et al., 2007). The first report of an engineered NP was presented by Kaegi et al. (2008), who found engineered nano- TiO_2 in surface water and traced the origin of the particles to leaching from facades that had been treated with nano- TiO_2 -containing paint.

3.7.2 EXPOSURE MODELING

Because analytical measurements of engineered NPs in the environment are missing, the expected concentrations of NPs in the environment have to be modeled with the help of extrapolations and analogies. The value derived from such modeling is the predicted environmental concentration (PEC). A recent study modeled Ag emissions from nano-Ag-containing biocidal products and compared the expected concentrations in the environment with a reference emission (Blaser et al., 2008).

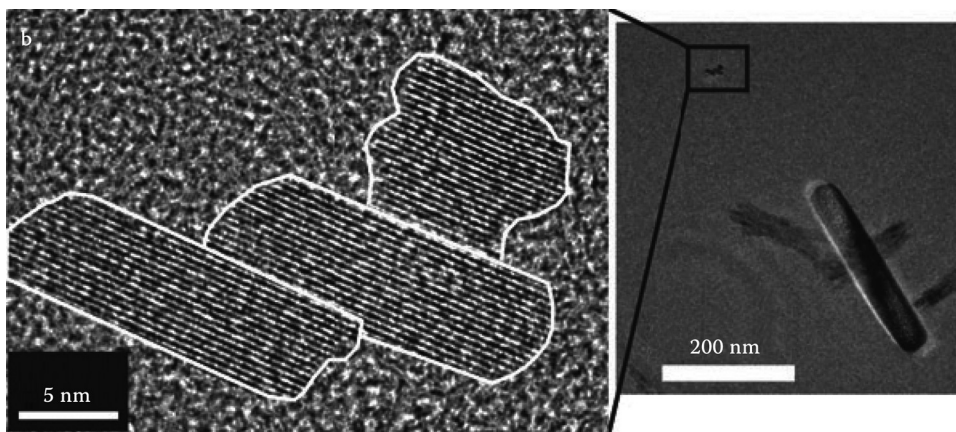


FIGURE 3.7 HR-TEM picture of crystalline TiO_2 nanoparticles from the Clark Fork River, Montana, U.S. (Adapted from Wigginton, N.S. et al., *J. Environ. Monit.* 9, 1306–1316, 2007.)

In this study, nano-Ag was assumed to be only an Ag^+ source and no particulate Ag emissions were considered; therefore, no concentrations of nano-Ag in the environment were modeled.

Another study used a life-cycle perspective to model the quantities of engineered NPs released into the environment (Mueller and Nowack, 2008). Inorganic NP nano-Ag and nano- TiO_2 were studied. The quantification was based on a substance flow analysis from products to air, soil, and water in Switzerland. The following parameters were used as model inputs: estimated worldwide production volume, allocation of the production volume to product categories, particle release from products, and flow coefficients within the environmental compartments. The PECs were then compared with the predicted no effect concentrations (PNEC) derived from the literature to estimate a possible risk. Table 3.2 shows that the expected concentrations of the three NPs in the different environmental compartments vary widely, caused by the different life cycles of the NP-containing products. The modeling suggests that currently nano-Ag poses little or no risk to soil organisms. The RQ (PNEC/PEC) water is less than one thousandth. Also in the high emission scenario, the modeling suggests that currently little or no risk is to be expected from nano-Ag in the soil compartment and the water in general. The PEC values for nano- TiO_2 in water are 0.7–16 $\mu\text{g/L}$. The modeling suggests that nano- TiO_2 may pose a risk to water organisms with an RQ between >0.73 and >16 . By contrast, the RQ air is smaller than one thousandth. The results of this study make it possible for

TABLE 3.2
PEC of Nano-Ag and Nano- TiO_2 in Air, Water, and Soil

	Unit	Nano-Ag		Nano- TiO_2	
		RE	HE	RE	HE
Air	$\mu\text{g/m}^3$	1.7×10^{-3}	4.4×10^{-3}	1.5×10^{-2}	4.2×10^{-2}
Water	$\mu\text{g/L}$	0.03	0.08	0.7	16
Soil	$\mu\text{g/kg}$	0.02	0.1	0.4	4.8

Source: Data from Mueller, N. C. and Nowack, B., *Environ. Sci. Technol.*, 42, 4447–4453, 2008.

Notes: HE, high emission scenario; RE, realistic scenario.

the first time to carry out a quantitative risk assessment of NPs in the environment and suggest further detailed studies of nano-TiO₂.

A similar study has been carried out for the United Kingdom (Boxall et al., 2007), although with a different approach. Based on assumed market penetrations of nanoproducts and the known usage of these products, concentrations in water, air, and soil were modeled. For the 10% market penetration model, which probably overestimates current exposure levels, concentrations of silver, aluminum, and fullerene were predicted to be in the ng/L range, whereas nano-TiO₂, ZnO, and hydroxyapatite are predicted to be in the µg/L range.

3.8 EFFECTS OF INORGANIC NPs ON ORGANISMS

3.8.1 TOXICOLOGY

The safety of NPs has been discussed extensively because they have properties that are clearly associated with pathogenicity (Donaldson et al., 2006). NPs may enter the body through the lungs, skin, or gut, depending on the type of exposure. Several recent papers have highlighted this area of toxicology, the gaps in research, and possible testing strategies for NPs (Oberdörster et al., 2005; Kreyling et al., 2006; Lewinski et al., 2008).

A consistent body of evidence shows that nanosized particles are taken up by a wide variety of mammalian cell types, are able to cross the cell membrane, and become internalized (Lynch et al., 2006; Rothen-Rutishauser et al., 2006; Smart et al., 2006). The uptake on NPs is size-dependent (Limbach et al., 2005; Chithrani et al., 2006). Aggregation and size-dependent sedimentation onto the cells or diffusion toward the cell were the main parameters determining uptake (Limbach et al., 2005). Uptake occurs via endocytosis or by phagocytosis in specialized cells. One hypothesis is that the coating of the NPs by protein in the growth medium results in conformational changes of the protein structure, which triggers uptake into the cell by specialized structures, limiting uptake to NPs below about 120 nm (Lynch et al., 2006). In general, cells can survive low concentrations of NPs (<10 mg/L); however, at high doses, cytotoxic effects emerge in a dose- and time-dependent manner for many NPs (Lewinski et al., 2008). While the causes for the increase in cell death observed at higher concentrations and longer exposure times are material specific, the generation of reactive oxygen species and the influence of cell internalization of NPs are two common findings throughout.

Within the cells, NPs are stored at certain locations (e.g., inside vesicles and mitochondria) and are able to exert a toxic response. The small particle size, a large surface area, and the ability to generate reactive oxygen species play a major role in the toxicity of NPs (Nel et al., 2006). Inflammation and fibrosis are effects observed on an organism level, whereas oxidative stress, antioxidant activity, and cytotoxicity are effects observed on a cellular level (Oberdörster et al., 2005).

3.8.2 ECOTOXICOLOGY

Most toxicology studies have been carried out with mammalian cells, and the NPs were exposed to a cell culture medium containing a mixture of proteins and other biological compounds. Results from such *in vitro* studies can therefore not be directly transferred to environmental conditions where the uptake of NPs into the aquatic biota is a major concern. However, the knowledge base on the ecotoxicology of NPs is expanding rapidly (Moore, 2006; Baun et al., 2008a; Navarro et al., 2008).

Potential uptake routes into organisms include direct ingestion, inhalation, or entry across epithelial boundaries such as gills or body wall. At the cellular level, prokaryotes such as bacteria may be largely protected against the uptake of many types of NPs since they do not have mechanisms for transport of colloidal particles across the cell wall (Moore, 2006). However, for eukaryotes, for example protists and metazoans, the situation is different since they have processes for the cellular internalization of nanoscale or microscale particles, namely endocytosis and phagocytosis (Moore, 2006).

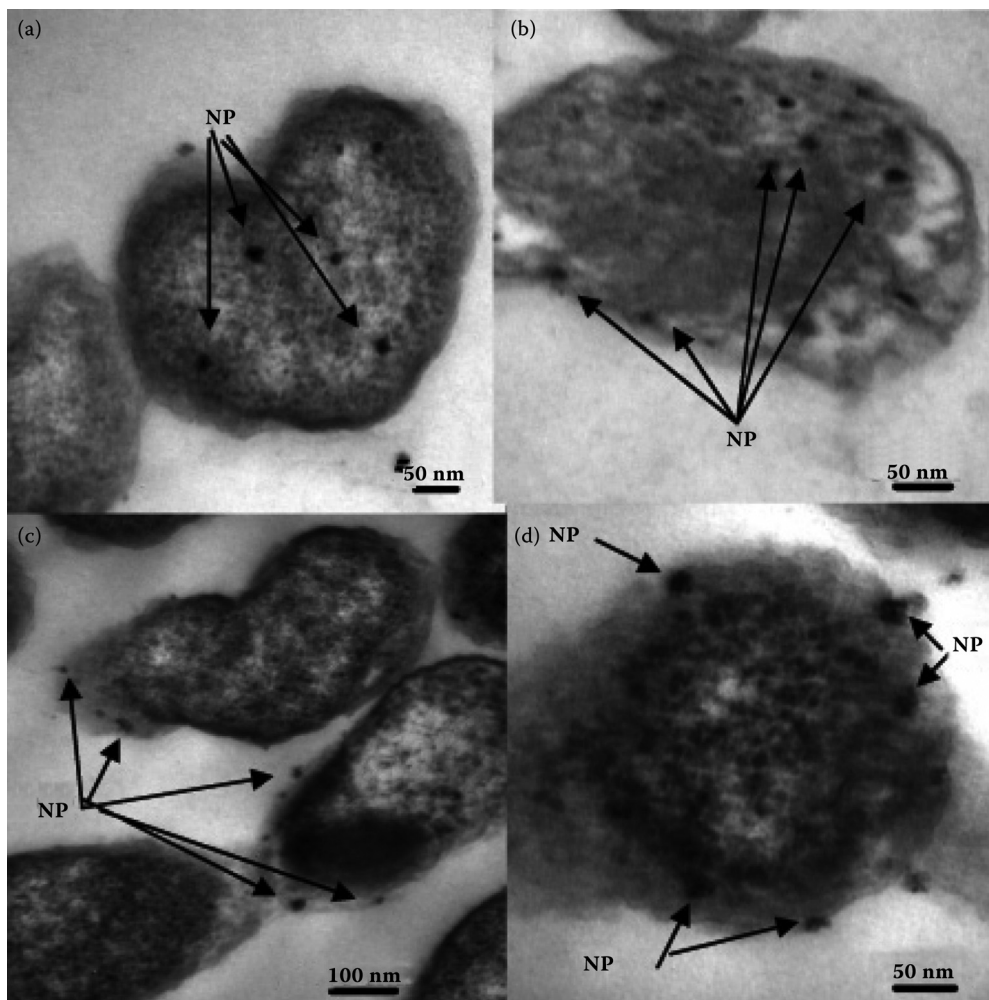


FIGURE 3.8 Incorporation of ZnO nanoparticles into *E. coli* bacteria. (Adapted from Brayner, R. et al., *Nano Lett.*, 6, 866–870, 2006.)

The uptake of different NPs has indeed been observed. Nanosized ZnO, for example, was internalized by bacteria (Brayner et al., 2006; see Figure 3.8). Also nanosized CeO₂ particles were adsorbed onto the cell wall of *Escherichia coli*, but the microscopic methods were not sensitive enough to discern whether internalization had taken place (Thill et al., 2006). Inorganic nanoparticulate TiO₂, SiO₂, and ZnO had a toxic effect on bacteria, and the presence of light was a significant factor increasing the toxicity (Adams et al., 2006). Whereas bulk TiO₂ is considered to have no health effects on aquatic organisms, this is clearly the case for nanosized TiO₂ (Lovern and Klaper, 2006). NPs that damage bacterial cell walls have been found to be internalized, whereas those without this activity were not taken up (Stoimenov et al., 2002). The LC₅₀ for *Daphnia magna* and nano-TiO₂ was reported to be 5.5 mg/L with complete mortality at 10 mg/L (Lovern and Klaper, 2006). There are also many studies that did not find any toxic effects of nano-TiO₂; for example, even at 20 g/L it was not toxic to the bacterium *Vibrio fischeri* and to the crustacean *D. magna* (Heinlaan et al., 2008). Also, studies with zebrafish did not find any toxic effect of both nano-TiO₂ and bulk-TiO₂ at 500 mg/L concentration (Zhu et al., 2008). Nano-TiO₂ did not have any behavioral effects on *D. magna* at concentrations of 2 mg/L (Lovern et al., 2007). Nano-TiO₂ can affect numerous body systems in rainbow

trout, for example, respiratory toxicity and disturbances to the metabolisms of some trace elements (Frederici et al., 2007). Because TiO_2 has a photocatalytic activity, the effect of light on toxicity has to be investigated (Hund-Rinke and Simon, 2006). A difference in toxicity to algae and daphnids was reported of illuminated and nonilluminated products.

With respect to plants, the effect of different NPs (aluminum, aluminum oxide, zinc, and zinc oxide) on seed germination and root growth was investigated (Lin and Xing, 2007). Seed germination was only affected by nano-zinc and nano-ZnO at concentrations of 2000 mg/L. The 50% root inhibition concentrations were about 50 mg/L for nano-Zn and nano-ZnO. Because filtered supernatants of the solution did not have the same effect, it was concluded that the toxicity was not due to dissolution and formation of Zn^{2+} , but due to the NP itself. Several articles by the group of Hong et al. (Hong et al., 2005a,b; Zheng et al., 2005; Gao et al., 2006; Yang et al., 2006) have shown that nanosized TiO_2 can have a positive effect on the growth of spinach when administered to the seeds or sprayed onto the leaves. Nano- TiO_2 was shown to increase the activity of several enzymes and to promote the adsorption of nitrate and accelerate the transformation of inorganic into organic nitrogen. Normal-sized TiO_2 did not have these effects. Magnetic iron NPs dispersed in liquid carriers added to nutrient solution stimulated plant growth at low concentrations and inhibited plant growth at higher concentrations (Racuciu and Creanga, 2007); it also induced chromosomal aberrations (Pavel et al., 1999). No information on their uptake is available, although it was suggested that the particles penetrated cell membranes.

Quite a lot of information is available on nanosized silver particles due to their use as bactericides. The cells of bacteria are damaged in the presence of nano-Ag, finally resulting in death of the organisms (Sondi and Salopek-Sondi, 2004). Interaction with the cells is size-dependent (Morones et al., 2005) and seems to also depend on the shape of the particles (Pal et al., 2007). Nano-Ag appears to be significantly more toxic than Ag^+ ions toward *E. coli* (Lok et al., 2006).

The toxicity of NPs is not always related to some “nano-identity,” but may also be due to dissolution of the particles. This has been shown for nano-ZnO, which had comparable toxicity to bulk ZnO and dissolved Zn (Franklin et al., 2007). The toxicity was attributed to the dissolution of NPs and toxicity by dissolved Zn^{2+} (Heinlaan et al., 2008). Furthermore, for nano-CuO the toxicity could be largely attributed to free Cu^{2+} (Heinlaan et al., 2008). However, another study with metallic Cu NPs and zebrafish showed that only a small part of the toxic effect could be attributed to toxicity of Cu^{2+} (Griffitt et al., 2007). A slight reduction in the root elongation of plants was found in the presence of uncoated alumina NPs, but not with NPs coated with phenanthrene (Yang and Watts, 2005). It was proposed that the surface characteristics of alumina played an important role in phytotoxicity and that adsorption of phenanthrene shielded the toxic alumina surface from the plant roots. However, the study is problematic as pointed out by Murashov (2006) because the authors did not take into account the fact that soluble Al^{3+} is a potent root toxicant and is known to inhibit root growth. The solubility of aluminum oxide is known to increase with decreasing particle size, and modification of the surface by adsorbed compounds is known to affect the dissolution rate.

These sometimes conflicting data show that the type of organisms and the characteristics of the NPs itself are dominant factors in determining the toxicity of NPs toward organisms.

3.8.3 “TROJAN HORSE” EFFECT

The interaction of NPs with toxic, organic compounds can both amplify and alleviate the toxicity of compounds. In the case of particle-mediated transport of toxicants into the cell and a greater toxic effect than without NPs, this effect is called the “Trojan horse” effect. Because NPs can be taken up by cells, they can transport toxicants that are otherwise not bioavailable into the cell. This effect is investigated extensively in medicine; see for example Tsapis et al. (2002).

In contrast to harmful effects, NPs can also have an advantageous influence on toxicants in the environment. NPs can reduce the free toxicant concentration by adsorption onto their surfaces, and hence reducing the toxicity of the pollutant. If NPs with the adsorbed pollutants are taken up by the cells, then a toxic effect may be the consequence, caused by the NPs, the pollutant, or in a

synergistic way by both. However, it could also be that no effect is observed if the bound pollutant is not bioavailable and the NPs itself is not toxic.

Some experimental information is available about the influence of organic NPs on toxicant uptake (Knauer et al., 2007; Baun et al., 2008b; Ferguson et al., 2008; Petersen et al., 2008a,b), but only very little about inorganic NPs. One study looking at an inorganic NP showed that carp exposed to As(V)-contaminated water in the presence of nanosized TiO₂ accumulated considerably more As than without NPs (Sun et al., 2007). Nanocomposites of SiO₂/TiO₂ were loaded with mercury and exposed to sedimentary microorganisms (Gao et al., 2008). The work showed that the sorbed Hg could become bioavailable when introduced into natural systems.

3.9 CONCLUSIONS

Whereas it is often stated that we have a very limited knowledge about the behavior and effects of NPs in the environment (Owen and Handy, 2007; Hannah and Thompson, 2008), this chapter shows that we have already acquired quite a large body of knowledge. There may be some areas with missing information, for example, about ecotoxicity to terrestrial species (Handy et al., 2008), but all in all we are starting to get an overview of the important processes in the environment. The most important property of NPs is their tendency to agglomerate, which leads to sedimentation and removal of wastewater or groundwater from water. Understanding the parameters that determine whether an NP is agglomerating or not is therefore crucial for understanding the fate of NPs in natural systems. With regard to ecotoxicity, we can already say that although many NPs can be toxic to organisms at high concentrations, most studies report little to no effects at lower, environmentally relevant concentrations. However, almost all studies so far have been short-term experiments, and long-term experiments have been almost completely missing so far.

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4 Heavy Metal Removal with Exopolysaccharide-Producing Cyanobacteria

Roberto De Philippis and Ernesto Micheletti

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4.1 INTRODUCTION

4.1.1 HEAVY METAL POLLUTION IN WATER BODIES: AN INCREASING CONCERN FOR HUMAN HEALTH

Heavy metals are one of the most widespread causes of pollution, both in water and in the soil, and the presence of increasing levels of these metals in the environment is causing serious concern in public opinion owing to the toxicity shown by most of them [1,2].

Heavy metals are usually defined as metals with a density greater than $4\text{--}5\text{gcm}^{-3}$, but in the literature it is possible to find so many different definitions that recently IUPAC defined the term “heavy metal” as a confusing and misleading one [3]. Generally speaking, metals are natural components of the Earth’s crust and some of them (e.g., copper, selenium, and zinc) are essential as trace elements to maintain the metabolism of the human body even if, at higher concentrations, they may have toxic effects. Many other metals (e.g., mercury, cadmium, lead, etc.) have direct toxic effects on human health. Owing to their chemical characteristics, metals remain in the environment, in many cases only changing from one chemical state to another one and eventually accumulating in the food chain. These pollutants enter the environment through a variety of human activities, such as mining, refining, and electroplating industries [4]. The effluents produced by these industries contain a variety of heavy metals, such as cadmium, copper, chromium, nickel, lead, and zinc, and their release in water bodies may significantly contribute to the increased presence of toxic heavy metals in aquatic environments. Owing to their high water solubility, heavy metals can be easily absorbed by living organisms and, due to their mobility in natural water ecosystems and their toxicity to living forms, have been ranked as major inorganic contaminants in surface and ground waters. Even if they may be present in dilute, almost undetectable quantities, their recalcitrance to degradation and consequent persistence in water bodies imply that, through natural processes such as biomagnification, their concentration may become elevated to such an extent that they begin exhibiting toxic effects. Of the 35 metals considered dangerous for human health, 23 have been defined as heavy metals: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [5]. However, the main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, and arsenic (this element is a metalloid but it is usually defined as a heavy metal). Large amounts of any of these metals may cause acute or chronic toxicity (poisoning), resulting in damaged or reduced mental and central nervous functions, modify blood composition, and damage the lung, kidney, liver, and other vital organs. Long-term exposure to the above-mentioned heavy metals may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer’s disease, Parkinson’s disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer [6]. Heavy metals may enter the human body through food, water, and air, or may be absorbed through the skin when they enter into contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings.

Although several adverse health effects of heavy metals have been known since a long time, exposure to these metals is continuing and even increasing in some parts of the world. Thus, the control of heavy metal dumpings and the removal of toxic heavy metals from waters has become a challenge for the twenty-first century.

4.1.2 HEAVY METAL REMOVAL: CONVENTIONAL TECHNOLOGIES

A number of techniques for the treatment of heavy metal-containing waste waters have been developed in recent years, in order to both decrease the amount of metal-containing waste waters produced by industrial activities and improve the quality of treated effluents. Various treatments, such as chemical precipitation, coagulation–flocculation, flotation, ion exchange, and membrane filtration, can be utilized to remove heavy metals from contaminated waste waters, each with their own inherent advantages and limitations in application.

4.1.2.1 Chemical Precipitation

Chemical precipitation is the most common technology used to remove dissolved (ionic) metals from water solutions, such as process waste waters containing toxic metals. The ionic metals are converted to an insoluble form (particle) by the chemical reaction between the soluble metal compounds and the precipitating reagent. Typically, the metal precipitated from the solution is in the form of hydroxide. The conceptual mechanism of heavy metal removal by chemical precipitation is represented as



where $M(OH)_n$ is insoluble metal hydroxide and M^{n+} and OH^- represent dissolved metal ions and precipitant, respectively. Therefore, the optimum pH for precipitation of one metal may cause another metal to solubilize, or start to go back into solution. Most process waste waters contain mixed metals and hence precipitating these different metals as hydroxides can be a tricky process. Chemical precipitation requires large amounts of chemicals to reduce the concentration of metals to an acceptable level for discharging waste waters into the environment. Other drawbacks of this method are related to the excessive sludge production that requires further treatments, the cost of sludge disposal, the slow kinetics of metal precipitation, the poor settling of metal hydroxides, the aggregation of metal precipitates, and the long-term environmental impact of sludge disposal.

4.1.2.2 Coagulation–Flocculation

Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing suspended particles, allowing particle collision and growth as flocks. If the first step is incomplete, the following one will be unsuccessful. The coagulation process destabilizes colloidal particles, constituting metal-containing compounds, by adding a coagulant and results in the sedimentation of these compounds. To increase the particle size, coagulation is followed by the flocculation of unstable particles into bulky flocs. The general approach for this technique includes a preliminary pH adjustment and involves the addition of ferric/aluminum salts as coagulants to overcome the repulsive forces between colloidal particles. Like chemical precipitation, a pH ranging from 11.0 to 11.5 has been found to be the most effective in maximizing the heavy metal removal obtained by means of this process. Improved sludge settling, dewatering characteristics, capability of inactivating bacterial activities, and sludge stability are reported to be the major advantages of lime-based coagulation. In spite of its advantages, coagulation–flocculation has limitations such as high operational costs due to the use of large amounts of chemicals. In addition to this drawback, the large volume of sludge generated from the coagulation–flocculation process may hinder its adoption as a global strategy for waste water treatment.

4.1.2.3 Flotation

This technology is used to separate solids or dispersed liquids from a liquid phase using bubble attachment. Flotation can be divided into five different kinds of processes: (i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) vacuum air flotation, (iv) electro-flotation, and (v) biological

flotation. Among the various types of flotation, DAF is the one most frequently used for the treatment of metal-containing waste waters. Adsorptive bubble separation utilizes foaming to separate the metal impurities.

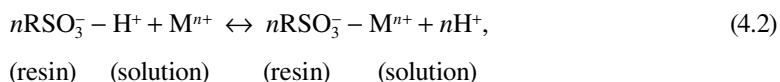
4.1.2.4 Membrane Filtration

Membrane technology has become a dignified separation technology over the past decennia. The main force of membrane technology is the fact that it works without the addition of chemicals, with a relatively low-energy use and easy and well-arranged process conductions. This technology is capable of removing not only suspended solids and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particles that have to be retained, various types of filtration techniques [i.e., ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)] can be utilized for the removal of heavy metals from waste waters. UF utilizes permeable membranes to separate heavy metals, macromolecules, and suspended solids from inorganic solutions on the basis of the size of the pores (5–20 nm) and the molecular weight (1000–100,000 Da) of the compounds that have to be separated. NF has unique properties between UF and RO membranes. In NF, the separation mechanism involves steric (sieving) and electrical (Donnan) effects. A Donnan potential is created between the charged anions in the NF membrane and the metal co-ions in the effluent, thus creating conditions for the rejection of the latter ones. NF membranes, generally, can treat inorganic effluents with a metal concentration of 2000 mg L⁻¹. In RO, the metal-containing solution is forced, by applying a pressure on the fluid, to pass through a membrane: heavy metals are retained and accumulated on one side while purified water is recovered on the other side of the membrane. In general, compared with UF and NF, RO is more effective for heavy metal removal from inorganic solutions, as indicated by the rejection percentage of over 97% with a metal concentration ranging between 20 and 200 mg L⁻¹, but its major drawback is related to the high operational costs.

4.1.2.5 Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion present in solution is exchanged with a similarly charged ion bound to a stationary solid phase (resin). Ion exchange can also be used for recovering valuable heavy metals from inorganic effluents. After separating the loaded resin, metals can be recovered in a more concentrated solution by eluting with suitable reagents.

Since the acidic functional groups of the resins consist of sulfonic acid, it is assumed that the physico-chemical interactions occurring during metal removal can be expressed as follows:



where (–RSO₃[–]) and Mⁿ⁺ represent the anionic group attached to the ion-exchange resin and the metal cation, respectively, while *n* is the coefficient of the reaction component, depending on the oxidation state of metal ions. Selecting the optimum dosage level depends mainly on the quality of finished water required, considering both economic and operating factors. Depending on the characteristics of the ion exchanger, heavy metal removal by ion exchange is effective in acidic conditions with pH ranging from 2 to 6. However, ion exchange also has some limitations in treating waste waters containing heavy metals. Prior to ion exchange, appropriate pretreatment systems for secondary effluent such as the removal of suspended solids from waste water are required. In addition, suitable ion-exchange resins are not available for all heavy metals and the capital and operational costs are high.

4.1.2.6 Electrochemical Treatment Techniques

Electro-dialysis (ED) is a membrane separation technique in which ionized species in the solution are passed through an ion-exchange membrane by applying an electric potential. The membranes

are thin sheets of plastic materials with either anionic or cationic charge. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations migrate toward the cathode, crossing the anion-exchange and cation-exchange membranes. Since ED is a membrane process, it requires clean feed, careful operation, and periodic maintenance to prevent any damage to the membranes.

In conclusion, it is possible to say that physico-chemical treatments offer various advantages but their benefits are counterbalanced by a number of drawbacks such as their high operational costs due to the chemicals used, high energy consumption, and handling costs for sludge disposal.

4.1.3 HEAVY METAL REMOVAL: USE OF MICROORGANISMS

The property of nonliving microbial biomass to accumulate heavy metal ions, a not metabolically driven process called *biosorption*, has been known for several decades [7].

In contrast, the term *bioaccumulation* describes an active process where the removal of metals requires the metabolic activity of a living organism. In recent years, research on the mechanisms of biosorption has intensified because biomass can be profitably utilized to sequester heavy metals from industrial effluents (e.g., produced by mining or electroplating industries) or to recover precious metals from processing solutions [7].

Microbial cells may represent excellent biosorbents owing to their high surface-to-volume ratios and a high content of potentially active chemo-sorption sites [8].

The use of biomass as adsorbent for the control of pollution due to heavy metals can generate revenue for those microbiological industries that are currently wasting the biomass derived from the industrial process and can also ease the burden of the costs associated with the disposal of the waste biomass produced. Alternatively, the biomass can also be grown using unsophisticated fermentation techniques and inexpensive growth media [9]. The use of dead biomass in industrial applications offers certain advantages over living cells. Systems using living cells are likely to be more sensitive to metal ion concentration (toxicity effects) and adverse operating conditions (pH and temperature). Furthermore, a constant nutrient supply is required for systems using living cells, resulting in high operating costs for waste streams devoid of nutrients, and the recovery of metals and the regeneration of biosorbent are more complex for living cells. Dead biomass can be obtained from industrial sources as a waste product derived from fermentation processes. Microbial cells can be killed by physical treatment methods using heat treatment [10,11], autoclaving, and vacuum drying [12,13], by using chemicals such as acids, alkalis, detergents [12,14–20], and other organic compounds (e.g., formaldehyde) [21], or by mechanical disruption [19,22]. The biosorption of metals is based on several mechanisms that quantitatively and qualitatively differ according to the species used, the origin of the biomass, and their method of processing. Metal sequestration follows complex mechanisms, mainly based on ion exchange, chelation, adsorption by physical forces, and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural polysaccharidic network of external cell layers. There are several chemical groups that could attract and sequester the metals in biomass, depending on a number of external environmental factors as well as on the type of metal, its toxic form in solution, and the type of active binding site responsible for the sequestration of the metal [23]. The most important binding compounds are acetamido groups of chitin, structural polysaccharides of fungi, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl, and carboxyl groups in proteins, and carboxyls, hydroxyls, and sulfates in polysaccharides (Table 4.1). However, it should be stressed that the presence of a specific functional group does not guarantee its accessibility for sorption, owing to possible steric and conformational barriers. Research on biosorption of heavy metals has led to the identification of a number of microbial biomass types that are extremely effective in concentrating metals. Some types of biomass are the waste of large-scale industrial fermentations (e.g., the bacterium *Bacillus subtilis*). Other metal-binding microbial types, such as certain abundant cyanobacterial strains, can be readily harvested from specific environments such as lakes or the sea, where they form superficial

TABLE 4.1
Most Important Heavy Metal-Binding Groups Present in the External Layers of Microbial Cells

Binding Group	pK _a	Occurrence in Selected Biomolecules
Hydroxyl	9.5–13	PS, UA, SPS, AA
Carbonyl (ketone)	—	Peptide bond
Carboxyl	1.7–4.7	UA, AA
Sulfhydryl (thiol)	8.3–10.8	AA
Sulfonate	1.3	SPS
Thioether	—	AA
Amine	8–11	Cto, AA
Secondary amine	13	Cti, PG, peptide bond
Amide	—	AA
Imine	11.6–12.6	AA
Imidazole	6.0	AA
Phosphonate	0.9–2.1/6.1–6.8	PL
Phosphodiester	1.5	TA, LPS

Source: Volesky, B. *Water Res.*, 41, 4017–4029, 2007.

Notes: AA = amino acids; Cti = chitin; Cto = chitosan; LPS = lipopolysaccharides; PG = peptidoglycan; PL = phospholipids; PS = polysaccharides; SPS = sulfated PS; TA = teichoic acid; UA = uronic acids.

blooms. These biomass types can accumulate considerable amounts of heavy metals, such as Pb, Cd, U, Cu, Zn, Cr, and others.

Large quantities of waste microbial biomass are produced in many industries such as those producing citric acid or penicillin. Berkeley [24] estimated that fermentation industries produce some 790,000 tons of microbial waste each year, with 41,000 tons resulting from citric acid production by *Aspergillus niger*. The use of dead rather than live biomass eliminates the problems of waste toxicity and nutrient requirements.

Some types of biosorbents could be broad range, binding and collecting the majority of heavy metals with no specific priority, whereas others can even be specific for certain types of metals [25,26].

An important consideration in studying biosorption is the solution chemistry of metals, particularly as it relates to their hydration and hydrolysis reactions. Biosorption of heavy metals usually leads to the acidification of solutions, because the biomass usually acts as a weakly acidic ion exchanger. Since deprotonation of each functional group depends on pH, the process of biosorption is strongly pH dependent. This was confirmed in the biosorption experiments carried out at different pH values. The contribution of functional groups in the biosorption process was confirmed by chemical modification of the groups. Chemically blocked groups did not show either biosorption or ion-exchange capabilities.

4.1.4 MODELING MICROBIAL BIOSORPTION

Sorption can be defined, in general terms, as a process in which a solid, named sorbent, interacts with a chemical species (sorbate) dissolved in a liquid phase (usually water); as a consequence of this interaction, the sorbate is removed from the liquid phase with an efficiency depending on its affinity for the sorbent. When the sorbent is a biological material (i.e., microbial cells, vegetable residues, wood residues, etc.), this process is defined as *biosorption* [27].

In order to evaluate the quality of a sorbing material, its capability of removing from water solutions the sorbate of interest is generally compared with the performances obtained with other sorbents previously reported in the literature. The parameter most frequently used for describing the

performances of sorbing materials is the metal uptake q , defined as the amount of sorbate bound per unit of sorbent. In studies aimed at defining a practical process for the removal of heavy metals, q is generally expressed in terms of milligrams of metal removed per gram of dry weight of the sorbent. When the stoichiometry of the process has to be defined, the amount of metal removed can be better expressed as millimoles (i.e., milligrams of sorbate removed divided by its atomic or molecular weight) or milliequivalents (i.e., millimoles removed divided by the ion valence of the sorbate) per gram of dry weight of sorbent.

In many papers, it is possible to find other parameters, such as the percentage of sorbate removed on the amount initially present in solution; however, these parameters are of limited significance for carrying out a sound comparison with sorption processes performed under different conditions or with different sorbents. In addition to these considerations, it has to be stressed that many factors affect the sorption processes (see [Section 4.3.3](#)), thus suggesting that one carefully check the operating conditions utilized before comparing the results obtained in different laboratories. Indeed, the sorption process is affected by the temperature; thus all the experiments must be carried out under controlled temperature and it is only possible to compare experiments carried out at the same temperature. Moreover, the q values are comparable only if they were calculated when the equilibrium between the amount of sorbate on the sorbent and in the liquid phase was attained. Finally, the sorption process is strongly affected by the pH and the ionic strength of the metal solution; thus any of these parameters should be maintained under strict control during the experiments aimed at characterizing the sorption performances of a new biosorbent.

The data obtained in the processes of metal biosorption with microorganisms are usually expressed utilizing the Freundlich or the Langmuir isotherms, the two most utilized adsorption models for single-solute systems [28].

4.1.4.1 Freundlich Adsorption Isotherm

The Freundlich isotherm relationship is an empirical exponential equation with the following form:

$$q = K C_e^{1/n}, \quad (4.3)$$

which can be linearized as

$$\ln q = \ln K + n^{-1} \ln C_e, \quad (4.4)$$

where q is the solute (metal) adsorbed per mass of adsorbent, typically expressed as mg g^{-1} , K is a constant, related to the adsorbent capacity, n is a constant, related to the energy of sorption, and C_e is the equilibrium (final) concentration of solute (metal) in the solution, typically expressed as mg L^{-1} .

The Freundlich isotherm, not indicating a finite uptake capacity, should only be utilized at low or intermediate values of the final metal concentration C_f [29].

4.1.4.2 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm has the following form:

$$q = b C_e q_{\max} / (1 + b C_e), \quad (4.5)$$

which can rearranged as

$$C_e q^{-1} = (b q_{\max})^{-1} + C_e (q_{\max})^{-1}, \quad (4.6)$$

where q is the solute (metal) adsorbed per mass of adsorbent, $q_{\max}$ is the metal adsorbed, at saturation, per mass of adsorbent, b is a constant, related to the energy of adsorption, and C_e is the equilibrium (final) concentration of solute (metal) in the solution.

The Langmuir isotherm is based on a number of assumptions: (i) the sorption process involves only a monolayer on the surface of the sorbent; (ii) there is only a fixed number of active sites on the sorbent; (iii) all the active sites are chemically equivalent; (iv) only one sorbate is present; (v) one active site reacts with only one molecule; and (vi) there are no interactions among the sorbed molecules.

It has to be stressed that in many, if not all, practical cases these assumptions are far from reality; however, the experimental data of most biosorption processes so far described in the literature fit rather well in the Langmuir isotherm and thus the use of this model allows the calculation of three very useful parameters such as q , $q_{\max}$, and b . The value of $q_{\max}$ can be considered as the maximum amount of sorbate that may theoretically be sorbed by the sorbent (i.e., the total number of binding sites available on the sorbent), whereas q is the number of binding sites really occupied by the molecules of sorbate; b is a parameter inversely related to the affinity of the sorbent for the sorbate.

Other, more complex isotherm relationships have been utilized in order to obtain more detailed models of the sorption process, even if none of them is actually related to the real physico-chemical mechanism of the sorption process. In particular, the Brunauer–Emmett–Teller (BET) model, which is based on the assumption that sorption is a multilayer process where the binding sites are independent one from the other, has been frequently utilized.

4.1.4.3 BET Adsorption Isotherm

The BET adsorption isotherm has the following form:

$$q = BQC_f \left\{ (C_s - C_f) \left[1 + (B - 1) \frac{C_f}{C_s} \right] \right\}^{-1}, \quad (4.7)$$

where q is the solute (metal) adsorbed per mass of adsorbent (mg g^{-1}), B is a constant related to the energy of interaction of the sorbate with the surface of the sorbent, Q is the number of moles of sorbate adsorbed per gram of sorbent in the formation of a complete monolayer, and C_s is the saturation constant of the sorbate.

Other more sophisticated models have been proposed, but they are empirical models. Indeed, the sorption process is very complex and not ascribable to a unique phenomenon; in addition, in the case of biosorption of heavy metals on biological materials, it has been suggested the occurrence of a process of formation of gels and the presence of a mechanism of exchange between the newly sorbed ions and those coming out from the gel. For the above reported reasons, the isotherms thus far proposed can only be considered as useful models for calculating the most important sorption parameters when the experimental data nicely fit one of them [29].

4.2 CYANOBACTERIA

4.2.1 GENERAL CHARACTERISTICS OF CYANOBACTERIA

Cyanobacteria are a wide group of Gram-negative, phototrophic prokaryotes characterized both by the capability of performing an oxygenic, plant-like photosynthesis and by autotrophy as their main mode of nutrition, even if the additional capability of growing under heterotrophic and/or mixotrophic growth conditions has been reported for a number of species [30]. In addition, some cyanobacterial strains were found to be capable of growing in the dark on organic substrates [31,32] or, under anaerobic conditions, of carrying out anoxygenic photosynthesis utilizing sulfide as the electron donor [33]. A large number of species possess the capability of fixing atmospheric dinitrogen, which is reduced to ammonia and utilized for the biosynthesis of nitrogen-containing cellular compounds. As a consequence of these metabolic features, cyanobacteria can be considered as the microbial group possessing the simplest nutritional requirements of all microorganisms [34,35]. Such trophic independence, along with their competitive ability and the relative ease of cultivation, makes cyanobacteria well suited for use in waste water treatment processes [102].

Cyanobacteria are characterized by great morphological diversity. They are included in the group of both unicellular and filamentous species, with large differences in their cell volume that range over more than five orders of magnitude [36]. They have been found in most of the natural illuminated environments, both aquatic and terrestrial, as a consequence of a broad spectrum of physiological properties and tolerance to environmental stress [37].

4.2.2 CHARACTERISTICS OF THE CYANOBACTERIAL CELL WALL

Cyanobacteria are classified as Gram-negative prokaryotes with regard to the organization of their cell walls. These microorganisms possess a four-layered cell wall that consists of a peptidoglycan layer (murein) surrounded by a lipopolysaccharidic layer (outer membrane), as is typical for Gram-negative bacteria [38]. However, there are some peculiarities in the cell wall of cyanobacteria in comparison with those of other Gram-negative bacteria. Indeed, the peptidoglycan layer is considerably thicker and with a higher degree of cross-linking between the polysaccharidic chains, reaching values close to those reported for Gram-positive bacteria [39]. On the other hand, most cyanobacteria showed the presence of the typical Gram-negative bacterial *meso*-diaminopimelic acid in the peptides linking the polysaccharidic chains.

Some other peculiarities of the cell walls of cyanobacteria, related to the composition of lipopolysaccharides (LPSs) and to the presence of unusual constituents (e.g., carotenoids), distinguish cyanobacterial cell walls from the typical cell wall of Gram-negative cyanobacteria.

4.2.3 CHARACTERISTICS OF THE POLYSACCHARIDIC EXTERNAL STRUCTURES IN CYANOBACTERIA

Several cyanobacteria possess, outside their outer membrane, additional surface structures mainly of polysaccharidic nature, which are usually defined as sheaths, capsules, and slimes. The sheath is defined as a thin layer that surrounds single cells, single filaments, or cell groups, reflecting their shape and microscopically visible without any staining (Figure 4.1); the sheath shows, in most cases, a microfibrillar substructure and is characterized by considerable mechanical and physico-chemical stability [40–42,48]. The capsule is a polysaccharidic, gelatinous layer, associated with the cell surface and characterized by sharp outlines (Figure 4.2); it is structurally coherent so as to exclude particles, and this characteristic is used for its negative staining with India ink [48]. The slime is an

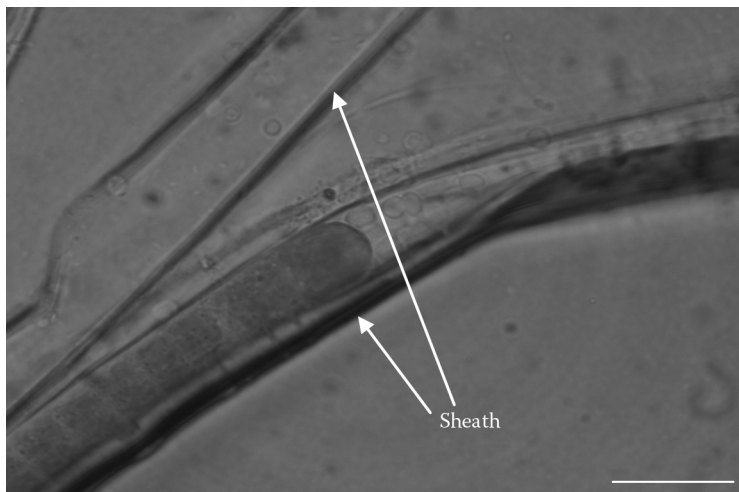


FIGURE 4.1 Example of sheath in cyanobacteria: Nomarski differential interference contrast photomicrograph of *Lyngbya* sp. (scale bar = 10 μ m).

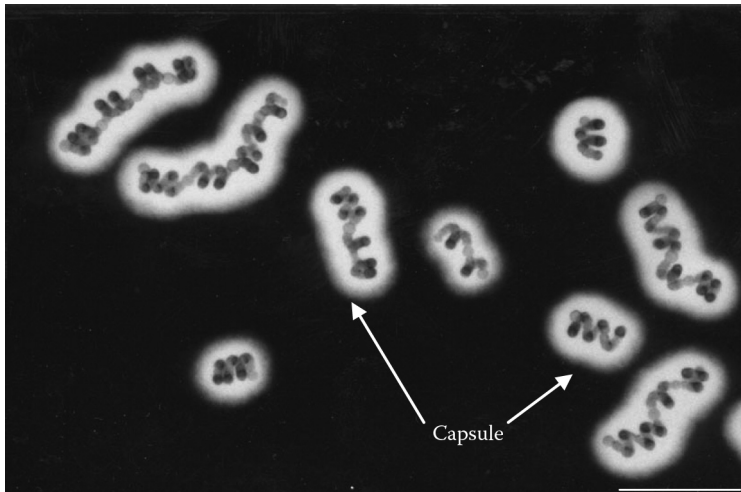


FIGURE 4.2 Example of capsule in cyanobacteria: Nomarski differential interference contrast photomicrograph of *Cyanospira capsulata* filaments stained with India ink (scale bar = 100 μm).

amorphous, mucilaginous shroud characterized by a non-well-defined structure; it may enclose a certain number of cells or filaments, which may show the additional presence of capsules (Figure 4.3). [43,44,48]. During cell growth in batch cultures, aliquots of the polysaccharidic material of sheaths, capsules, and slimes may be solubilized into the surrounding medium, constituting the so-called released polysaccharides (RPSs), which, depending on their molecular weight and concentration, may cause a significant increase in the viscosity of the culture medium.

From the data so far available in the literature, based on the characterization of more than 150 cyanobacterial RPSs, it appears that they can be defined as complex heteropolymers, containing three to fourteen different kinds of monosaccharides. Indeed, about 80% of the polymers described so far showed the presence of six or more different monomers; a feature peculiar to this group of microorganisms is that the polysaccharides produced by other microbial groups are generally constituted by a much lower number of monomers [45]. Another important feature of cyanobacterial

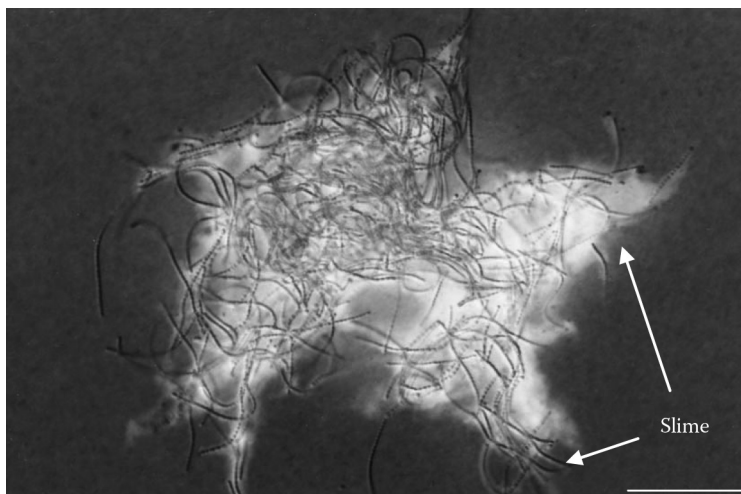


FIGURE 4.3 Example of slime in cyanobacteria: Nomarski differential interference contrast photomicrograph of *Nostoc* PCC7936 filaments stained with India ink (scale bar = 150 μm).

polysaccharides represents their anionic character, with more than 90% of them being characterized by the presence of one or two uronic acids, namely galacturonic and/or glucuronic acid. In about half of the RPSs studied, the amount of uronic acids is higher than 20% of the RPS dry weight. A certain number of charged, nonsaccharidic constituents, such as sulfate and ketal-linked pyruvyl groups, have also been found in many cyanobacterial RPSs, contributing to the global negative charge of these macromolecules [46]. A rather large number of cyanobacterial RPSs also showed the presence of peptidic moieties, which, depending on their amino acidic composition, may contribute either to the electrostatic charge of the macromolecules or to their hydrophobicity [47,48].

Owing to the presence of a large number of negative charges on the external layers of the exopolysaccharide-producing cyanobacteria, these microorganisms and the polymers that they produce have been considered as very promising chelating agents for the removal of positively charged heavy metal ions from water solutions [46,47].

4.3 HEAVY METAL REMOVAL WITH CYANOBACTERIA

4.3.1 PUTATIVE MECHANISMS OF METAL BIOSORPTION WITH CYANOBACTERIA

The ability of microorganisms to accumulate and remove heavy metals from water has been widely reported in the literature [4,8,23]. The complexity of the structure of microbial cells implies that there are many possible ways for the metal to be captured by the cell. Sorption mechanisms are therefore various and in some cases still not completely understood; however, generally speaking, it is possible to classify these processes as (i) active, metabolically driven or (ii) passive, not metabolically driven processes.

In active processes, the sorption, named *bioaccumulation*, is due to the transport of the metal across the cell membrane, with a consequent intracellular accumulation of the metal depending on cell metabolism. As a consequence, bioaccumulation occurs only with viable cells and is often associated with an active defense system of microorganisms, which reacts in the presence of a toxic metal. In this case, metal sorption is not immediate, since it requires time for reaction of the microorganism to the presence of the metal; thus the occurrence of bioaccumulation is evidenced by the kinetics of the metal sorption, which is slower in this metabolically driven process in comparison with the mere physico-chemical adsorption on the cell surface. When both processes occur, the slope of the line representing metal uptake versus time shows an inflexion point, which is due to the temporal sequence of passive adsorption, characterized by a steep slope, followed by active bioaccumulation, characterized by a less steep slope.

In the case of physico-chemical interactions (based on physical adsorption, ion exchange, and complexation) between the metal and functional groups present on the cell surface, the sorption process is not dependent on the metabolism. Cell walls, mainly composed of polysaccharides, proteins, and lipids, may offer particularly abundant sites for the binding of metals. These not metabolically driven, physico-chemical processes are relatively fast and usually reversible [26]. In the presence of such mechanisms, the microbial biomass acts as an ion-exchange resin. Ion exchange is an important concept in biosorption, because it explains many of the observations made during heavy metal uptake experiments. However, it should be pointed out that the term ion exchange does not explicitly identify the binding mechanism. The precise mechanism(s) may range from physical (i.e., electrostatic or London–van der Waals forces) to chemical binding (i.e., ionic and covalent).

Like other microbial biomasses tested, cyanobacteria also have a cell wall that is capable of passively adsorbing high levels of dissolved metals, usually via a charge-mediated attraction. Cell walls present, in fact, functional groups, such as carboxylate, hydroxyl, sulfate, phosphate, and amino groups (see [Sections 4.2.2](#) and [4.2.3](#)). In addition, many strains are characterized by the presence of outermost polysaccharidic envelopes, often coupled with the capability of releasing exocellular polysaccharides (EPSs) into the culture medium during cell growth [48]. Most of these polymers are characterized by anionic nature, owing to the presence of uronic acids and/or other charged groups

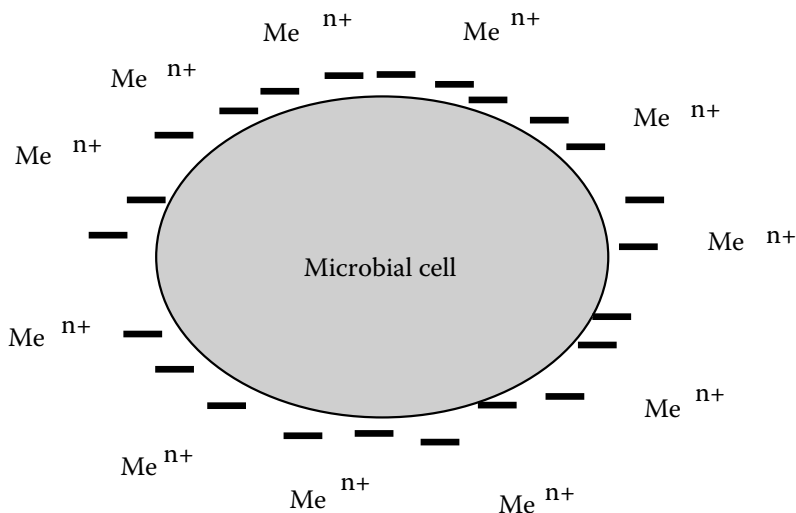


FIGURE 4.4 Interactions of metal cations with negative charges on the cell surface.

that contribute to give to these macromolecules a rather high anion density [48]. For this reason, the biomass of EPS-producing cyanobacteria can be considered very promising as a chelating agent for the removal of heavy metals from water [46], with a larger number of binding sites for metal ions compared with the biomass of other microorganisms.

In EPS-producing cyanobacteria, it is possible to hypothesize a complex mechanism of interaction with positively charged metal ions due to the presence of more than one negatively charged external cell structure. Indeed, the metal cations can be taken up by the negatively charged groups present on the cell wall (Figure 4.4), those present on the polysaccharidic layers surrounding the cell wall (sheath, capsule, and/or slime) (Figure 4.5), and those present in the RPSs released by the cells into the surrounding environment (Figure 4.6).

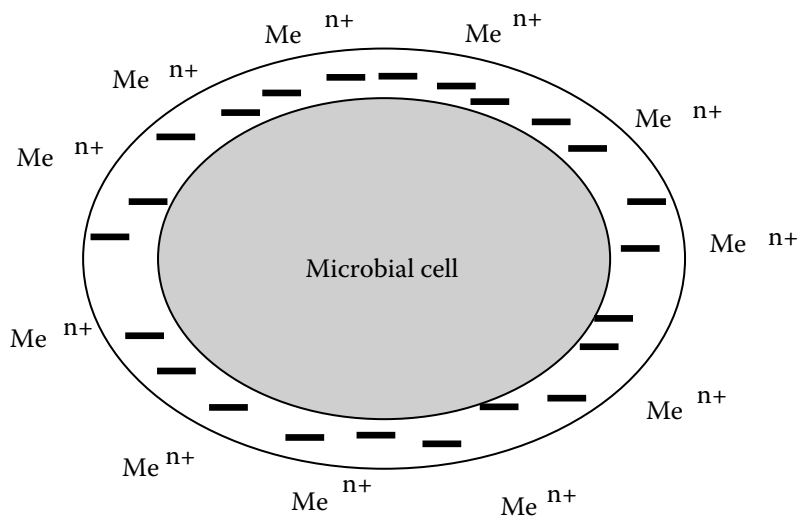


FIGURE 4.5 Interactions of metal cations with negative charges on the polysaccharidic exocellular layers (sheath or capsule).

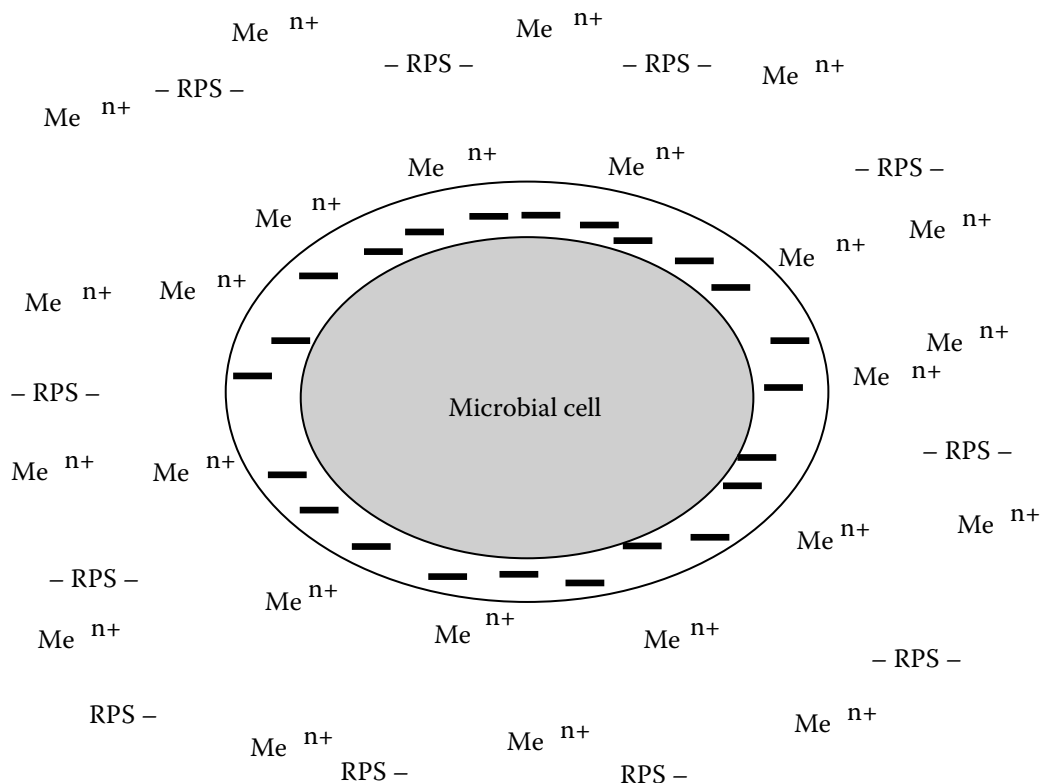


FIGURE 4.6 Interactions of metal cations with negative charges of the polysaccharide released (RPS) into the water medium.

4.3.2 HEAVY METAL REMOVAL WITH CYANOBACTERIA

The ability of cyanobacterial biomass to accumulate and remove heavy metals from water solutions has been widely reported in the literature. Up to now, a very large number of cyanobacterial strains have been screened with regard to their capability of removing heavy metals from metal solutions, mostly operating under laboratory conditions with pure metal solutions. As is evident from Table 4.2, a large number of papers describe experiments performed using cyanobacteria for the removal of metals with a high level of toxicity, such as Cd, Hg, Ni, Zn, and Pb. *Tolypothrix tenuis* and *Calothrix parietina* showed a very high capability of removing Hg [49], *Scytonema schmidlei*, *Anabaena cylindrica*, and *A. torulosa* removed 96–98% of Cd from 1 mg L⁻¹ solutions of this metal [50], and *Gloeocapsa* sp., *Nostoc paludosum*, *N. piscinale*, *N. punctiforme*, *N. commune*, *Oscillatoria agardhii*, *Phormidium molle*, and *Tolypothrix* removed 90–96% of Pb from 1 mg L⁻¹ solutions [51]. In addition to studies on the removal of toxic metals, the biosorption of nontoxic, but economically valuable, metals was also studied, often using the same cyanobacterial strains utilized with toxic heavy metals (Table 4.2). However, as already discussed in the previous sections, one of the problems arising when one intends to make a sound comparison among the performances of cyanobacteria reported in the literature comes from the different experimental conditions frequently utilized by different authors and from the uncertainty, in many cases, that the equilibrium in the sorption process was actually attained, a condition indispensable for giving sense to the comparison of the results obtained by different authors [52].

In spite of the large number of data available on the metal removal capability of cyanobacteria, the presence and the possible role of their extracellular polysaccharidic layers in the biosorption

TABLE 4.2

Heavy Metal Removal by Cyanobacteria: Results Obtained with the Cyanobacteria and the Metals So Far Tested

Metal	Cyanobacterium	Sorption (mmol g ⁻¹) ^a or Metal Removal Efficiency (%) ^b	References
Al	<i>Spirulina platensis</i>	0.0045 ^{a,c}	[76]
	<i>Spirulina maxima</i>	0.0145 ^{a,c}	[76]
	<i>Mastigocladus laminosus</i> #113	0.0284 ^{a,c}	[76]
Co	<i>Oscillatoria angustissima</i>	0.26 ^a	[77]
	<i>Spirulina</i> sp.	0.0002 ^a	[72]
	<i>Phormidium valderianum</i> BDU 30501	n.r.	[78]
Cd	<i>Anabaena nodosum</i>	0.087 ^a	[79]
	<i>Anabaena nodosum</i>	0.81 ^a	[80]
	<i>Anabaena</i> sp. BCC 2	85 ^b	[50]
	<i>Anabaena variabilis</i> NIES 23	57 ^b	[67]
	<i>Anacystis nidulans</i>	n.r.	[81]
	<i>Aphanocapsa halophytia</i>	n.r.	[82]
	<i>Calothrix</i> sp.	n.r.	[83]
	<i>Calothrix marchica</i> BCC 4	57 ^b	[50]
	<i>Calothrix marchica</i> BCC 6	87 ^b	[50]
	<i>Calothrix parietina</i> TISTR 8093	0.70 ^a	[50]
	<i>Calothrix</i> sp. BCC 8	88 ^b	[50]
	<i>Calothrix</i> sp. BCC 10	89 ^b	[50]
	<i>Calothrix</i> sp. TISTR 8130	82 ^b	[50]
	<i>Chlorococcus paris</i>	n.r.	[84]
	<i>Cylindrospermum</i> sp. BCC 20	65 ^b	[50]
	<i>Gloeocapsa</i> sp. BCC 25	96 ^b	[50]
	<i>Gloeotheca magna</i>	3.78 ^{a,c}	[85]
	<i>Hapalosiphon hibernicus</i> BCC 27	90 ^b	[50]
	<i>Hapalosiphon</i> sp. BCC 30	62 ^b	[50]
	<i>Hapalosiphon welwitschii</i> BCC 34	75 ^b	[50]
	<i>Lyngbya hieronymusii</i> BCC 41	97 ^b	[50]
	<i>Lyngbya spiralis</i> BCC 42	80 ^b	[50]
	<i>Lyngbya taylorii</i>	0.37 ^a	[86]
	<i>Mastigocladus laminosus</i> #113	0.0048 ^{a,c}	[76]
	<i>Mastigocladus</i> sp. BCC 36	78 ^b	[50]
	<i>Nostoc rivularis</i>	n.r.	[87]
	<i>Microcystis</i> sp.	1.28 ^a	[88]
	<i>Microcystis aeruginosa</i> f. <i>aeruginosa</i> NIES 44	95.3 ^b	[67]
	<i>Microcystis aeruginosa</i> f. <i>flos-aquae</i> C3-40	1.23 ^{a,c}	[89]
	<i>Nostoc linckia</i>	n.r.	[87]
	<i>Nostoc</i> sp. BCC 50	94 ^b	[50]
	<i>Nostoc commune</i> . BCC 76	69 ^b	[50]
	<i>Nostoc micropicum</i> BCC 77	72 ^b	[50]
	<i>Nostoc piscinale</i> . BCC 47	82 ^b	[50]
	<i>Nostoc punctiforme</i> BCC 48	73 ^b	[50]
	<i>Nostoc punctiforme</i> BCC 49	84 ^b	[50]
	<i>Oscillatoria amoena</i> BCC 53	83 ^b	[50]
	<i>Oscillatoria jasorvensis</i> BCC 56	94 ^b	[50]
	<i>Oscillatoria agardhii</i> BCC 52	90 ^b	[50]

continued

TABLE 4.2 (continued)

Metal	Cyanobacterium	Sorption (mmol g ⁻¹) ^a or Metal Removal Efficiency (%) ^b	References
Cr	<i>Phormidium angustissimus</i> BCC 68	87 ^b	[50]
	<i>Phormidium molle</i> BCC 7193	95 ^b	[50]
	<i>Phormidium valderianum</i> BDU 30501	83 ^b	[78]
	<i>Rivularia</i> sp. BCC 80	88 ^b	[50]
	<i>Spirulina platensis</i>	0.0035 ^{a,c}	[76]
	<i>Spirulina maxima</i>	0.0017 ^{a,c}	[76]
	<i>Spirulina platensis</i>	0.33 ^a	[90]
	<i>Spirulina platensis</i>	1.07 ^a	[91]
	<i>Spirulina</i> sp.	0.004 ^a	[72]
	<i>Spirulina vulgaris</i>	1.00 ^a	[92]
	<i>Stigonema</i> sp. BCC 90	89 ^b	[50]
	<i>Stigonema</i> sp. BCC 92	80 ^b	[50]
	<i>Synechococcus</i> sp. PCC 7942	0.06 ^a	[93]
	<i>Tolypotrix tenuis</i> TISRT 8063	0.80 ^a	[50]
	<i>Tolypotrix tenuis</i>	0.18 ^a	[67]
	<i>Tolypotrix tenuis</i> BCC 100	53 ^b	[50]
	<i>Aphanocapsa halophytia</i>	0.29 ^a	[82]
	<i>Cyanospyra capsulata</i>	0.36 ^a	[74]
	<i>Cyanothece</i> CE 4	1.83 ^a	[74]
	<i>Cyanothece</i> ET 5	0.59 ^a	[74]
Cu	<i>Cyanothece</i> PE 14	0.26 ^a	[74]
	<i>Cyanothece</i> TI 4	1.29 ^a	[74]
	<i>Cyanothece</i> VI 13	0.93 ^a	[74]
	<i>Cyanothece</i> VI 22	1.08 ^a	[74]
	<i>Cyanothece</i> 16Som 2	3.77 ^a	[74]
	<i>Nostoc</i> PCC 7936	0.07 ^a	[74]
	<i>Spirulina</i> sp.	0.19 ^a	[72]
	<i>Synechococcus</i> sp. PCC 7942	0.10 ^a	[93]
	<i>Anabaena variabilis</i> NIES 23	35.4 ^b	[67]
	<i>Anacystis nidulans</i>	n.r.	[81]
	<i>Aphanocapsa halophytia</i>	n.r.	[82]
	<i>Calothrix</i> sp.	n.r.	[83]
	<i>Chroococcus paris</i>	n.r.	[84]
	<i>Cyanospyra capsulata</i> PCC 9502	3.65 ^a	[94]
	<i>Cyanospyra capsulata</i>	1.97 ^a	[47]
	<i>Cyanospyra capsulata</i>	2.25 ^a	[74]
	<i>Cyanothece</i> CE 4	0.52 ^a	[74]
	<i>Cyanothece</i> ET 5	1.78 ^a	[74]
	<i>Cyanothece</i> PE 14	0.16 ^a	[74]
	<i>Cyanothece</i> TI 4	0.50 ^a	[74]
	<i>Cyanothece</i> VI 13	0.95 ^a	[74]
	<i>Cyanothece</i> VI 22	0.98 ^a	[74]
	<i>Cyanothece</i> 16Som 2	3.17 ^a	[74]
	<i>Gloeotheca</i> sp. PCC 6909	0.41 ^a	[69]
	<i>Microcystis</i> sp.	2.91 ^a	[88]
	<i>Microcystis aeruginosa</i> f. <i>flos-aquae</i> C3-40	4.1 ^{a,c}	[89]
	<i>Nostoc</i> PCC 7936	1.465 ^a	[47]
	<i>Oscillatoria angustissima</i>	4.22 ^a	[95]

continued

TABLE 4.2 (continued)

Metal	Cyanobacterium	Sorption (mmol g ⁻¹) ^a or Metal Removal Efficiency (%) ^b		References
Fe	<i>Phormidium laminosum</i>	97.5 ^c		[58]
	<i>Spirulina</i> , sp.	0.19 ^a		[72]
	<i>Synechococcus</i> sp. PCC 7942	0.18 ^a		[93]
	<i>Tolypotrix tenuis</i> TISTR 8063	0.18 ^a		[67]
Hg	<i>Phormidium laminosum</i>	94.8 ^b		[58]
Hg	<i>Anabaena</i> sp. BCC 2	68 ^b		[50]
	<i>Calothrix marchica</i> BCC 4	84 ^b		[50]
	<i>Calothrix</i> sp. BCC 8	86 ^b		[50]
	<i>Calothrix</i> sp. BCC 10	92 ^b		[50]
	<i>Calothrix parietina</i> TISTR 8093	50 ^b		[50]
	<i>Calothrix</i> sp. TISTR 8130	40 ^b		[50]
	<i>Cylindrospermum</i> sp. BCC 20	83 ^b		[50]
	<i>Gloeocapsa</i> sp. BCC 25	50 ^b		[50]
	<i>Hapalosiphon hibernicus</i> BCC 27	84 ^b		[50]
	<i>Hapalosiphon welwitschii</i> BCC 34	85 ^b		[50]
	<i>Lyngbya hieronymusii</i> BCC 41	92 ^b		[50]
	<i>Lyngbya spiralis</i> BCC 42	96 ^b		[50]
	<i>Mastigocladus laminosus</i> #113	0.005 ^{ac}		[76]
	<i>Mastigocladus</i> sp. BCC 36	89 ^b		[50]
	<i>Nostoc</i> sp. BCC 50	86 ^b		[50]
	<i>Nostoc commune</i> sp. BCC 76	43 ^b		[50]
	<i>Nostoc micropicum</i> BCC 77	26 ^b		[50]
	<i>Nostoc piscinale</i> sp. BCC 47	22 ^b		[50]
	<i>Nostoc punctiforme</i> sp. BCC 48	66 ^b		[50]
	<i>Nostoc punctiforme</i> sp. BCC 49	49 ^b		[50]
	<i>Oscillatoria amoena</i> BCC 53	12 ^b		[50]
	<i>Oscillatoria jasorvensis</i> BCC 5689	89 ^b		[50]
	<i>Oscillatoria agardhii</i> BCC 52	73 ^b		[50]
	<i>Phormidium angustissimus</i> BCC 68	74 ^b		[50]
	<i>Phormidium molle</i> BCC 71	93 ^b		[50]
	<i>Rivularia</i> sp. BCC 80	86 ^b		[50]
	<i>Spirulina maxima</i>	0.00125 ^{ac}		[76]
	<i>Spirulina platensis</i>	0.00055 ^{ac}		[76]
	<i>Stigonema</i> sp. BCC 90	92 ^b		[50]
	<i>Stigonema</i> sp. BCC 92	94 ^b		[50]
	<i>Tolypotrix tenuis</i> BCC 100	94 ^b		[50]
Mn	<i>Microcystis aeruginosa</i> f. <i>flos-aquae</i> C3-40	2.84 ^{ac}		[89]
Ni	<i>Aphanocapsa halophytia</i>	n.r.		[82]
	<i>Cyanospyra capsulata</i>	1.41 ^a		[74]
	<i>Cyanothece</i> CE 4	1.24 ^a		[74]
	<i>Cyanothece</i> ET 5	0.24 ^a		[74]
	<i>Cyanothece</i> PE 14	0.19 ^a		[74]
	<i>Cyanothece</i> TI 4	0.62 ^a		[74]
	<i>Cyanothece</i> VI 13	0.39 ^a		[74]
	<i>Cyanothece</i> VI 22	0.59 ^a		[74]
	<i>Cyanothece</i> 16Som 2	0.96 ^a		[74]
	<i>Lyngbya taylorii</i>	0.65 ^a		[86]
	<i>Microcystis aeruginosa</i>	4.26 ^a		[96]

continued

TABLE 4.2 (continued)

Metal	Cyanobacterium	Sorption (mmol g ⁻¹) ^a or Metal Removal Efficiency (%) ^b	References
Pb	<i>Nostoc</i> PCC 7936	0.032 ^a	[74]
	<i>Phormidium laminosum</i>	85 ^b	[58]
	<i>Spirulina</i> sp.	0.003 ^a	[72]
	<i>Synechococcus</i> sp. PCC 7942	0.05 ^a	[93]
	<i>Synechocystis</i> sp.	3.23 ^a	[97]
	<i>Anabaena</i> sp. BCC 2	29 ^b	[50]
	<i>Anabaena variabilis</i> NIES 23	48.92 ^b	[67]
	<i>Aphanothece halophytica</i>	22 ^b	[98]
	<i>Calothrix</i> sp. BCC 8	59 ^b	[50]
	<i>Calothrix</i> sp. BCC 10	13 ^b	[50]
	<i>Calothrix</i> sp. TISTR 8130	86 ^b	[50]
	<i>Calothrix</i> sp.	n.r.	[83]
	<i>Cylindrospermum</i> sp. BCC 20	52 ^b	[50]
	<i>Gloeocapsa</i> sp. BCC 25	96 ^b	[50]
	<i>Hapalosiphon hibernicus</i> BCC 27	13 ^b	[50]
	<i>Hapalosiphon welwitschii</i> BCC 34	47 ^b	[50]
	<i>Lyngbya heironymusii</i> BCC 41	80 ^b	[50]
	<i>Lyngbya spiralis</i> BCC 42	73 ^b	[50]
	<i>Lyngbya taylorii</i>	1.47 ^a	[86]
	<i>Mastogocladus</i> sp. BCC 36	29 ^b	[50]
	<i>Microcystis aeruginosa</i> f. <i>flos-aquae</i> C3-40	1.50 ^{a,c}	[89]
	<i>Nostoc</i> sp. BCC 50	58 ^b	[50]
	<i>Nostoc commune</i> BCC 76	94 ^b	[50]
	<i>Nostoc piscinale</i> BCC 47	94 ^b	[50]
	<i>Nostoc punctiforme</i> BCC 48	98 ^b	[50]
	<i>Nostoc punctiforme</i> BCC49	51 ^b	[50]
	<i>Oscillatoria agardhii</i> BCC 52 73	96 ^b	[50]
	<i>Oscillatoria amoena</i> BCC 53	89 ^b	[50]
	<i>Oscillatoria jasorvensis</i> BCC 56 89	85 ^b	[50]
	<i>Phormidium angustissimum</i> BC 68	77 ^b	[50]
	<i>Phormidium molle</i> BCC 71	90 ^b	[50]
	<i>Rivularia</i> sp. BCC 80	76 ^b	[50]
	<i>Spirulina maxima</i>	84 ^b	[71]
	<i>Spirulina platensis</i>	35 ^b	[98]
	<i>Spirulina platensis</i>	0.08 ^a	[79]
	<i>Spirulina</i> , sp.	0.00005 ^a	[72]
	<i>Stigonema</i> sp. BCC 90	52 ^b	[50]
	<i>Stigonema</i> sp. BCC 92	59 ^b	[50]
	<i>Synechococcus</i> sp. PCC 7942	0.15 ^a	[93]
	<i>Tolypothrix tenuis</i> TISTR 8063	88 ^b	[50]
	<i>Tolypothrix tenuis</i> BCC 100	90 ^b	[50]
	<i>Tolypothrix tenuis</i> TISTR 8063	0.15 ^a	[67]
Sn	<i>Aphanocapsa halophytia</i>	82 ^b	[82]
Zn	<i>Anabaena variabilis</i> NIES 23	67.7 ^b	[67]
	<i>Anacystis nidulans</i>	n.r.	[81]
	<i>Aphanocapsa halophytia</i>	n.r.	[82]
	<i>Aphanothece halophytia</i>	2.03 ^a	[99]
	<i>Chroococcus paris</i>	n.r.	[84]

continued

TABLE 4.2 (continued)

Metal	Cyanobacterium	Sorption (mmol g ⁻¹) ^a or Metal Removal Efficiency (%) ^b	References
	<i>Lyngbya taylorii</i>	0.49 ^a	[86]
	<i>Mastigocladus laminosus</i> #113	0.00856 ^{a,c}	[76]
	<i>Microcystis aeruginosa</i> f. <i>flos-aquae</i> C3-40	1.23 ^{a,c}	[89]
	<i>Microcystis</i> sp.	15.29 ^a	[96]
	<i>Nostoc linckia</i>	n.r.	[87]
	<i>Nostoc rivularis</i>	n.r.	[87]
	<i>Oscillatoria angustissima</i>	0.33 ^a	[100]
	<i>Oscillatoria angustissima</i>	9.81 ^a	[101]
	<i>Phormidium laminosum</i>	78.2 ^b	[58]
	<i>Spirulina maxima</i>	0.0023 ^{a,c}	[76]
	<i>Spirulina platensis</i>	0.0046 ^{a,c}	[76]
	<i>Spirulina platensis</i>	0.11 ^a	[79]
	<i>Spirulina</i> sp.	0.003 ^a	[72]
	<i>Tolypotrix tenuis</i> TISTR 8063	0.14 ^a	[67]

^a Sorption, expressed as millimoles of metal removed per gram of dry biomass.

^b Metal removal efficiency, expressed as percent of metal removed on its initial concentration.

^c Bioremoval carried out with solutions of the pure polysaccharide produced by the cyanobacterium.

n.r. = quantitative data not reported.

process were almost neglected until a few years ago. Indeed, even if since the late 1980s it was hypothesized that the metal-binding process occurs by the complexation of metal ions with the polysaccharidic, mucilaginous material covering the cell wall or released by the cell surface [53,54], most of the studies on the role of polysaccharides in metal uptake date from the beginning of this century.

The comparison between metal biosorption in capsulated and decapsulated cells of field samples and laboratory-grown cultures of the unicellular cyanobacterium *Microcystis* showed a higher biosorption capability of the cells surrounded by the polysaccharidic capsular layer, pointing out a significant role of the polysaccharides in heavy metal removal [55]. Similar results were obtained in experiments of Cu biosorption with laboratory monocultures of microalgae and cyanobacteria, demonstrating the importance of surface mucilage in the adsorption process [56]. Mucilaginous algal species (e.g., *Anabaena* spp. and *Eudorina elegans*) showed a higher copper sorption in comparison with nonmucilaginous ones (*Chlorella vulgaris*), suggesting that this gelatinous layer increased the number of binding sites [56].

Inthorn et al. [50] reported that the cyanobacterium *Calothrix marchica* was able to remove Pb from waste water, and Ruangsomboon et al. [57] demonstrated that cells of this cyanobacterium, covered with a mucilaginous sheath, were able to remove Pb ions also owing to the contribution of polysaccharidic material. The accumulation of heavy metals in capsular polysaccharide was also reported for *Phormidium laminosum*, which showed the capability of adsorbing Pb, Fe, Cd, Cu, Zn, and Ni [58]. Capsular polysaccharides of *Microcystis aeruginosa* and *M. flos-aquae* showed the capability of adsorbing iron ions [59,60].

A wide difference in the metal-binding capacity of capsulated and uncapsulated cyanobacterial strains has been demonstrated [61]. A cyanobacterial strain, characterized by the presence of a thick capsule surrounding the cells, showed higher metal-binding capacity than strains devoid of or with only a thin capsule [47,62]. However, the presence of gelatinous capsules surrounding cyanobacterial

cells may also cause the slowing down of the diffusion rate of metal ions into the chelating matrix of the cell wall [63].

The role of RPSs was demonstrated by the work carried out by De Philippis et al. [64], who pointed out the significant contribution of the solubilized polysaccharidic fraction in the bio-removal of copper by two cyanobacteria, *Cyanospira capsulata* and *Nostoc* PCC 7936, comparing the results previously obtained with the sole biomass [47] with those obtained with the whole cultures confined to dialysis tubings.

Tien et al. [56] confirmed, by scanning electron microscopy x-ray microanalysis, that the higher binding capacity of mucilaginous cyanobacterial species is consistent with the hypothesis of the role of the polysaccharidic layer in metal uptake, having shown that about 40% of the adsorbed copper ions are bound to the mucilage. The longer adsorption time and the higher copper adsorption per unit of surface area of mucilaginous algae compared to *Chlorella* also supported this conclusion [56]. Parker et al. [65] and Li et al. [66] have found that the mucilaginous sheaths isolated from *M. aeruginosa* and *Aphanothece halophytica* exhibited strong affinity for metal ions. A high copper uptake by two mucilaginous cyanobacteria, *C. capsulata* and *Nostoc* PCC7936, was also shown by De Philippis et al. [47] in comparison with other microbial biomass.

A number of papers have been dedicated to the identification of the functional groups involved in the uptake of metal cations. The functional groups involved in metal sorption cyanobacteria have been identified by FTIR spectroscopy, pH and potentiometric titrations, and specific chemical modification of the biomass, with the block of functional groups with specific chemical reagents. There is a general agreement on the very important role carried out by carboxyl groups in the binding of positively charged metal ions by cyanobacterial cells [67–69], and this role is of particular importance in the polysaccharide-producing cyanobacteria, which are in most cases characterized by the presence of significant amounts of galacturonic and/or glucuronic acids (see [Section 4.2.3](#)). In the capsulated *Microcystis*, it was shown that the slime interacts with Cd, Ni, and Cu cations due to the presence of galacturonic acid [70]. The predominance of galacturonic acid in the capsule of *M. flos-aquae* suggested that the binding of Fe cation was due to carboxyl groups present in this polysaccharidic layer [60]. However, other groups have also been reported to be involved in the heavy metal-binding process by cyanobacterial cells. For instance, infrared (IR) data [71] showed that amino and hydroxyl groups play a predominant role (at high pH) in the binding of Pb by *Spirulina maxima*. Chojnacka [72] found that the process of Cr removal by *Spirulina* sp. was hindered when carboxyl and phosphate groups were esterified, showing the important role of these groups in the biosorption process. An insignificant decrease in the biosorption properties of the biomass after methylation of hydroxyl groups showed that these groups do not significantly contribute in the biosorption process.

The above reported results strongly support the conclusion, reported in [Section 4.3.3](#), that at low pH values carboxyl groups of EPSs play a predominant role in heavy metal sorption by algae and cyanobacteria. Other functional groups, such as sulfonate and amino groups, play a relatively minor role in metal sorption, even if at high pH values amino groups start to significantly contribute to metal uptake.

In any case, it is worth stressing that the mere determination of the quantity of charged groups is not sufficient for anticipating the actual metal-binding capability of a polymer, because, depending on the conformation of the macromolecules, some of the charged groups might be hardly accessible by metal ions. Hence, it is possible to say that the uptake of metal ions depends on charge density, their distribution on the polymers, and their accessibility by metal ions. Indeed, Tien [73] reported that *Oscillatoria limnetica*, even if it did not produce large amounts of surface mucilage in comparison with *Anabaena spiroides* and *Eudorina elegans*, which produced large amounts of dense and thick mucilages, showed the highest Cu and Pb uptake capacity per volume unit of mucilage. As a consequence of these results, the author infers that the metal-binding activity of surface mucilage depends on the characteristics and not on the amount of mucilage produced. These findings were confirmed by a recent study carried out by Micheletti et al. [74], who investigated

the role of outermost polysaccharidic investments in the process of copper removal by using the sheathed unicellular cyanobacterium *Gloeotheca* PCC 6909 and its sheathless mutant PCC 6909/1. In this study, both the wild type and the sheathless mutant were able to remove copper ions from metal solutions, but the specific metal uptake of the sheathed cells was slightly higher in comparison with the unsheathed mutant strain. On the other hand, the polysaccharide released by the two strains into the culture medium showed a different metal uptake, with the specific metal removal of the polysaccharide released by the mutant strain being higher than that of the polysaccharide released by the wild type. These results are discussed by the authors in terms of the type and number of binding sites present in the polysaccharide released by the mutant strain, underlining that the metal removal process depends not only on the amount of EPS produced but also on its quality and structure.

Thus, it is possible to conclude that, although various potential functional groups have been demonstrated to be present on the external cell layers of microalgae and cyanobacteria, their mere presence is not sufficient for demonstrating their participation in the biosorption of metals. Indeed, steric hindrance, conformational changes, or cross-linking may prevent some of the surface functional groups from being involved in the binding of metal ions [75]. As a consequence, the only way to evaluate the potential of a cyanobacterial strain in metal removal is the experimental evaluation of its performances.

4.3.3 FACTORS AFFECTING METAL UPTAKE BY CYANOBACTERIA

Metal biosorption has been described as being dependent on the cyanobacterial species used and on the differences in the composition of their cell walls. However, many other factors may affect the biosorption of metals in addition to cell wall composition and structure, beginning from differences in cell size and shape between species [29,52]. Also, the concentration of biomass in solution seems to influence specific uptake, that is specific metal uptake, expressed as mg of metal removed per gram of biomass, the highest in correspondence with the lowest biomass concentration [77]. The decrease in the specific metal uptake observed with the increase in biomass concentration was explained by hypothesizing that an increase in biomass concentration leads to a negative interference between binding sites [47].

The pH of the metal solution is one of the most important factors affecting the biosorption process: it influences the chemistry of the metal in solution, the activity of the functional groups present on the biomass, and the competition among metallic ions for the binding sites [19]. The amount of ions bound at a given pH is, in fact, determined by the affinity constants of the metal-binding functional groups. The value of these constants depends on the kind and valence of the metal ion and on the pK_a value of the functional group (see Table 4.1). Depending on pH, different functional groups participate in the metal-binding process: at pH ranging from 2 to 5, the active functional groups are carboxyl groups, at pH ranging from 5 to 9, the active functional groups are carboxyl and phosphate groups, at pH ranging from 9 to 12, the active functional groups are carboxyl, phosphate, and hydroxyl (or amine) groups [69,72].

The simultaneous presence of more than one metal in solution usually depresses the biosorption of the metal of interest or the biosorption of other cations. Such an effect can be explained in terms of competition between metal ions for the same binding sites on the biomass. Studies on the effect of this competition and on the selectivity of biosorption in mixtures of metal cations will be discussed in Section 4.4.3.

Temperature does not seem to significantly affect biosorption performances in the range 20–35°C [78]; for this reason, most biosorption studies with microalgae and cyanobacteria were performed at room temperature, without a strict control of this parameter [1]. However, if the aim of the experiments is to build up the adsorption isotherms of the metal removal process and also to allow a sound comparison among experimental data obtained in different laboratories, the experiments should be carried out in a thermostatic chamber in order to maintain a constant temperature.

It also has to be stressed that the physiological state of the biomass significantly affects its metal removal capability; a large difference between the amounts of metal uptake by dead or live microbial biomass has been reported by many authors. In most studies, biosorption of metals is greater with dead biomass as compared to equal amounts of living biomass. When biomass is in the dead state, the cells are permeable and this permeability allows metals to enter the cells and bind on intracellular constituents and surfaces as well as on the external surface, thus increasing the amount of metal uptake [67]. In addition, metal uptake is not affected by toxicity of the metal, which could affect the active transport of metal ions into living cells.

Other important factors that significantly affect metal uptake by microbial biomass are the electric charge and the chemical characteristics of the metal ions that interact with the cells [1]. Indeed, it has been demonstrated that metal ions with small ionic radius are sorbed onto a fixed surface area of a sorbent more quickly than metal ions characterized by larger ionic radii [13]. In accord with these results, it was found that Cu (ionic radius = 0.72 Å) was taken up in larger amounts than Zn (ionic radius = 0.74 Å) and Cd (ionic radius = 0.96 Å) by biomass of *Microcystis* sp. [62]. These results are in good accordance with previous results obtained by Cho et al. [103] and the hypothesis formulated by Lee [104].

Another very important factor affecting the performances of microbial biomass in the removal of heavy metals is the physical or chemical pretreatment of cells before their contact with metal ions. Not much research has been dedicated to this aspect with cyanobacterial biomass, but it was clearly demonstrated that the pretreatment may significantly improve the metal removal capability of biomass. In the case of *Oscillatoria* sp. biomass, an acid pretreatment with 0.01 N HCl induced a 10% increase in Cu adsorption in comparison with the metal uptake obtained with native biomass. Sampedro et al. have reported increased biosorption in the filamentous cyanobacterium *P. laminosum* after NaOH treatment, whereas HCl treatment was ineffective. An extensive study, carried out with several different pretreatment agents (i.e., with acid, alkaline, or chelating compounds), showed that, in the case of the biomass of two capsulated filamentous cyanobacteria, *C. capsulata* and *Nostoc* PCC 7936, the best performances were obtained after a pretreatment with a 0.1 N NaOH solution, which induced a 10% increase in the Cu removal of the treated biomass [94]. Moreover, the same authors demonstrated that the biomass of *C. capsulata* can withstand eight sorbing–desorbing cycles, carried out with 0.1 N HCl or 0.1 N NaOH as desorbing agents for removing adsorbed Cu ions during the previous sorbing cycle, without any degradation and while continuing to maintain a high sorbing capacity, averaging about 90% with both desorbing agents, as was previously found with other cyanobacteria [58,105,106].

4.4 METAL REMOVAL IN MULTIMETAL SOLUTIONS

4.4.1 MODELING MICROBIAL BIOSORPTION IN MULTIMETAL SOLUTIONS

Biosorption has been often studied in simple sorption systems, usually containing only one heavy metal. This is an inappropriate simplification for the understanding of the real process, because industrial waste waters usually simultaneously contain more than one metal ion. For this reason, in studies aimed at realistically representing the situation of metal-containing waste waters, it is necessary to develop models on the metal-binding process in multimetal solutions.

Metal sorption in binary metal systems may be described by the three-parameter extended Langmuir equation given below [107]:

$$q_1 = \frac{q_{\max 1} b_1 C_{f1}}{1 + b_1 C_{f1} + b_2 C_{f2}}, \quad (4.8)$$

where q_1 is the equilibrium sorption (mmol g⁻¹) of the first metal; $q_{\max 1}$ is the maximum sorption of the first metal at equilibrium (final) concentration of metal in solution (C_{f1} and C_{f2} , expressed as mM);

b_1 and b_2 are constants for the first and second metal, respectively; and subscripts 1 and 2 represent the metal of primary interest and the second metal, respectively.

In multimetal solutions, q (mmol g⁻¹) can be calculated by using the multicomponent extended Langmuir model with four parameters, as reported by Chong and Volesky [77]:

$$q(M_i) = \frac{(q_{\max}/K_i)C_f[M_i]}{1 + (1/K_1)C_f[M_1] + (1/K_2)C_f[M_2] + (1/K_3)C_f[M_3]}, \quad (4.9)$$

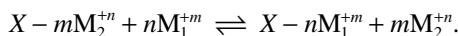
where i ($= 1, 2, 3$) represents the metal of interest and $C_f[M_1]$, $C_f[M_2]$, and $C_f[M_3]$ are the residual concentrations of metals 1, 2, and 3, respectively. The four parameters ($q_{\max}$, K_1 , K_2 , and K_3) of the above model could be evaluated using an appropriate software package. Although the above model is empirical, it is very often used to describe the equilibrium isotherm data of multicomponent systems.

A model represented in Equation 4.10 has also been proposed; it is a combination of the conventional Langmuir and Freundlich models [107]:

$$q_1 = \frac{q_{\max 1} b_1 C_{f1}^{n_1}}{1 + b_1 C_{f1}^{n_1} + b_2 C_{f2}^{n_2}}. \quad (4.10)$$

The parameters of the above model ($q_{\max}$, b_1 , b_2 , n_1 , and n_2) for sorption of metal ions from a multicomponent system may be obtained by fitting the data using suitable software. In the same way, sorption of the second metal (q_2) may also be represented.

Models focused on the ion-exchange mechanism are a closer representation of metal sorption, confirming the experimental evidences that cyanobacterial biomass is protonated or contains other cations that are released when heavy metal ions are taken up by the biomass. The ion exchange isotherm model represents ion-exchange reaction between the metal species, M_1 and M_2 (metal ions or cations bound on biosorbent (X) [108]. Ion-exchange reaction is given by



For this reaction, the equilibrium constant is represented as

$$K_{M_1 M_2} = \frac{q_{M_1}^n C_{fM_2}^m}{q_{M_2}^m C_{fM_1}^n}. \quad (4.11)$$

By assuming the above ion-exchange reaction, the ion-exchange isotherm equation can be derived [109] as

$$\begin{aligned} q_{M_1} &= \frac{Q}{1 + C_{fM_2}/K_{M_1 M_2} C_{fM_1}}, \\ q_{M_2} &= \frac{Q}{1 + C_{fM_2}/K_{M_1 M_2} C_{fM_2}}, \end{aligned} \quad (4.12)$$

where M_1 and M_2 are heavy metal ions to be sorbed and already bound on the biosorbent, respectively; m and n are the valences of M_1 and M_2 , respectively; Q is the total number of binding sites in algal biomass; C_{fM_1} and C_{fM_2} are the equilibrium (final) concentrations of metals M_1 and M_2 in

solution, respectively; and q_{M_1} and q_{M_2} are the contents of M_1 and M_2 in the biosorbent. In this model, M_2 can be replaced by proton $[H]$ if biomass is protonated.

However, it has to be stressed that important variables (such as metal and biomass concentration, pH and ionic strength) are not taken into account in such models.

There are many equilibrium models, which incorporate metal ion concentration, pH, ionic strength, and biomass swelling [110,111]. One of them is the two-site model for predicting ion-exchange and pH effect [112]. This model is based on the fact that in the ion-exchange process, $2H^+$ ions are released from previously protonated biomass for each divalent metal ion bound. The two-site ion-exchange model assumes two types of binding sites, carboxyl (C) and sulfate (S) groups, to be present in the biomass. Considering metal and proton binding on these two sites, Schiewer and Volesky [109] derived an isotherm equation that is able to predict the binding of protons and metal ions as a function of metal concentration and pH:

$$qH = C_t(K_{CH}[H])/(1 + K_{CH}[H] + (K_{CM}[M])^{0.5}) + S_t(K_{SH}[H])/(1 + K_{SH}[H] + (K_{SM}[M])^{0.5}), \quad (4.13)$$

$$qM = C_t(K_{CM}[M]^{0.5})/(1 + K_{CH}[H] + (K_{CM}[M])^{0.5}) + S_t(K_{SM}[M]^{0.5})/(1 + K_{SH}[H] + (K_{SM}[M])^{0.5}), \quad (4.14)$$

where C_t and S_t are the total number of carboxylic and sulfate sites, respectively. Constants K_{CH} and K_{SH} are equal to $10^{4.8}$ (pK_a for carboxyl group, 4.8) and $10^{2.5}$ (pK_a for sulfate group, 2.5) [110]. K_{CM} and K_{SM} represent metal-binding constants for the binding of metal (M) on carboxyl and sulfate groups, respectively. qH and qM represent proton and metal uptake, respectively, by biosorbent. Values of C_t and S_t need to be determined for different algal biosorbents. Constants K_{CH} and K_{SH} can be used for binding any metal on a biosorbent. Parameters K_{CM} and K_{SM} have to be determined for binding individual metal. Although the applicability of this model has not been tested other than by its developer, Schiewer [110] pointed out that being pH sensitive, the two-site model could successfully predict the binding of both protons and metal at different pH values and metal concentrations. Because the two-site model considers the effect of pH and proton binding, it has a better predictive power than the Langmuir model.

4.4.2 METAL BIOSORPTION BY CYANOBACTERIA IN MULTIMETAL SOLUTIONS

Many industrial waste waters contain high concentrations of several different metal ions. For instance, the waste water arising from a fur cleaning and dyeing industry has been shown to contain 7.04, 20.14, 0.17, 1.73, and 0.12 mg L⁻¹ of Cu, Cr, Ni, Zn, and Cd, respectively [113]. Similarly, Cr and Cu are frequently encountered together in industrial waste waters, for example, from mining, metal cleaning, plating, electroplating, metal processing, dyeing, and oil industries. In metal cleaning, plating, and metal processing industries, Cu and Cr concentrations may approach 100–120 mg L⁻¹ and 10–270 g L⁻¹, respectively [114]. Effluents from mining operations have Cu, Zn, Pb, Cr, As, and Se together [115]. Cr, Ni, Cd, and Zn are reported to occur together in effluents generated during electroplating operations [115]. Most of the industrial effluents have high concentrations of Al along with other metal ions. Although Al is not a major environmental problem, its ubiquitous presence in solution interferes with the sorption of many other metals [116]. While the accumulation of single species of heavy metal ions by cyanobacterial biomass has been extensively studied, less attention was given to the study of multimetal solutions. The presence of a multiplicity of metals leads to interactive effects on physiological and biochemical processes and on the growth and metal uptake of various organisms [117]. Studies on multimetal systems clearly revealed that sorption may be species and metal specific as well as variable in single- and multimetal solutions, showing, in most cases, competitive interactions among metals for the binding on sorption sites.

Singh et al. [62] examined the competitive biosorption of Pb^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} in single, bi-, tri-, and multimetal mixtures by using as biosorbents biomasses derived from field-grown and laboratory-grown *Microcystis* cultures. In single-metal solutions, the cyanobacterial strains exhibited the following order of metal biosorption: $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$. In sharp contrast, the biosorption of Cd was greater than Zn in tri- and multimetal solutions. All bimetal and trimetal solutions tested with any of the biomass showed antagonistic behavior for Cu, Zn, and Cd biosorption, resulting in a 12–49% reduction in the amount of metal uptake in comparison with removal in single-metal solutions. In multimetal biosorption tests, the decrease ranged from 33.8% to 59% in comparison with the single-metal systems. It has to be stressed that the biosorption of Pb was less affected, or not affected at all, by the presence of other metals [62].

Pradhan and Rai [88] provided information on the biosorption of Cu, Zn, and Cd by *Microcystis* sp. in single-, bi-, and trimetal solutions. The highest biosorption was observed for Cu, followed by Zn and Cd, both in single- and in multimetal solutions. This observation was confirmed by the Freundlich adsorption isotherm: Cu showed the highest K_f value ($K_f = 45.18$), followed by Zn ($K_f = 16.71$) and Cd ($K_f = 15.63$) in single-metal solutions. The decrease in Cu, Zn, and Cd biosorption observed in bi- and trimetal solutions suggested the presence of a competition among metal ions for binding sites on the cell surface [88].

The next study on *Microcystis* sp. demonstrated that this cyanobacterium possesses the highest affinity for Fe, followed by Ni and Cr, in single-, bi-, and trimetal solutions [68]. Fe was not only preferentially adsorbed from trimetal solutions, but the presence of the other two metals did not cause any decrease in its biosorption. The experimental data of Fe biosorption fitted well in the Langmuir model, suggesting monolayer sorption and the existence of a constant sorption energy under the experimental conditions utilized. Maximum Fe, Ni, and Cr uptake, at the equilibrium concentration, was 240, 100, and 65 mg (g dry wt)⁻¹, respectively. Fe biosorption was not much affected by Ni and Cr in bi- and trimetal solutions. In contrast, Ni biosorption decreased in multimetal in comparison with single-metal solutions. The presence of Ni and Cr did not affect Fe sorption, whereas the presence of Fe reduced Ni and Cr sorption. Interestingly, in contrast with Fe and Ni biosorption, Cr biosorption increased in trimetal solutions of Cr–Ni–Fe in comparison with Cr–Ni solutions [68].

Parker et al. [89] demonstrated that the order in which metals are added to solutions may play an important role in the biosorption capacity exhibited by the biosorbent. In this study, the sorption of cadmium, copper, lead, manganese, and zinc by purified capsular polysaccharide from the cyanobacterium *M. aeruginosa* f. *flos-aquae* strain C3-40 was evaluated. Competition between bimetal solutions was tested with simultaneous and sequential additions of metal. The results showed that cadmium and lead, as well as lead and zinc, competed relatively equally and reciprocally for polymer-binding sites. In contrast, manganese strongly inhibited the binding of cadmium and lead, but was itself not substantially inhibited by either the prior or simultaneous adsorption of cadmium or lead. This result suggests that manganese can indirectly affect the access of lead and cadmium to their sites, perhaps causing an altered polymer conformation or a cross-linking [89].

Another way to study biosorbent behavior in multimetal solutions is to consider the total amount of metal ions sorbed in these conditions and to compare this result with the highest q value obtained in single metal solutions. Micheletti et al. [74] tested nine EPS-producing cyanobacteria for their ability to remove Cr, Cu, and Ni in both single- and multimetal solutions. The comparison between the total number of millimoles of the three metals adsorbed per gram of dry biomass in multimetal solutions and the number of millimoles of the metal removed with the highest q value in single-metal solutions (usually Cu) pointed out different behaviors among the cyanobacterial strains. Two strains removed the same millimoles of metals in single- and trimetal solutions, showing noninteractive action between the metal ions, which seem to progressively saturate the available binding sites on the biomass without any preferential order and without any reciprocal hindrance. Four strains showed antagonistic action between metal ions, which was explained by hypothesizing the setting up of competitive interaction among metals for the binding sites on the biomass. In the other three

strains, a synergistic action between metals was observed, which caused an increase in the global amount of metal ions adsorbed. This behavior was explained by hypothesizing that the sorption on the biomass of ions with the highest affinity has induced a modification of the specific binding sites for ions with the lowest affinity, increasing their sorption capability.

The above reported studies clearly point out that the sorption process by cyanobacterial biomass can be species and metal specific and variable in the single- and multimetal solutions, the combined effects of two or more metals on the metal uptake capability of the microorganisms depending on the number of metals competing for binding sites, metal combination, levels of metal concentration, order of metal addition, and also on the surface-specific properties of the biosorbent utilized.

4.4.3 SELECTIVITY IN METAL REMOVAL IN MULTIMETAL SOLUTIONS

One of the difficulties most frequently faced in the removal of heavy metals from industrial waste waters is connected with the possible contemporaneous presence of different metal ions in the waste stream that has to be treated. This situation may have significant consequences on the treatment of heavy metal-containing waste waters, because the presence of several different metals can reduce the capability of the biosorbent to take up the desired element. Recent research in the area of heavy metal removal from waste waters and sediments has focused on the development of biomaterials with increased affinity, capacity, and selectivity for target metals.

As stated earlier, many functional groups, such as hydroxyl, phosphoryl, amino, carboxyl, sulfhydryl, and so on, present on the cell surface or on exocellular structures, may confer negative charge on the cells, giving them the capability of binding metal cations in solution (see [Section 4.1.3](#)).

The affinity of various cyanobacterial species for binding to metal ions shows different hierarchies. In general, metal ions with greater electronegativity and smaller ionic radii are preferentially sorbed by algal biomass. In most cases, the lowest affinity was found for Ni, with the exception of *M. aeruginosa*, which possesses a very high Ni sorption capability [96].

In a screening carried out with nine exopolysaccharide-producing cyanobacteria tested with the aim of assessing their capability of selectively removing Cu, Cr, or Ni, an interesting behavior was observed for the strain *Nostoc* PCC 7936 [74]. In the trimetal solutions, this strain removed Cu at the same q value observed in the absence of Cr and Ni, showing a very high selectivity of its binding sites for copper. The metal affinity of the nine cyanobacteria tested generally decreased in the order $\text{Cu} > \text{Cr} > \text{Ni}$. The specific metal uptake was, for some of the strains, very high, in particular toward copper and chromium. Another strain, *Cyanothece* 16Som 2, showed a very high affinity for both Cu and Cr, either in single or in trimetal solutions, while the q value for Ni dramatically decreased in the presence of the other two metals, pointing out a selective affinity of the cultures of this strain for Cu and Cr. 16Som 2 can be considered a very promising biosorbent for the selective removal of Cu and Cr from aqueous solutions, having shown q values toward these two metals that are among the highest so far reported for other cyanobacteria and microorganisms [62,72,73].

Also, *Microcystis* showed high affinity for Cu in bi- and trimetal solutions, probably due to the existence of a greater number of active sites with high specificity for this metal [61]. Biosorption of Cu and Cd from Cu–Cd solutions indicated a greater affinity for Cu and a strong inhibition of Cd biosorption caused by the presence of Cu. High-affinity sites only include carboxyl groups, which are rapidly occupied by Cu [61]. In a subsequent study, *Microcystis* has been tested with Fe, Ni, and Cr in single-, bi-, and trimetal solutions [68]. This study demonstrated that the specific metal uptake of *Microcystis* was greatest with Fe, followed by Ni and Cr. IR spectroscopy, utilized to determine the functional groups present on the surface of *Microcystis*, pointed out the role of a large number of —COO^- groups and of a limited number of amino groups in the metal removal process. Extra peaks present in the spectra obtained with the cells analyzed after the contact with Ni and Cr suggested that amino groups were responsible for Ni and Cr biosorption, whereas carboxyl groups were responsible for Fe biosorption. This study suggests the excellent biosorption potential of naturally

abundant and cheap microbial biomass, which can be successfully and economically used in the selective removal of Fe from waste waters.

Singh et al. [62], using the technique of differential pulsed anodic stripping voltammetry, showed a significant difference in Pb, Cu, Zn, and Cd binding efficiencies of the macrophyte *Lemna*, of the colonial cyanobacterium *Microcystis*, and of the filamentous green alga *Spirogyra*. The order of metal biosorption was $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$. Differences in metal biosorption efficiencies were due to the presence of various functional groups on the surface of the biosorbents, which were identified by IR spectra. In this work, it was also demonstrated that the binding process of different metal ions on biomaterials having different functional groups depends on the properties of the metals (electronegativity, ionization potential, ionic radius, and redox potential). It was suggested that the higher the electronegativity of a metal, the higher its affinity toward negatively charged sorbents, as indicated by the smaller uptake of Cu (electronegativity 1.75, Pauling scale) in comparison with Pb (electronegativity 1.8, Pauling scale). Tobin et al. [13] suggested that ions with smaller ionic radii can be more quickly sorbed onto a fixed surface area of sorbent.

Parker et al. [65], using bi- and trimetal solutions of Cd, Cu, Mn, Pb, and Zn, showed that the order in which metals are added in water solution (simultaneously or with subsequent additions) may influence the affinity and selectivity of biosorbent toward metals. These authors showed that lead and cadmium, at saturation conditions, compete fairly equally for similar or overlapping sites on the capsular polysaccharide. On the other hand, roughly 80% of the manganese-binding sites on the capsule are not the same as, or overlap substantially with, those of lead or cadmium. This effect was explained by suggesting that manganese indirectly affects the access of lead and cadmium to their sites, perhaps by means of an alteration of the polymer conformation or by a cross-linking of the binding sites. Similar phenomena, involving conformational changes, cation bridging, and modified solvation, have been invoked to explain the effects of these same metals on the viscosity of the capsular polysaccharide produced by strain C3-40 [70]. De Philippis et al. [64] tested the metal removal capacity of the cultures of two exopolysaccharide-producing cyanobacteria, *Cyanospira capsulata* and *Nostoc* PCC7936. Part of this study focused on the interference of Zn(II) and Ni(II) ions with copper removal. Both cyanobacteria removed metals from the multimetal solutions containing Cu, Zn, and Ni, but copper was removed in larger amounts than Zn or Ni, showing a great degree of affinity toward this ion.

4.5 FIELD APPLICATIONS: CASE STUDIES

In the literature, a large number of studies on the metal sorption carried out by microbial biomasses operating under laboratory conditions in single-metal systems are available. On the other hand, only a limited number of studies have been dedicated to the competitive interactions occurring among metals when the microbial biomass operates in multimetal solutions (see [Section 4.4](#)), even if these systems are very similar to what occurs in many kinds of industrial wastes. These studies were mostly dedicated to testing metal bioremoval operating in pure multimetal solutions under well-controlled, laboratory conditions, whereas very few studies have been dedicated to metal bioremoval from real industrial waste waters by using microbial biomass. In particular, the use of cyanobacteria for metal uptake from industrial waste waters was almost completely neglected, and only in the last few years a limited number of patents for this application have been reported (for a review of the U.S. patents, see [118]), together with some preliminary case studies.

4.5.1 CASE STUDY 1: *CYANOSPIRA CAPSULATA* FOR THE REMOVAL OF METALS FROM INDUSTRIAL WASTE WATERS

The EPS-producing filamentous, heterocystous cyanobacterium *C. capsulata* was tested with regard to its capability of removing heavy metals from two kinds of industrial waste waters [119]. The experiments were carried out with the percolate of two different industrial solid wastes stored

TABLE 4.3
Metal Composition of the Percolates of Two Wastes Derived from Industrial Fermentations Utilized for Experiments of Biosorption with the EPS-Producing Cyanobacterium *Cyanospira capsulata*

Metal	Metal Concentration (mg L ⁻¹)	
	Waste Water A	Waste Water B
Ba	1.87	1.39
Cr	1.60	3.84
Mn	6.54	6.32
Fe	44.00	57.10
Ni	0.61	0.80
Al	8.99	27.40
Cu	Not present	9.39
Pb	Not present	6.49
Zn	Not present	6.54
Hg	Not present	5.20

Source: De Philippis et al., In: *Proceedings of the European Symposium on Environmental Biotechnology*, Verstraete, W., Ed., A.A. Balkema Publishers, Leiden, pp. 459–462, 2004.

outdoors for several months. The two percolates, named A and B by the authors, contained respectively six and ten different metals at various concentrations, ranging from less than 1 to about 60 mg L⁻¹ (Table 4.3), and were characterized by COD values of about 12–15,000 mg L⁻¹. For carrying out the tests, various amounts of fresh biomass of the cyanobacterium, obtained from the centrifugation of cultures carried out under laboratory conditions, were directly suspended into the waste water at pH 5.5. When the biomass of *C. capsulata* was suspended, at a concentration of 140 mg (dry weight) L⁻¹, into waste water A, a reduction of about 60% of the initial concentration of each metal was observed, with the exception of Ba, which showed a reduction of about 40%. An increase in the biomass concentration, up to 190 and 280 mg (dry weight) L⁻¹, increased the global amount of metals removed. However, the correlation between the increase in the amount of biosorbent and the increase in metal removal was not linear, a phenomenon that was explained by hypothesizing an increase in the competitive interactions among the binding sites due to their increased proximity. For increasing the effectiveness of the treatment, the authors treated the waste water using three consecutive cycles carried out with small amounts of fresh cyanobacterial biomass operating on the same water sample. After the second cycle, the amount of metals removed reached values of about 80–90% of the amount present before the biological treatment, and after the third cycle, the removal reached values corresponding to about 95–97% of the initial metal concentrations, thus demonstrating the good efficiency of *C. capsulata* in the biosorption of metals contained in waste water A. Among the metals present, the highest value of specific metal uptake was observed for iron (20.4 mg of Fe removed per gram of biomass dry weight).

Better results were obtained when *C. capsulata* was utilized for the removal of heavy metals from waste water B. Under this condition, the amount of metals removed at the end of the first cycle already reached values higher than 80% of the initial metal concentration. After the second cycle, the removal attained values higher than 97% for each metal, thus demonstrating that the system was very efficient, in spite of the presence of a large number of different metals. In such a complex system, the highest value of specific metal uptake was again found for iron, with a value of 24.8 mg Fe (g biomass dry wt)⁻¹.

4.5.2 CASE STUDY 2: EPS-PRODUCING CYANOBACTERIA FOR THE REMOVAL OF Cr(VI) FROM WASTE WATERS OF PLATING INDUSTRIES

The aim of this experimentation was assessment of the capability of some EPS-producing cyanobacteria to remove chromate from the waste waters of a plating industry in laboratory and in semipilot devices (Colica, 2009). A preliminary screening, carried out under laboratory conditions with seven EPS-producing cyanobacteria, pointed out the good efficiency of one *Nostoc* strain for the removal of chromate from waste waters of a plating industry. In laboratory experiments, a complex role of the cyanobacterial biomass of this strain in the removal of Cr(VI) was observed: the cells, when subjected to treatments removing the external polysaccharidic structures, carried out the reduction of Cr(VI) to Cr(III), while the polysaccharidic fraction, previously released and solubilized by cells in the culture medium, was capable of removing the Cr(III) cations formed in the reduction process. This behavior was confirmed in field experiments carried out with the cyanobacterial biomass confined to three different experimental devices (a filter press, a filter column, and a dialysis membrane system) and operating with 50 L of Cr(VI)-containing waste waters of a plating industry. The results obtained, presented at the last Congress of the International Society for Applied Phycology held in Galway, Ireland, in June 2008, showed the potential of using EPS-producing cyanobacteria in the removal of heavy metals present in anionic form in water solutions.

4.6 CONCLUSIONS

The above reported results, obtained by a large number of research groups utilizing cyanobacterial biomass for the removal of heavy metals from water solutions, pointed out very promising performances for some of the species tested. In particular, some of the EPS-producing cyanobacteria showed a very high uptake of positively charged metal ions in comparison with other microbial sorbents previously utilized. For instance, the results obtained in the removal of copper ions with the cultures of *Cyanothece* 16Som 2, a unicellular cyanobacterium characterized by a thick polysaccharidic capsule surrounding the cells (Figure 4.7), were the highest so far reported for bacterial, algal, and fungal biosorbents (Table 4.4).

However, as is evident from Section 4.5, very few case studies have been published, showing that this kind of biomass is still far from being utilized at the industrial level in the treatment of waste waters containing heavy metals. Two main reasons can be suggested to explain this situation: (i) the

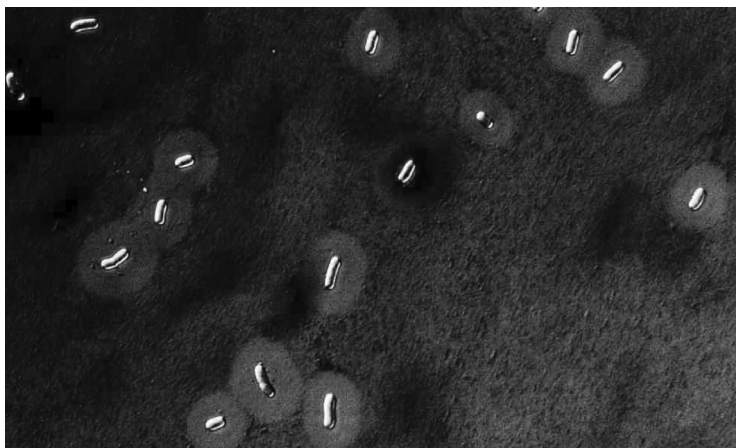


FIGURE 4.7 Nomarski differential interference contrast photomicrographs of the capsulated strain *Cyanothece* 16Som 2 stained with India ink (scale bar = 10 μ m).

TABLE 4.4
Comparison of the Best Results Obtained in the
Bioremoval of Cu with Microorganisms and Macroalgae

Species	$q_{\max}$ (mg g ⁻¹)	References
<i>Cyanothece</i> 16Som 2	201	[74]
<i>Spirulina</i> sp.	196	[72]
<i>Oscillatoria</i> sp.	165	[95]
<i>Arthrobacter</i> sp.	148	[120]
<i>Cyanospira capsulata</i>	143	[74]
<i>Sargassum</i> sp.	140	[27]
<i>Candida tropicalis</i>	107	[55]

production costs of cyanobacterial biomass, which are still too high to be attractive for industrial applications of this kind of biosorbent, and (ii) a lack of research oriented to the setting up of a suitable device that could be profitably used with exopolysaccharide-producing cyanobacteria for metal bioremoval. A possible solution of the former problem may reside in the use of bloom-derived biomass, which is freely available at no production cost. Indeed, in many water bodies there is a periodic unrestrained growth of microalgal and cyanobacterial blooms due to the introduction of inorganic nutrients into the environment. Recently, preliminary experiments carried out by our research group together with the group headed by Professor Liu Yong ding (Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, China) on the use of bloom-derived biomass withdrawn from Lake Dian Chi, Yunnan Province, China, showed a promising capability of this biomaterial to act as sorbent toward metals in aqueous solutions. Studies are now in progress for the optimization of operational conditions. Another interesting development that could attract interest in the use of EPS-producing cyanobacterial biomass is the use of this biosorbent for the recovery of metals with high economical value such as gold, ruthenium, palladium, copper, and so on. In this connection, our research group is carrying out a study with a large number of EPS-producing cyanobacterial strains for the removal of these valuable metals from waste waters and for finding the best conditions for recovering the metals from the biomass.

As a general conclusion, it is possible to say that interactions between cyanobacteria and metals are very complex, depending on a large number of factors that are related to the chemical and morphological features of microbial cells, to the chemical and physical properties of metals to be removed, and to the operational conditions utilized in the treatment. For these reasons, the selectivity, a characteristic that may have great interest for many industrial applications, as well as the good metal uptake capability shown by some of the cyanobacteria tested in the laboratory must be confirmed under conditions reproducing the specific industrial application that is of interest. In any case, the promising results so far obtained, the increase in the prices of chemical products, the possibility of using free cyanobacterial biomass derived from microalgal blooms, and the increasing public perception of the interest in using green biotechnologies for the resolution of problems derived from the pollution of water bodies seem to open up new perspectives in the use of cyanobacteria for the removal of heavy metals from waste waters.

ACKNOWLEDGMENTS

The authors gratefully acknowledge all the members of the research group operating at the Department of Agricultural Biotechnology of the University of Florence (Dr Giovanni Colica and the graduate/undergraduate students Giacomo Bertini, Pier Cesare Mecarozzi, Simone Petreni, and

Federico Rossi) for their enthusiastic activity in the laboratory and in the field, which made it possible to obtain the unpublished results mentioned in this review. The authors also thank Dr Claudio Sili (ISE, CNR, Firenze, Italy) for some of the photomicrographs shown in this chapter, Federico Rossi for his contribution in editing the manuscript, and Ente Cassa di Risparmio di Firenze, which supported, in the framework of the *Firenze Hydrolab* project, the purchase of the culture devices and analytical instruments utilized for all the research that was carried out at the Department of Agricultural Biotechnology.

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5 Environmental Geochemistry of High-Arsenic Aquifer Systems

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5.1 INTRODUCTION

Arsenic (As) is a carcinogenic, mutagenic, and teratogenic element [1]. Most As compounds are odorless and tasteless and readily dissolve in water. As poisoning can cause skin diseases, cardiovascular, neurological, hematological, renal, and respiratory diseases, as well as lung, bladder, liver, kidney, and prostate cancers [2]. The World Health Organization (WHO) has set a provisional guideline limit of 10 $\mu\text{g/L}$ for As in drinking water [3], which was subsequently adopted by the European Union [4]. United States Environmental Protection Agency (U.S. EPA) lowered the maximum contaminant level (MCL) for As in drinking water from 50 to 10 $\mu\text{g/L}$, effective in January 2006 [5]. The provisional guideline value for As concentration in drinking water of China has been lowered from 50 to the WHO's recommendation of 10 $\mu\text{g/L}$ since 2007. In Bangladesh and India, the guideline value for As in drinking water is still 50 $\mu\text{g/L}$.

As is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activities, and volcanic emissions as well as through a range of anthropogenic activities such as mining and pesticide production. Most waterborne As problems, however, are the result of As mobilization in shallow aquifers under natural conditions, in different parts of the world [6]. In Asia, for example, the presence of elevated concentrations of As in groundwaters has become a major threat to the health of people in Bangladesh, India [7–10], China [11–19], Vietnam [20–23], Cambodia [24–25], Nepal [26], Pakistan [27], and Indonesia [28].

To assess the environmental and toxicological effects of As, it is important to ascertain the source of As in groundwaters and to understand its geochemical behavior in aquifers. In this chapter, we will first review the fundamentals of As geochemistry that control the abundance, aqueous speciation, mineralogy, and geochemical behavior of As in groundwater. The complex controls that govern As mobilization and transport in groundwaters in South and Southeast Asia and northern China are then discussed. More detailed information about the hydrogeochemistry of As can be found in a series of previous publications as well [6,29–35,37].

5.2 OCCURRENCE, DISTRIBUTION, AND SOURCE OF As IN THE NATURAL ENVIRONMENT

5.2.1 OCCURRENCE AND DISTRIBUTION OF As IN ROCKS, SEDIMENTS, AND SOILS

As is a natural constituent of the Earth's crust and ranks 20th in abundance in relation to the other elements, with an average As content in continental crust varying between 2 and 3 mg/kg [29]. As is found in more than 200 minerals, which include arsenates (60%), sulfides, and sulfosalts (20%), and minor amounts of arsenides, arsenates, oxides, silicates, and As in its native form [34].

As occurs at crustal concentrations in many rock-forming minerals because it can substitute for Si^{4+} , Al^{3+} , Fe^{3+} , and Ti^{4+} in their structures [6]. Major As-containing primary minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3). Realgar (As_4S_4) and orpiment (As_2S_3) are the two common reduced forms of As. As occurs in oxidized form in the mineral arsenolite (As_2O_3). Other naturally occurring As-bearing minerals include loellingite (FeAs_2), saffrolite (CoAs), niccolite (NiAs), rammelsbergite (NiAs_2), arsenopyrite (FeAsS), cobaltite (CoAsS), enargite (Cu_3AsS_4), gersdorffite (NiAsS), glaucodot ($(\text{Co,Fe})\text{AsS}$), and elemental As [35].

Interaction of groundwater with host rocks drives the multiphase cycling of As in aquifer systems. Typical concentrations of As in crustal rocks are presented in Table 5.1. Relative to igneous rocks, As concentrations are significantly higher in fine-grained and organic-rich sedimentary rocks and their metamorphic equivalents. As concentrations in sedimentary rocks can be more variable. The highest As concentrations (20–200 mg/kg) are typically found in organic- and sulfide-rich shales, sedimentary ironstones, phosphate rocks, and some coals [6]. Although As concentrations in coals can reach up to 3.5×10^4 mg/kg, concentrations in the range from <1 to 17 mg/kg are more typical [36].

TABLE 5.1
Natural Abundance of As (mg/kg) in Crustal Materials

Rock Type	As Concentration Average (and/or Range)
Igneous rocks	
Ultrabasics	1.5 (0.03–15.8)
Basalts	2.3 (0.18–113)
Andesites	2.7 (0.5–5.8)
Granites/silicic rocks	1.3 (0.2–13.8)
Sedimentary rocks	
Shales and clays	3–15 (up to 490)
Phosphorites	21 (0.4–188)
Sandstones	4.1 (0.6–120)
Limestones/dolomite	2.6 (0.1–20.1)
Iron formations and Fe-rich sediment	(1–2900)
Evaporites (gypsum and anhydrite)	3.5 (0.1–10)
Metamorphic rocks	
Quartzite	5.5 (2.2–7.6)
Hornfels	5.5 (0.7–11)
Phyllite/slate	18 (0.5–143)
Schist/gneiss	1.1 (<0.1–18.5)
Amphibolite and greenstone	6.3 (0.4–45)
Coal	
Bituminous ^a	9.0 ± 0.8
Lignites ^a	7.4 ± 1.4
Peat	(16–340)

Source: Modified from Smedley, P.L. and Kinniburgh, D.G. *Appl. Geochem.*, 17, 517–568, 2002 and Nriagu, J.O. et al., In: Bhattacharya, P. et al., (Eds), *Trace Metals and Other Contaminants in the Environment*, Vol. 9, pp. 3–60. Elsevier, 2007.

Note: Coal Clarke value of As.

^a Yudovich, Y.E. and Ketris, M.P., *Int. J. Coal Geol.*, 61, 141–196, 2005.

In sedimentary rocks, As is concentrated in clays and other fine-grained sediments, especially those rich in sulfide minerals, organic matter (OM), secondary iron oxides, and phosphates. The average concentration of As in shale is an order of magnitude greater than that in sandstone, limestone, and carbonate rocks. As is strongly sorbed by oxides of iron, aluminum, and manganese as well as by some clay minerals, leading to its enrichment in ferromanganese nodules and manganese deposits.

Alluvial sands, glacial till, and lake sediments typically contain <1–15 mg/kg As. Stream sediments from England and Wales had a median As concentration of 10 mg/kg [39]. The median As concentration in stream sediments from 20 study areas across the United States collected as part of the National Water Quality Assessment (NAWQA) program was 6.3 mg/kg [40]. The As concentration in soils shows a range similar to that in sediments, except in places contaminated by industrial or agricultural activities.

5.2.2 OCCURRENCE AND DISTRIBUTION OF AS IN GROUNDWATERS

As is perhaps unique among the heavy metalloids and oxyanion-forming elements such as As, Se, Sb, Mo, V, Cr, U, and Re in its sensitivity to mobilization at the pH values typically found in groundwaters (6.5–8.5) and under both oxidizing and reducing conditions [6].

The concentration of As in most groundwaters is $<10 \mu\text{g/L}$ [41–42] and often below the detection limit of routine analytical methods. A survey of groundwaters used for public supply in the United States showed that only 7.6% exceeded $10 \mu\text{g/L}$ and 64% contained As $<1 \mu\text{g/L}$ [43]. Nonetheless, naturally occurring high-As groundwaters have been found in aquifers in many parts of the world and their As concentrations occasionally reach the mg/L level [6], in a range of four orders of magnitude, from <0.5 to $5,000 \mu\text{g/L}$ [44]. Industrial activities can also give rise to very high dissolved As concentrations in groundwater, but the affected areas are usually localized. For example, Kuhlmeier [45] found concentrations of As up to $4.08 \times 10^5 \mu\text{g/L}$ in groundwater close to a herbicide plant in Texas [45].

Although most high-As groundwater provinces are the result of natural occurrences of As, high concentrations of As have been found in groundwater in different environments. These include both oxidizing and reducing aquifers and areas affected by geothermal, mining, and industrial activities (Table 5.2). Cases of mining-induced As pollution are numerous in the literature, but are mostly localized. As mobilization and enrichment in groundwater are discussed in more detail in [Section 5.4](#).

Reducing conditions favorable for As mobilization have been reported most frequently from Quaternary basins and/or deltaic regions where strong neotectonic processes have resulted in

TABLE 5.2
Concentration Ranges of As in Various Aquifers of the World

Country/Region Location	As Concentration: Average or Range ($\mu\text{g/L}$)	References
Bangladesh	<0.5 –2500	[46]
West Bengal, India	<10 –3700	[9]
China		
Taiwan, Chianan Plain	<10 –1300	[47]
Xinjiang, Tianshan Plain	40–750	[48]
Inner Mongolia, Huhhot Basin	<1 –1480	[17]
Inner Mongolia, western Hetao Plain	76–1093	[18]
Shanxi, Datong Basin	9–1530	[12]
Red River Delta, Vietnam	1–3050	[20]
Mekong Plain, Cambodia	1–1700	[25]
Terai Basin, Nepal	<10 –740	[26]
Kalalanwala area, Punjab, Pakistan	32–1900	[27]
Lowlands of Sumatra, Indonesia	<0.1 –65	[28]
Pannonian Basin, Hungary	0–300	[49]
La Pampa Province, central Argentina	<4 –5300	[44]
Rio Loa (Second Region), northern Chile	100–1000	[50]
Zimapán Valley, Mexico	<50 –1100	[51]
United States		
California, Owens Dry Lake	100–96,000	[52]
Southeast Michigan	0.5–278	[53]
Central New Hampshire	1.95–397.5	[54]
Eastern Wisconsin, Fox River Valley	2–12,000	[55]
Central Arizona, Verde Valley	10–210	[56]
Central Illinois	<1 –266	[57]
Western Nevada	Nondetectable–6000	[58]
Maine, Northport	0.75–1900	[59]
New England	<5 –1100	[60]

continued

TABLE 5.2 (continued)

Country/Region Location	As Concentration: Average or Range (µg/L)	References
Okavango Delta, NW Botswana	1.8–112	[61]
Various areas in Canada	0.5–11,000	[62]
Fukuoka Prefecture, Japan	1–293	[63]
Mineralized area, Bavaria, Germany	<10–150	[64]
Western Anatolia, Turkey	0–10,500	[65]
South-western Uruguay	0.1–58	[66]
Duero Cenozoic Basin, Central Spain	0.42–613.45	[67–68]
Volcanic areas in southern Italy	0.1–6940	[69]
Porphyry Cu deposits, Chile	<10–278	[70]
Coastal sand aquifer, Australia	52–337	[71]

complex patterns of sedimentation and rapid burial of large amounts of sediment containing fresh OM during basin/delta development. Thick sequences of young sediments are quite often the sites of high As concentrations in groundwater. The most notable example of these conditions is the Bengal Basin, which includes Bangladesh and West Bengal [46]. Other examples include Nepal, Myanmar, Cambodia [33], parts of northern China [11–19,72], the Great Hungarian Plain of Hungary and Romania [49,73], the Red River floodplain of Vietnam [20,23], and parts of the western USA [42]. Recent groundwater extraction in many of these areas, either for public supply or for irrigation, has induced an increase in both groundwater flow and As transport in aquifer systems [74].

High concentrations of naturally occurring As are also found in oxidizing conditions where groundwater pH values are high (usually >8) [6]. In such environments, inorganic As(V) predominates and As concentrations are positively correlated with those of other anion-forming species such as HCO_3^- , F^- , H_3BO_3 , and H_2VO_4^- . Examples include San Joaquin Valley, California [75], the Lagunera region of Mexico [76], the Antofagasta area of Chile [50], and the Chaco-Pampean Plain of Argentina [44] (Table 5.2). These high-As groundwater provinces are usually located in arid or semiarid regions where groundwater salinity is high. Evaporation has been suggested to be an important additional cause for As accumulation in groundwater from arid areas [75].

High concentrations of As in groundwater have also been found in areas of hard rocks and polymetallic mines. As concentrations of up to 5000 µg/L have been found in groundwater associated with the former tin-mining activity in the Ron Phibun area of Peninsular Thailand, the source most likely being oxidized arsenopyrite (FeAsS) [77]. Similar cases have been reported in the United States, Canada, Poland, and Austria [6,62,71]. Groundwater As problems in areas of unexploited ore deposits are less common. But Boyle et al. [78] found concentrations up to 580 µg/L in groundwater from the sulfide mineralized areas of Bowen Island, British Columbia [78]. Heinrichs and Udluft [64] also found As concentrations up to 150 µg/L in groundwater from a mineralized sandstone aquifer in Bavaria.

5.2.3 SOURCE AND BIOGEOCHEMICAL CYCLE OF AS IN THE ENVIRONMENT

As is ubiquitous in different compartments of the ecosystem, as is shown in Figure 5.1. The most common primary sources of As in the natural environment are volcanic rocks, marine sedimentary rocks, hydrothermal ore deposits and associated geothermal waters, and fossil fuels [6]. As is released from these sources into the environment through various natural processes such as weathering, volcanic eruption, geothermal activity, and forest fires. Wind-blown dust and seasalt spray may transport As over long distances as suspended particulates or gases through the atmosphere.

The conceptual model for biogeochemical cycling of As species in the environment is shown in Figure 5.2. The occurrence of As in natural water is dependent on the geology, hydrogeology,

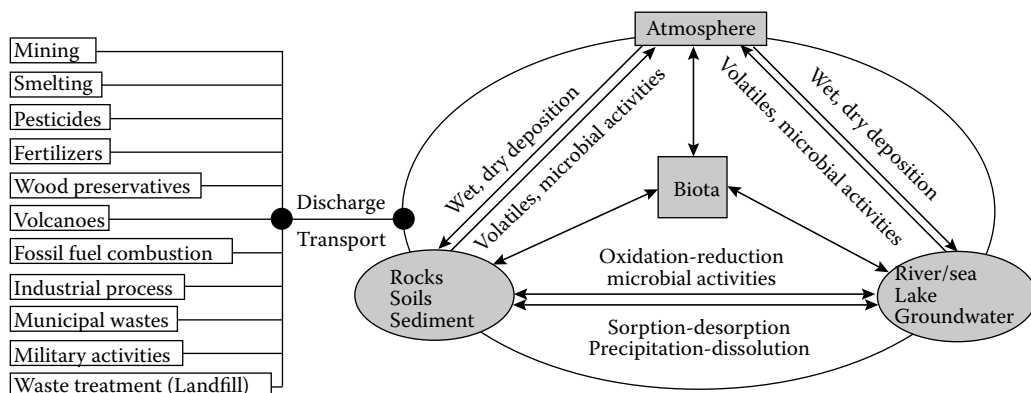


FIGURE 5.1 Sources and distribution pathways for As in the environment. (Modified from Wang, S.L. and Mulligan, C.N., *Sci. Total Environ.*, 366, 701–721, 2006.)

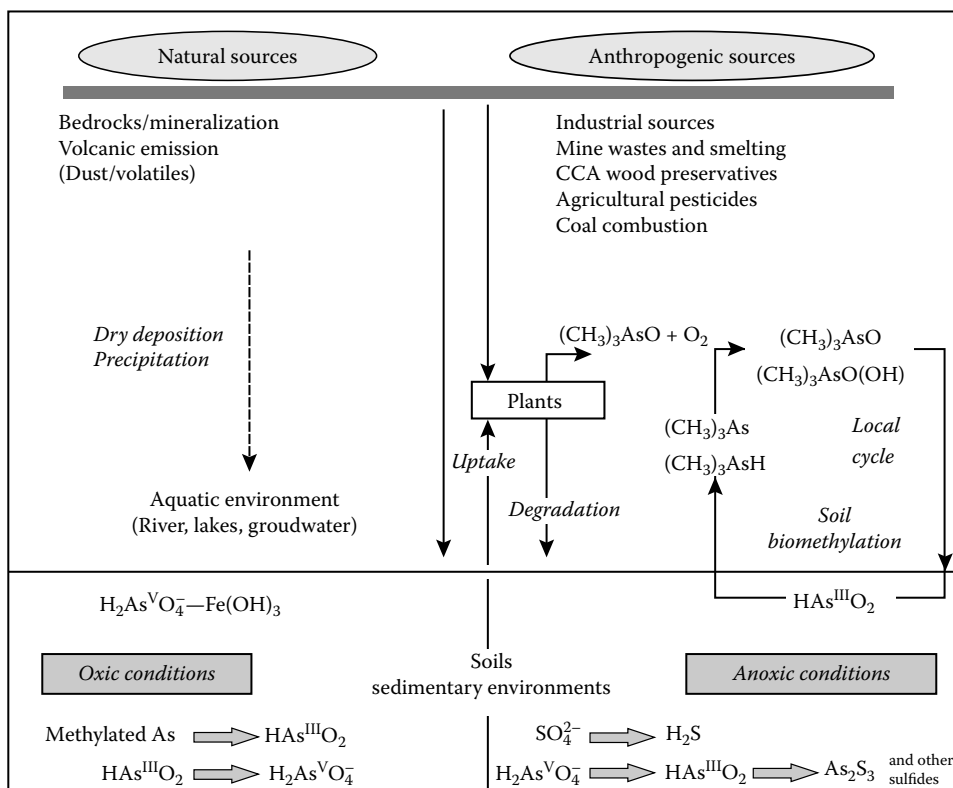


FIGURE 5.2 Conceptual model of As biogeochemical cycling in the environment. (Modified from Nriagu, J.O. et al., In: Bhattacharya, P. et al. (Eds), *Trace Metals and Other Contaminants in the Environment*, Vol. 9, pp. 3–60. Elsevier, 2007.)

and geochemistry of the aquifer, climate conditions, and human activities. Natural sources of As in water have been attributed to several natural geochemical processes, including oxidation of As-bearing sulfides, desorption of As from (hydro)oxides (e.g., iron, aluminum, and manganese oxides), reductive dissolution of As-bearing iron (hydro)oxides, release of As from geothermal water, and evaporative concentration, as well as leaching of As from sulfides by carbonates [6,79].

5.3 As SPECIES IN NATURAL WATERS

There are four valence states (−3, 0, +3, and +5) of As. Metallic As rarely occurs and the (−III) oxidation state is found only in extremely reduced environment. Arsenate ions (As(V)) occur under aerobic conditions, whereas arsenite ions (As(III)) occur in anaerobic environments. Methylated As species, such as monomethylarsonous acid (MMA(III)), monomethylarsonic acid (MMA(V)), dimethylarsinous acid (DMA(III)), dimethylarsinic (DMA(V)), trimethylarsine (TMA(III)), and trimethylarsenic oxide (TMAO), can be formed through biomethylation by microorganisms under favorable conditions [29,80]. Arsenobetaine and arsenosugar occur commonly in marine animals and show no potential toxicity at any dose [81]. Generally, inorganic forms are more toxic than organoarsenic species, while arsenite is considered to be more toxic than arsenate.

Inorganic speciation is important since the varying protonation and charge of the As species present at different oxidation states have a strong effect on their behavior, for example, their adsorption [6]. By contrast, the concentrations of organic As species are generally low or negligible in most groundwaters [82]. For instance, Bednar et al. [83] tested various As species in more than 100 surface water, groundwater, and acid mine drainage samples, and found that methylated As species concentrations were less than 100 µg/L and were detected only in some surface water samples [83].

The mobility of As in groundwater environment is usually controlled by redox conditions, pH, biological activity, and adsorption–desorption reactions, rather than solubility control of As. Factors such as pH, Eh (thermodynamic redox potential), solution composition, competing and complexing ions, mineralogy, reaction kinetics, and hydraulics of aquifer systems can all potentially affect As speciation and concentrations. The major As species in groundwater are inorganic arsenite (As(III)) and arsenate (As(V)). Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (less than about pH 6.9), whereas at higher pH, HAsO_4^{2-} becomes dominant (H_3AsO_4^0 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions, respectively). Under reducing conditions at pH less than 9.2, the uncharged arsenite species H_3AsO_3^0 will predominate [84,85] (Figure 5.3). The distribution of the species as a function of pH is shown in Figure 5.4.

The Eh–pH diagrams for the As–O–S system are useful, since they necessarily simplify highly complex natural systems. In practice, most studies in the literature report speciation data without consideration of the degree of protonation. In the presence of extremely high concentrations of reduced S, dissolved As-sulfide species can be significant. In sulfide-concentrated solutions, dissolved thioarsenic species such as $\text{H}_2\text{AsOS}_2^-$ and H_2AsS_3^- can be formed under near-neutral to alkaline conditions [87]. Reducing and acidic conditions favor the precipitation of orpiment (As_2S_3), realgar (As_4S_4), or other sulfide minerals containing coprecipitated As [29]. Therefore high-As waters are not expected where there is a high concentration of free sulfide [88]. In reducing waters containing free sulfide, a large fraction of the dissolved As can be present in the form of soluble As–S compounds [89]. Four currently unidentified As–S species encountered are probably monomeric thioarsenites or thioarsenates, which have been found to play a key role in the dissolution of As-sulfide minerals under alkaline conditions [89].

Sulfur and iron play important roles in influencing As speciation and its transport. As has a high adsorption affinity on iron oxides. Sulfides can be a source or sink for As under different conditions [42]. Dissolution of sulfide minerals or iron oxides may contribute As to groundwater. The precipitation of sulfide minerals, which can occur in sulfide-rich water or sorption by iron oxides, can in turn remove As from water.

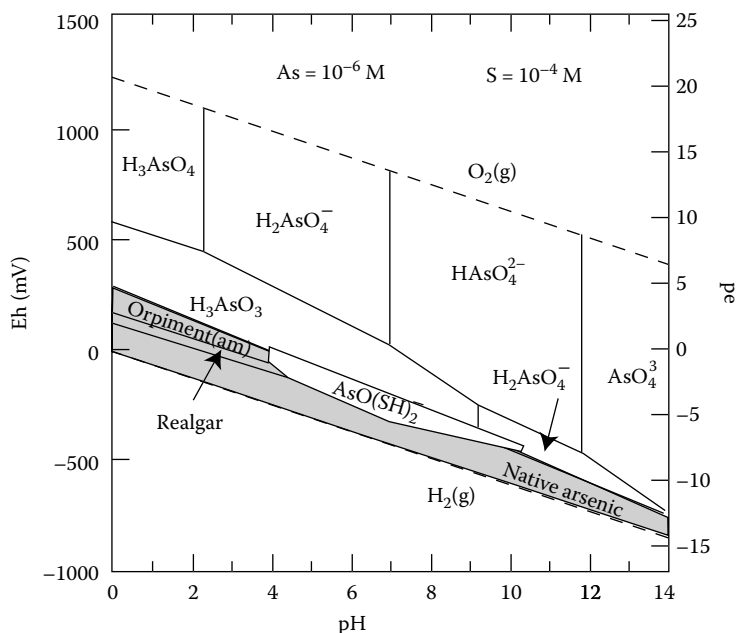


FIGURE 5.3 Eh–pH stability diagram for the As–O–S system at 25°C and 1 bar total pressure. The dashed lines indicate stability field for water. The gray area represents a solid phase. (Modified from Plant, J.A. et al., In: Holland, H.D. and Turekian, K.K. (Eds), *Treatise on Geochemistry*, Chapter 9.02, pp. 17–66. Elsevier, 2004.)

The Eh–pH diagram for the As–Fe–S–O–H₂O system is shown in Figure 5.5. It can be seen that an overwhelmingly large field exists for the ionic arsenate and arsenite species, but mostly combined with hematite (Fe₂O₃). Under reducing alkaline conditions, realgar (As₂S₂) coexists with magnetite (Fe₃O₄), whereas arsenopyrite (FeAsS), the most common mineral of As, is stable only under extremely reducing and alkaline conditions.

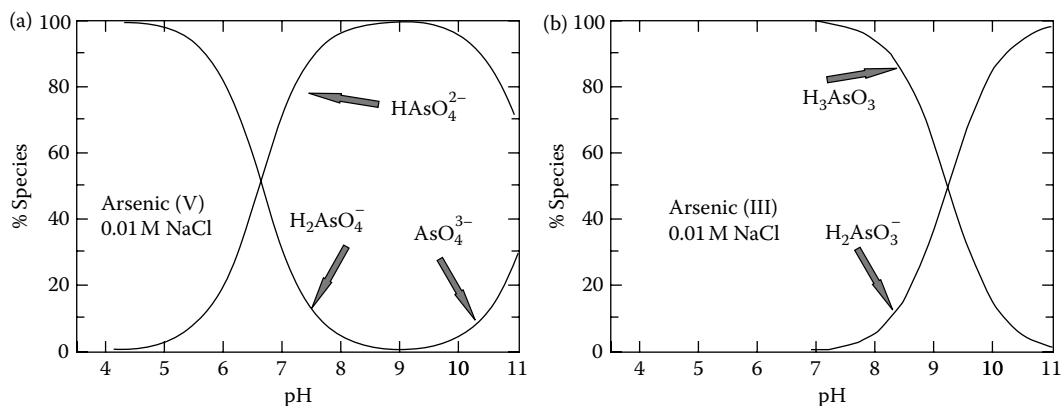
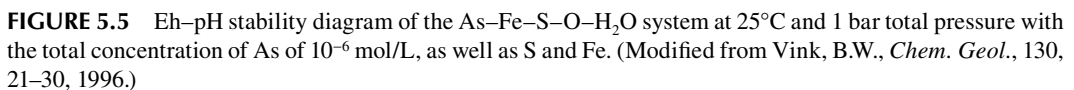


FIGURE 5.4 Speciation of: (a) As(V) and (b) As(III) in a 0.01 M NaCl medium as a function of pH at 25°C. (Modified from Smedley, P.L. and Kinniburgh, D.G., *Appl. Geochem.*, 17, 517–568, 2002.)



As with most trace metals, the concentration of As in aquifer systems is controlled by mineral–water interactions. Knowing the types of processes involved is important not only for understanding the response of As to changes in groundwater chemistry, but also for determining the modeling approach to predict the trend of change in As concentration. Mineral–water interactions can be divided into

four major types from a geochemical point of view: precipitation–dissolution, adsorption–desorption, oxidation and reduction, and microbial activities. Besides, natural organic matter (NOM) and microbes have a strong impact on the behavior of As in various biogeochemical processes.

5.4.1 PRECIPITATION AND DISSOLUTION

Precipitation–dissolution reactions involve the growth or erosion of a mineral structure and therefore only involve structural ions, that is, the elements included in the chemical formula of the mineral. The solubility of minerals can in principle be described quite well by a solubility product, although this may vary with the particle size and crystallinity of the mineral. Moreover, the rate of dissolution or precipitation can be very slow and thermodynamic equilibrium is therefore often not attained in practical time scales.

Coprecipitation is also a common natural process whereby minor constituents are incorporated or scavenged into a mineral structure as it forms. For instance, As can be coprecipitated during the formation of pyrite. Furthermore, both phosphate and As are coprecipitated during the formation of iron oxides.

Arsenian pyrite, $\text{Fe}(\text{As,S})_2$, is probably the most significant reservoir of mineral As in nature. Pyrite can incorporate up to a maximum of 8 wt% As into its structure, and it was speculated that pyrite may form a solid solution with arsenopyrite, FeAsS [91–92]. The so-called authigenic pyrite is typically formed when OM is introduced into an iron- and sulfur-rich system, which causes redox potentials to drop. Highly insoluble ferric iron (iron oxide) is first reduced by the OM to soluble ferrous iron, and then sulfate is reduced to sulfide. The dissolved As concentrations then decline as pyrite forms through a complex process that coprecipitates As [93].

5.4.2 ADSORPTION AND DESORPTION

Under oxidizing conditions, As concentrations in water are mostly controlled by adsorption rather than mineral solubility. Sorption of As to solid phases has been proposed as a principal control on its mobility (Table 5.3), which can transfer soluble or mobile As to particulate phases, thus immobilizing it.

TABLE 5.3
Effects of the Main Aquifer Materials on As Immobilization and Transformation in Adsorption–Desorption Processes

Aquifer Materials	Main Affecting Mechanism
Fe hydroxides	As(V), $\text{CH}_3\text{AsO}_2(\text{OH})^-$, and $(\text{CH}_3)_2\text{AsOOH}$ adsorption at pH 4–7, maximized around pH 4 As(III) adsorption at pH 7–10, maximized around pH 7 Desorption when pH increases Amorphous phases of a higher adsorption capacity than crystalline phases Releasing sorbed As during chemical and microbial reductive dissolution As(III) oxidation, catalyzed by light or H_2O_2 in alkaline pH
Al hydroxides	As(V), $\text{CH}_3\text{AsO}(\text{OH})_2$, and $(\text{CH}_3)_2\text{AsOOH}$ adsorption up to pH 7 and decreases significantly at higher pH As(III) adsorption at pH 6–9.5 and decreases at higher pH Amorphous phases of a higher adsorption capacity than crystalline phases
Mn hydroxides	Negligible As(V) adsorption, but increased in the presence of other divalent cations Slightly greater As(III) oxidation at low pH (pH 4) Poorly crystalline phases with high surface areas are more efficient

continued

TABLE 5.3 (continued)

Aquifer Materials	Main Affecting Mechanism
Clay	As(V) adsorption up to pH 7 and decreases with pH increases Low As(III) adsorption at low pH and increases with pH Clays with high surface areas showing a higher adsorption capacity As(III) oxidation in the presence of trace amounts of impurities such as Fe or Mn oxides, iodide, or TiO ₂
Sulfides	As substitution for S in sulfides, forming of As sulfide precipitates in the reduced environment Releasing As during chemical and microbial oxidation of As-bearing sulfides
Calcite ^a	Equilibrium data of As(III) sorption onto calcite depicts an S-shaped sorption isotherm At low concentrations, As(OH) ₃ is adsorbed by complexation to surface Ca surface sites Sorbed As increases linearly with solution concentration, up to the saturation of As with respect to the precipitation of CaHAsO ₃ (s)
Muscovite and mica ^b	Function of solution pH (pH 3–8 for muscovite, and 3–11 for biotite), amount of As adsorbed increases with increasing pH, exhibiting a maximum value, before decreasing at higher pH values Maxima correspond to 3.22 ± 0.06 mmol/kg As(V) at pH 4.6–5.6 and 2.86 ± 0.05 mmol/kg As(III) at pH 4.1–6.2 for biotite, and 3.08 ± 0.06 mmol/kg As(III) and 3.13 ± 0.05 mmol/kg As(V) at pH 4.2–5.5 for muscovite
NOM	Enhancing As release mainly through competition for active adsorption sites, forming aqueous complexes, and changing the redox chemistry of site surfaces and As species Inhibiting As mobility by serving as a binding agent and/or by forming insoluble complexes, especially when saturated with metal cations
Anions	Competition for active adsorption sites, influenced by pH and concentration ratios between anion and As
Cations	Enhancing As sorption by increasing the amount of positive charge on the oxide surfaces and/or forming a positively charged surface

Source: Modified from Wang, S.L. and Mulligan, C.N., *J. Hazardous Mater. B*, 138, 459–470, 2006.

^a Román-Ross, G., Cuello, G.J., Turrillas, X., Fernández-Martínez, A., and Charlet, L., *Chem. Geol.*, 233, 328–336, 2006.

^b Chakraborty, S., Wolthers, M., Chatterjee, D., and Charlet, L., *J. Colloid Interface Sci.*, 309, 392–401, 2007.

Especially, (hydro)oxides of Fe, Al, and Mn are ubiquitous in soils and sediments, either as discrete particles or as coatings on other mineral solids, with corresponding high surface areas, and are potentially the most important As adsorbents [94].

Spectroscopic studies have confirmed that both As(III) and As(V) may form inner-sphere complexes on the surfaces of the (hydro)oxides and clay minerals through ligand exchange with OH and OH₂⁺ surface functional groups [98]. As(III) may also form outer-sphere complexes by simple coulombic (electrostatic) interactions on the surface of amorphous Al hydroxides and sulfide minerals. Inner-sphere complex bonds are much stronger than outer-sphere complex bonds, resulting in stronger adsorption, which makes the immobilization more persistent [95]. Although surface complexation models developed to predict arsenate adsorption behavior have included the formation of only inner-sphere species (e.g., [99–102]), Catalano et al. [103] observed arsenate adsorption on corundum and hematite using resonant surface x-ray scattering measurement, and the results demonstrated that arsenate surface complexation is unexpectedly bimodal, adsorbing simultaneously as inner- and outer-sphere species [103].

5.4.2.1 As Sorption to Fe, Al, and Mn (Hydro)oxides

Fe hydroxides, such as goethite (α-FeOOH), ferrihydrite (β-FeOOH), and lepidocrocite (γ-FeOOH), have high isoelectric points of about 8.6 and possess net positive charges in most geological

environments, showing high affinities for As species. Their adsorption affinity is higher for As(V) and As(III) at lower and higher pH values, respectively [6].

Al (hydro)oxides are ubiquitous in acidic soils and aquatic environments. Amorphous $\text{Al}(\text{OH})_3$ has an isoelectric point of 8.5, and thus is an extremely efficient adsorbent to immobilize As. Previous studies indicated that As(III) and As(V) adsorption on an Al oxide ($\gamma\text{-Al}_2\text{O}_3$) and gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) formed inner-sphere complexes [95].

Mn hydroxides have an isoelectric point of about 2.3, and therefore carry a net negative charge at pH 3–9 in ordinary natural waters. In other words, it is difficult for them to adsorb As anions. It was observed that the negatively charged As(V) species, H_2AsO_4^- , was adsorbed negligibly onto the negatively charged birnessite surface at a pH range of 4–7 [104]. However, Mn hydroxides have the capacity to oxidize As(III) to As(V) [105,106], which may create fresh adsorption sites for As(V) on the oxide surface.

The crystallinity and surface area of the (hydro)oxides have demonstrated significant effects on their sorption capacity. Generally, poorly crystalline hydroxides with a higher surface area show a higher As sorption capacity by providing more active sorption sites [95]. For example, the adsorption of As(III) and As(V) was two or three times greater (on a surface area basis) on ferrihydrite than on goethite [107].

However, desorption and remobilization of the sorbed As from the (hydro)oxides may occur when biogeochemical conditions change with time. Significant As(V) remobilization from Fe hydroxides can occur at pH above 8, due to the increase of electrostatic repulsion on the negatively charged oxide surface, and the rate of As(V) desorption can be quite high [108]. In reducing sediments, As sorbed on Fe(III) hydroxides could be remobilized and released into groundwater as a result of the microbial reduction of Fe(III) to Fe(II) and the reduction of As(V) to As(III) [74,109,110]. But there is no clear correlation between the concentrations of dissolved As and Fe as can be expected from this hypothesis. Horneman et al. [111] suggested that this poor As–Fe correlation could be due to the formation of secondary Fe(II) or mixed Fe(II)/Fe(III) phases such as siderite (FeCO_3), green rust, and magnetite (Fe_3O_4) [111]. Jönsson and Sherman [112] found that As(V) can be sorbed to fougurite, magnetite, and siderite by forming inner-sphere surface complexes, and no evidence for As(V) reduction was found [112]. Their work also demonstrated that As(III) can form inner-sphere surface complexes on magnetite and fougurite but only a (presumably) weak outer-sphere complex on siderite, and no evidence for As(III) oxidation was found. Besides, As(V) desorbs from magnetite, fougurite, and siderite at pH > 8; however, As(III) sorption to these minerals is enhanced with increasing pH.

5.4.2.2 As Sorption to Clay Minerals

Ubiquitous in the terrestrial environment, clay minerals largely consist of aluminosilicates with alternating layers of silica oxide and aluminum oxide. Fourier transform infrared spectroscopy analyses (FTIR) indicated that the retention of As(V) by halloysite was likely due to the formation of hydroxy-As(V) interlayers in crystals. It was also reported that nearly all As(III) and As(V) were physisorbed to smectite, and only a portion of them was chemisorbed on kaolinite forming inner-sphere complexes [95].

As(V) adsorption to kaolinite, montmorillonite, illite, halloysite, and chlorite occurs up to pH 7 and then decreases with a pH increase [95]. As(III) adsorption by the same clay minerals is minimal at low pH and increases with increasing pH. As(V) is adsorbed to a greater extent than As(III) on all clay minerals at a pH below 7 [95]. At higher pH values, adsorption behaviors of As(V) and As(III) are more comparable. Moreover, the poorly crystallized clay minerals of larger surface area have higher As sorption capacity, and the presence of mineral impurities such as Fe species may further enhance the capacity [113].

5.4.2.3 Enhanced Sorption by Cations

Cations, such as Ca^{2+} and Fe^{2+} , may increase As adsorption by increasing the amount of positive charge on the oxide surface and/or forming a positively charged surface [114]. Ghosh and Teoh [115]

observed that the adsorption of As(V) onto Al oxides was enhanced in the presence of Ca^{2+} at pH above 8 [115]. The addition of Ca^{2+} also increased As(V) adsorption onto ferrihydrite at pH 9 [116]. Meng et al. [117] reported that the addition of Ca^{2+} and Mg^{2+} to the suspension of ferrihydrite negated part of the competitive effect of silicate on As adsorption [117]. The formation of CaCO_3 minerals can restrict the development of high pH, thus inhibiting As(V) release from oxides and clays.

Once the oxides have an adsorbed load, any change in their surface chemistry or the solution chemistry can lead to release of adsorbed As, and thereby increase of As concentration in groundwater. The extremely high solid/solution ratio of soils and aquifers makes them highly sensitive to such changes [118,119].

5.4.2.4 Competing Sorption by Anions

A complicating factor in As adsorption is competition by other oxyanions. In reducing groundwaters, these include phosphate, silicate, bicarbonate, and fulvic acids (FAs) [117,120–122]. As(V) and phosphorus sorption on hydrous ferric oxides (HFOs) are broadly similar, although there is usually a slight preference for phosphorus. Not surprisingly, As(V) is much more strongly affected by phosphate competition than As(III) [120]. Sulfate has essentially no effect on As(V) adsorption but may compete with As(III) adsorption when the pH is below 7 [117,120]. Generally, carbonate exhibits little effect on As(III) and As(V) adsorption [117], but the presence of bicarbonate (HCO_3^-) can facilitate As mobilization from As-containing sulfides such as orpiment in both oxic and anoxic environments [79]. As mobilization increases with increasing HCO_3^- concentrations and pH. Silicate reduces the adsorption of As(III) and As(V) on ferrihydrite at pH 6.8 [117]. Competitive adsorption between arsenate and molybdate was also observed [123]. The competing sorption between As species and other anions can inhibit As sorption and thus increase As mobility.

Anion displacement as a mechanism for As release has received less attention compared with the reductive dissolution of iron oxides, although several laboratory and field studies have demonstrated the ability of naturally occurring (in)organic ions to displace adsorbed As or inhibit its absorption. Most studies focused on phosphate-promoted desorption of As due to the increasing use of fertilizers. Fewer researchers evaluated the potential roles of silicate, carbonate, and sulfate, the three ubiquitous anions in groundwaters. For sulfate, it is not an effective desorbent [6,124]. The results of studying the influence of bicarbonate on As desorption have shown that in a neutral to basic pH environment of groundwaters, bicarbonate concentrations exceed the reactive surface site densities of iron (hydro)oxides and may promote As desorption [114,125]. Latest research on the importance of silicate on displacing As from goethite demonstrated that silicate can reduce arsenite adsorption rates, block potential adsorption sites, and irreversibly displace 0.3–1.5% absorbed arsenite, resulting in As concentration increase from 9 to 266 $\mu\text{g/L}$ [126].

5.4.3 OXIDATION AND REDUCTION

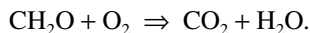
Redox reactions are important for controlling the behavior of many major and minor species in natural waters, including that of As [6]. In practice, redox equilibrium is hardly achieved and the redox potential tends to be controlled by major redox-sensitive elements (O, C, N, S, and Fe), and redox-sensitive minor and trace elements such as As respond to these changes rather than control them.

A well-known sequence of reduction reactions occurs when lakes, sediments, and aquifers become anaerobic [127,128]. The processes causing changes in Fe redox chemistry are particularly important since they can directly affect the mobility of As. One of the principal causes of high As concentrations in subsurface waters is the reductive dissolution of hydrous Fe oxides and/or the release of adsorbed or combined As [6]. This sequence begins with the consumption of O_2 and an increase in dissolved CO_2 from the decomposition of OM. Next, NO_3^- decreases by reduction to NO_2^- and the gases N_2O and N_2 . Insoluble manganese oxides dissolve by reduction to Mn^{2+} and hydrous ferric oxides by reduction to Fe^{2+} . These processes are followed by SO_4^{2-} reduction to S^{2-} ,

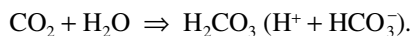
then CH_4 production from fermentation and methanogenesis, and finally reduction of N_2 to NH_4^+ . During SO_4^{2-} reduction, the consequent S^{2-} reacts with any available Fe^{2+} to produce FeS and ultimately pyrite, FeS_2 . As(V) reduction would normally be expected to occur after Fe(III) reduction but before SO_4^{2-} reduction [6].

Bhattacharya et al. [129] postulated that the principal redox reactions controlling As release in the groundwater of the Bengal Delta are given by the following scheme [129]:

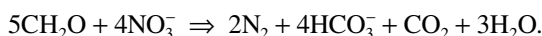
(Organic matter oxidation by O_2)



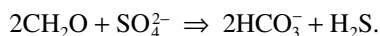
(Dissolution and hydrolysis)



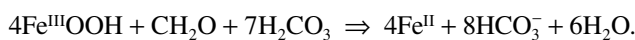
(Denitrification)



(Sulfate reduction)



(Reductive dissolution Fe oxides)



The As sorbed onto iron oxides is vulnerable to release by changing geochemical conditions, especially a decrease in redox potential. When the redox potential drops, the ferric iron is reduced to the highly soluble ferrous iron, and As is released from the surface of oxides into the solution. The reduction is generally driven by introduction of OM into the aquifer as well as by microbial activities [74,110].

Saunders et al. [130,131] and Lee et al. [132] proposed that As was mobile under Fe-reducing conditions and immobile under SO_4 -reducing conditions, given an ample supply of necessary electron donors and acceptors. Kirk et al. [133] reached a similar conclusion in studying As-rich groundwater in Illinois [133]. Further, Saunders et al. [131] proposed that As-bearing pyrite should be the most important solid As phase formed under SO_4 -reducing conditions in natural systems [130,131]. In contrast, O'Day et al. [134] and O'Day [135] reported pure As-S phases including realgar (As_4S_4) and orpiment (As_2S_3) from an industrial As-contaminated site, and proposed that these As solid phases would have formed under reducing conditions. Recently, As-bearing pyrite has been found in alluvial sediments in Bangladesh [136] and West Bengal, India [137], as previously in the United States [130,138,139].

5.4.4 MICROBIAL TRANSFORMATION

As with most redox reactions in the natural environment, both the oxidation of arsenite and the reduction of arsenate can be bacterially catalyzed. Microbial activity plays an important role dictating the fate of As in the environment, as shown in [Figure 5.6](#).

5.4.4.1 Microbial Arsenite Oxidation

The microbial oxidation of As(III) is of considerable environmental importance because it can impact the mobility and speciation of As in the environment. Oxidation of As(III) can be performed

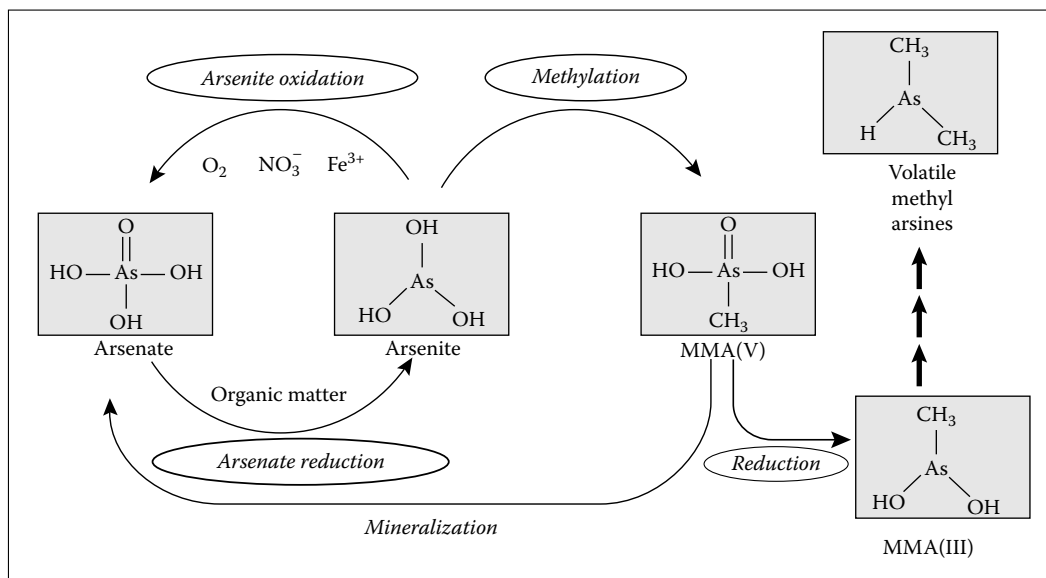


FIGURE 5.6 Microbial transformation in As cycling in the environment. (Modified from López, I.C. Microbial transformation of arsenic and organoarsenic compounds in anaerobic environments. PhD Dissertation Thesis, University of Arizona, 236 pp., 2007.)

by heterotrophic (HAOs) and chemolithoautotrophic arsenite oxidizers (CAOs). As(III) oxidation by HAOs microorganisms is utilized as a detoxification mechanism, and occurs in the cell's outer membrane [141]. CAOs utilize arsenite as electron donor to fix CO_2 for growth. Oxidation of As(III) coupled to the reduction of oxygen [142], nitrate to nitrite [143], or nitrate to nitrogen gas [144] has been reported.

5.4.4.2 Microbial Arsenate Reduction

There are two main mechanisms responsible for reduction of As(V) to As(III) [140]: (a) As(V) reduction as a detoxification pathway and (b) by the dissimilatory reduction of As(V).

5.4.4.2.1 Arsenate Reduction as a Detoxification Mechanism

Similarly to As(III) oxidation, reduction of As(V) is implicated in the mechanisms of detoxification developed by a wide variety of microorganisms. A well-studied mechanism of detoxification is the *ArsC* system developed in *Escherichia coli* and *Staphylococcus aureus* [145]. *ArsC* is an enzyme that reduces As(V) to the more toxic As(III) in the cytoplasm. Reduced glutathione serves as an electron donor for the As(V) reduction. Although As(III) is more toxic, it serves as a substrate for the *ArsB* transport protein. As(V) conversion seems counterproductive, but it is a mechanism to differentiate As(V) from PO_4^{3-} and avoid extrusion of PO_4^{3-} from the cell. Macur et al. [146] reported reduction of As(V) by aerobic bacteria isolated from mine tailings [146].

5.4.4.2.2 Dissimilatory Arsenate Reduction

Although As is normally associated with poisoning and death, this metalloid also serves to support bioenergetic reactions in certain types of microorganisms. As described above, many microorganisms have evolved capabilities of resistance involving redox reactions to protect themselves from the negative effect of As [147]. Some anaerobic bacteria and archaea can actually conserve the energy gained via oxidation of organic compounds or H_2 coupled to the reduction of As(V) to As(III). This process is termed dissimilatory arsenate reduction, and it is a means of anaerobic respiration that supports the growth of a number of microorganisms [148].

5.4.4.3 As Biomethylation

As can be biomethylated by algae, fungi, and a wide variety of bacteria mainly as a detoxification mechanism. Volatile (methylarsine, dimethylarsine, and trimethylarsine) and nonvolatile As compounds (mainly MMA^V and DMA^V) are formed by biomethylation. Microbial methylation is a process that has been reviewed recently [141,149,150].

5.4.4.4 Microbial Mobilization of Sorbed As

As sorbed onto iron hydroxides can be mobilized under anaerobic conditions by the reductive dissolution of iron hydroxides, allowing release of As(V) into the aqueous phase, followed by a rapid reduction of aqueous As(V) to As(III) via either biotic or abiotic pathways. Alternatively, As(V) may be reduced to As(III) on the surface, and then released upon reductive dissolution of the iron hydroxide phase [151,152].

Korte [153] first proposed that the As enrichment of alluvial aquifer groundwater was caused by the codeposition of HFOs containing sorbed As and NOM in river floodplain alluvium, and that the OM caused reductive dissolution of HFOs, releasing both Fe(II) and As to groundwater [153]. The scale of As enrichment of groundwater was recognized in Southeast Asia in the mid-to-late 1990s. Saunders et al. [130], Penny et al. [154], and Lee et al. [155] extended the geochemical model of Korte [153] to include the metabolic effects of Fe-reducing bacteria (FeRB) and Mn-reducing bacteria for releasing Fe and As (and other trace elements such as Mn, Co, Ni, Ba, V, and rare earth elements) in alluvial aquifers in the United States. Further, Saunders et al. [130] showed that SO₄-reducing bacteria removed As, Fe, Co, and Ni by coprecipitating them in biogenic pyrite [130]. Later, other researchers showed that FeRB were apparently responsible for causing As enrichment of Holocene alluvial aquifers in Bangladesh and India (e.g., [8,156,157]). Laboratory investigations by Islam et al. [158] on sediment cores from Southeast Asia showed that FeRB such as *Geobacter* could liberate As from minerals [158]. Field investigations by Saunders et al. [131] at Korte's [153] discovery location (Kansas City, MO, USA) showed that FeRB (of the genus *Geobacter*) were abundant in groundwaters containing elevated As and absent in groundwaters without As. Sulfate reducing bacteria (principally *Desulfovibrio desulfuricans*) were also present in As-enriched groundwater. Saunders et al. [131] proposed that such bacteria were also important in As geochemical cycling in Southeast Asia [131].

As-respiring bacteria are capable of reducing not only soluble arsenate but also adsorbed arsenate [159] and arsenate within solids such as scorodite [160], with recent evidence suggesting that reduction proceeds first through a dissolution step [161]. Dissimilatory arsenate reduction may enhance the solubility of As, particularly in environments with low iron (hydro)oxide content. Zobrist et al. [119], for example, showed that reduction of As(V) adsorbed or coprecipitated on amorphous aluminum hydroxides by *Sulfospirillum barnesii* greatly increased dissolved As(III) concentrations.

5.4.5 ROLE OF NOM

NOM such as humic acid (HA) and FA is an inherently complex mixture of polyfunctional organic acids derived from the decomposition of terrestrial and aquatic animals and plants. Prevalent in the subsurface, NOM is highly reactive toward both metals and surfaces, and therefore may play an important role in governing the mobility and bioavailability of As [162]. NOM has great potential in influencing As sorption behavior and its speciation by interacting with mineral surfaces and/or with As itself, and thus may play a major role in the release of As from soils and sediments into the groundwater [162,163].

Ubiquitous in aquatic environments, NOM may interact strongly with As. A number of studies have been performed to elucidate the effects of NOM on the sorption behavior of As species and the consequential influence on their mobility [107,110,163–170]. The interactions between NOM and As can be influenced by various factors such as pH, redox potential, As speciation and concentration, other competing ions and complexing ligands, aquifer mineralogical properties, and reaction kinetics [171].

The presence of NOM may enhance As release mainly through three main pathways [162]: (a) competition for available adsorption sites; (b) change of the redox chemistry of site surface and As species; and (c) formation of aqueous complexes.

5.4.5.1 Competitive Adsorption of As and NOM

Organic acids such as HA and FA may compete strongly with As(III) and As(V) for active adsorption sites on mineral surfaces. Competition between organic acids and As species can be an important factor in influencing the mobilization of As. The competition for active-binding sites on mineral surfaces between organic acids and As species may result in lowering the levels of As retention, especially under acidic conditions.

Grafe et al. [107] studied the adsorption of As(III) and As(V) on goethite in the presence of a peat HA, a Suwannee River FA, and citric acid (CA) [107]. HA inhibited As(V) adsorption starting at pH 9, reaching a maximum at pH 6.5. The inhibition effects of FA were slighter, starting at pH 5 and increasing as the pH decreased. CA showed no effect on As(V) adsorption. As(III) adsorption is inhibited by HA starting at pH 7 and increased when pH decreased, whereas FA and CA reduced As(III) adsorption starting at pH 8, with a continuous reduction as pH decreased. It was also observed that the adsorption of all three organic acids on the goethite surface was reduced in the presence of both As(V) and As(III). Grafe et al. [166] subsequently examined the effects of the organic acids on the adsorption of As(V) and As(III) on ferrihydrite [166]. However, some researchers reported that the presence of OM might increase the adsorption of As, thus reducing As mobility [164,165,168].

5.4.5.2 Effect of Site Surface and As Species on Redox Chemistry

It has been shown that NOM may catalyze both the oxidation and reduction reactions among chemical species, in part by the quinone-mediated formation of free radicals [167,172]. They may serve as an electron shuttle between kinetically inert redox species or between microorganisms and As species [172]. Hydroxides may act as a surface catalyst or as an electron-transfer intermediate. As release may be enhanced by the redox reactions among NOM, As, and substrates, resulting in As(V) reduction to the more labile and mobile form, As(III).

Redman et al. [167] observed the reduction of As(V) to free As(III) by the Inangahua River NOM, and the reversed process of As(III) oxidation to free As(V) by all other experimental NOM samples [167]. The authors postulated that hematite might have acted as a surface catalyst or as an electron-transfer intermediate in this process.

Palmer et al. [173] found that inorganic arsenates were reduced to arsenite by homogeneous aqueous solutions of several HAs and FAs [173]. The fraction of arsenate that was reduced initially increased with humic concentration, but leveled off as the reduction potential decreased at higher concentrations. Reoxidation of As(III) in humic solutions could be achieved by extended bubbling with air.

Tongesayi and Smart [174] investigated the reduction of inorganic As(V) with Suwannee River FA in aqueous solutions where the pH and concentrations of FA, As(V), As(III), and Fe(III) were independently varied. The results demonstrated that FA can significantly reduce As(V) to As(III), and both dark and light conditions promote reduction of As(V) to As(III). Besides, the addition of Fe(III) speeded up the reduction reaction [174].

5.4.5.3 NOM–As Complexation

NOM may form both aqueous and insoluble surface inner-sphere complexes with metal cations due to their strong affinity to metal cations and metal oxides. Aqueous NOM–metal complexes may, in turn, associate strongly with other dissolved anions, presumably by metal-bridging mechanisms, diminishing the tendencies of such anions to form surface complexes [167,169]. Factors influencing the quantity of ions bound by NOM include pH, ionic strength, molecular weight, and functional group content as well as the presence of competing ions [167,169]. The formation of soluble As complexes with NOM may enhance As solubility and therefore As release into groundwater.

Moreover, complexation may also affect the partitioning of As to suspended solids in the water column and the sequestration of As to sediments [162].

Infrared spectroscopy studies have confirmed that COOH groups play a predominant role in the complexation of metal ions by HA and FA [175]. Some evidence indicates that OH, C=O, and NH groups may also be involved [165,168].

Mukhopadhyay and Sanyal [176] studied As–humic/fulvic complexation equilibrium, and proposed that the equilibrium process depends on the nature and properties of the humic substance, which would affect the retention/release of As from the sediments matrix [176].

Warwick et al. [170] characterized the interaction of As with HA in a system consisting of HA with As(III) and As(V), and dimethylarsinic acid (DMAA) [170]. The interaction is postulated to involve bridging metals and deprotonated functional groups within the HA.

5.5 MECHANISM OF As MOBILIZATION AND RELEASE IN SHALLOW AQUIFERS: CASE STUDIES IN SOUTHERN ASIA AND NORTHERN CHINA

5.5.1 AS IN SHALLOW REDUCING AQUIFERS IN SOUTHERN ASIA

In southern Asia, major alluvial and deltaic plains composed of Quaternary sediments are prone to developing groundwater As problems, particularly around the perimeter of the Himalayan mountain range. High concentrations have been found in the groundwater from such aquifers in the Bengal Basin of Bangladesh and eastern India, the lowland Terai region of Nepal, the Mekong valley of Cambodia, the Red River Delta of Vietnam, and the Irrawaddy Delta of Myanmar [21,33,177,178]. Similar problems may occur in similar alluvial and deltaic environments elsewhere in the world. Unfortunately, such flat-lying fertile plains are often densely populated and poor groundwater quality can have a major impact on large numbers of people. At present, the Ganges–Brahmaputra–Meghna Plain and Delta in India and Bangladesh represent the most acutely As-contaminated site in the world, with concentrations sometimes $>4000\text{ }\mu\text{g/L}$ [179,180]. It has been estimated that more than 50 million people ingested As-contaminated water in this area alone [6]. Consequently, most of the groundwater As studies in recent years have been concentrated in this area (Table 5.4).

5.5.1.1 Common Hydrological and Hydrochemical Features of These Aquifers

The Ganges–Meghna–Brahmaputra Delta [46], the Mekong Basin near Phnom Penh [24,25], and the Red River Basin near Hanoi [20] have three features in common [33]: (a) River drainage from the rapidly weathering Himalayas. Although groundwater contamination has also been reported upstream, for example, in Nepal and in Bihar, India, the major concerns are the delta areas of these river systems because of the high populations they support and will continue to support in the near future. (b) In these delta areas, the three systems are characterized by rapidly buried OM-bearing, relatively young (ca. Holocene) sediments. (c) Very low, basin-wide hydraulic gradients. In all the three systems, the spatial heterogeneity of As content distribution occurs on very small scales, with high concentrations ($>50\text{ ppb}$) commonly found within tens of meters of low concentrations. This may reflect the complex lithological structures of the aquifers, which include highly permeable channel fills as well as very low-permeability scoured channels filled with organic-rich overbank deposits. The interconnectivity of highly permeable channel sand units may be critical to determining groundwater As distribution because of its control on groundwater flow patterns [32] and on the rate of flushing of As from the system.

A common feature of all these As-contaminated waters is their anoxia. This anoxia may be inherited from the conditions prevailing at the time of sediment deposition, as discussed below, or may result from the surface input of organic material. As Eh decreases, the classical cascade of electron acceptors involved in the oxidation of this organic material leads to the successive appearance of Mn^{2+} , Fe^{2+} , NH_4^+ , acid volatile sulfides (AVSs), and methane.

TABLE 5.4
Summary of Documented Cases of Naturally Occurring As Problems in Southern Asian Aquifers

Country/Region	Area (km ²)	As		Aquifer Type	Groundwater Conditions	Sediments/As Contents	References
		Population Exposed	Concentration Ranges (µg/L)				
Bangladesh	150,000	35,000,000	<1–2300	Holocene alluvial/deltaic sediments. Abundance of solid OM	Strongly reducing, neutral pH, high alkalinity, occurrence of CH ₄ , slow groundwater flow rates	Fine- to medium-sized sand shallow: brown to gray; deep: orange; As: 2–10 µg/g	[46]
West Bengal, India	23,000	5,000,000	<10–3200	As Bangladesh	As Bangladesh	Similar to those in Bangladesh	[181]
Vietnam Red River Delta	1200	10,000,000	1–3050	Holocene alluvial/deltaic sediments	Reducing, high Fe, Mn, NH ₄ , high alkalinity, Ca-HCO ₃ or Mg-HCO ₃ type, rich in CH ₄	Brown to black-brown clay 6–33 µg/g As; gray clay 2–12 µg/g; brown to gray sand 0.6–5 µg/g; average 7.5 µg/g As	[20,21]
Cambodia	3700	120,000	1–1340	Unconsolidated alluvial deposits of the Quaternary	Neutral pH, low Eh, high Fe and bicarbonate contents, moderate salinities, and low dissolved sulfate	As-rich area: gray clays, silts, and sands. As and Fe decrease with depth; near surface, As(V) dominated; 35–60% As reduced to As(III) by 17 m depth	[182,183]
Terai Region, Nepal	30,000	550,000	1.7–404	Thick sand and gravel deposits of Holocene age. Interlocked with alluvium flood plains	High HCO ₃ ⁻ and low SO ₄ ²⁻ , high Fe and Mn	Average As: 9 µg/g; iron oxide, titanium oxide, and calcium oxide concentration were 5%, 0.7%, and 3.9%, respectively	[26,184]
Punjab, Pakistan	?	3040	32–1900	Quaternary alluvial and deltaic sediments	Alkaline pH (7.3–8.7); high F, As, SO ₄ ²⁻ ; water type: Na–HCO ₃ or Na–HCO ₃ –SO ₄ dominant	Mostly coarse sand, containing high percentage of fine to very fine sand and silt	[27]

The most common feature of all these groundwaters is their high concentration of Fe^{2+} , often close to the level required for siderite saturation, in many of the Bengali, Cambodian, and Vietnamese shallow aquifers [8,20,24].

5.5.1.2 As Mobilization in Aquifers

Groundwater As enrichment in these deltas has been largely attributed to coupled redox cycling of As-bearing iron (oxy)hydroxides [6]. Reductive dissolution of Fe(III) phases may release sorbed As. Aqueous Fe concentrations and redox potential are important indicators of aqueous As enrichment in many environments [74,157].

There are a variety of proposed mechanisms for As release within these reducing aquifers. For example, the oxidation and breakdown of As-bearing pyrites by the drawdown of oxygenated water [186–187] was one possible mechanism, although this process has been contested, as the products of the breakdown of pyrite under the neutral conditions of the aquifer would act as a sink for As as opposed to releasing it to the groundwater [7,8]. The association of As with Fe(III) oxides within As-rich aquifers of Bangladesh and West Bengal [7,8,129,157,187–189], coupled with the reducing conditions of the aquifers, could also lead to As release. Microbial degradation of the naturally occurring OM drives the aquifer to anoxia where, under such conditions, Fe(III) oxides become unstable and dissolve, releasing As as well as Fe and HCO_3^- into the groundwaters. Such a process would be expected to produce correlations between these three components [6–8,46]. In addition, microbes can play a more direct role in mediating As release rather than just altering the redox conditions. Microcosm-based geomicrobiological studies on sediments from West Bengal and Bangladesh show that stimulation of the indigenous microbial community leads to increased As release and Fe(III) reduction [74,158,189–191].

Although the mechanism of release is generally agreed upon, other natural processes obscure a simple relationship between dissolved Fe and As levels [111,190]. Among these additional natural processes, sulfur redox cycling may impact Fe and As geochemistry [133,135]. A mechanistic understanding of these processes is necessary to explain the spatial heterogeneity and extent of As enrichment.

Iron mineralogical transformations are intrinsically linked to the cycling of other components, including OM which drives reduction [183]. Sulfur cycling, which can also undergo redox cycling to form sulfide ions as a product of dissimilatory reduction of SO_4^{2-} , may also affect the fate of As by leading to the formation of As sulfides [135,192]. Although Fe reduction is more thermodynamically favorable than SO_4 reduction, the latter often precedes Fe reduction for kinetic reasons [193] and, as a result, sulfide and Fe(III) oxides often occur together [194] and can thus react chemically in these environments. OM-driven reduction of Fe (oxy)hydroxides via sulfide is, therefore, common in anoxic settings [183].

Fluvial geomorphological processes influence sediment OM content, composition, and mineralogy, all of which may influence the distribution of As in the environment [25,131,182,195]. Widespread and heterogeneous As enrichment is commonly associated with the large deltas of south Asian rivers. These high flux, sediment-laden, tropical to subtropical river systems have the potential for rapid and recent major sediment deposition. Deltaic, localized depositional environments such as scroll sequences, avulsions, oxbows, abandoned chutes, and channel islands can capture suspended sediment [183]. Suspended OM as well as surficial plants and woody debris will be incorporated into these rapidly buried sediment strata. Sedimentary OM from overbank deposits, channel deposits, and suspended or dissolved OM may differ considerably in composition and reactivity. These differences may impact the fate of As indirectly by influencing Fe and S reduction, and the sequestration of As in the solid phase [183].

Ultimately, a complex array of geochemical processes may impact the fate of As. For example, the mechanism of Fe mineral dissolution, whether direct or indirect, or the extent of competing sequestration reactions, through secondary (diagenetic) mineral precipitation, may conceal the root cause of As enrichment [183].

5.5.2 FORMATION OF SODA WATERS AND GROUNDWATER AS PROBLEMS IN NORTHERN CHINA

The presence of endemic As poisoning has been recognized in China since the 1980s, and today the scale of the problem is known to be large. As poisoning due to long-term intake of high-As groundwater from Quaternary aquifers was first identified in Taiwan and Xinjiang, and more recently in parts of Inner Mongolia and Shanxi Province. Up to now, cases of waterborne endemic As poisoning have been reported in Taiwan, Xinjiang, Inner Mongolia, Shanxi, Ningxia, Jilin, Qinghai, and Anhui provinces, and in some villages close to Beijing [196]. Most of these areas are located in large Quaternary basins under arid and semiarid conditions. Groundwater in the As-affected areas appears to be strongly reducing. The population exposed to drinking water with concentrations in excess of 50 µg/L (the old Chinese standard) has been estimated to be around 3 million [197]; if accounted according to the latest data and national standard (10 µg/L), the population may reach 14.66 million [198].

Datong Basin in Shanxi and Hetao Basin in Inner Mongolia are two representative As poisoning-affected areas in China. They are both located in an arid/semiarid region of northwestern China with the mean annual rainfall less than 400 mm and the mean annual evaporation rate exceeding 2000 mm.

Endemic disease due to long-term intake of high-As groundwater was identified in these two basins in the early 1990s. Since the late 1990s, great effort has been made to characterize the main hydrogeochemical features and understand the mechanisms responsible for the natural As enrichment in the groundwater of these two basins through detailed hydrogeological and hydrochemical investigation [11–19,72,199–200].

The hydrochemical features of Datong Basin and western Hetao Basin are summarized in Table 5.5. The common hydrochemical features of the high-As groundwater from these two areas can be summarized as follows: the groundwaters are near-neutral to weakly alkaline with high alkalinity; most water samples contain high total dissolved solids (TDS), with HCO₃⁻ (and Cl⁻) as the dominant anion(s) and Na as the dominant cation; and As and fluoride are enriched simultaneously in groundwater.

TABLE 5.5
Comparison of the Hydrochemical Features of High-As Aquifers between Datong Basin and Western Hetao Basin

Hydrochemical Parameter	Datong Basin (2005)	Western Hetao Basin (2007)
pH	7.2–9.1	7.3–8.3
TDS (mg/L)	262–8870	444–7460
HCO ₃ ⁻ (mg/L)	72–1080	284–1290
Cl ⁻ (mg/L)	11–3170	37–4531
SO ₄ ²⁻ (mg/L)	0.7–2240	<0.1–1130
Na ⁺ (mg/L)	59–2395	74–1834
As (µg/L)	8–1550	1–1093
F (mg/L)	0.2–9.2	0.3–6.1
HPO ₄ ²⁻ (mg/L)	<0.1–3.8	<0.1–3.21
Fe (mg/L)	<0.01–5.44	<0.01–5.26
DOC (mg/L)	nd	0.73–35.7
NH ₄ ⁺ (mg/L)	nd	<0.2–10.5
Dissolved sulfide (mg/L)	nd	<0.01–0.37
Water chemical type	Na–HCO ₃	Na(–Mg)–Cl or Na(–Mg)–Cl–HCO ₃ or Na(–Mg)–HCO ₃ –Cl
Note	Strong odor of H ₂ S, occasionally high contents of methane	Strong odor of H ₂ S, occasionally high contents of methane (up to 5110 µg/L)

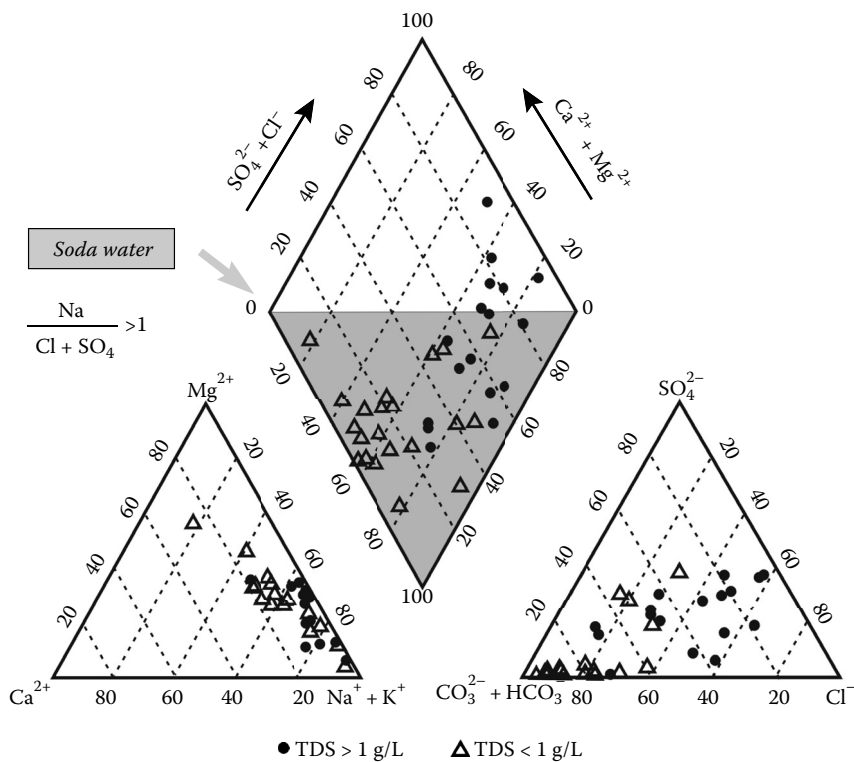


FIGURE 5.7 Piper diagram of high As and fluoride groundwaters in Datong Basin, Northern China.

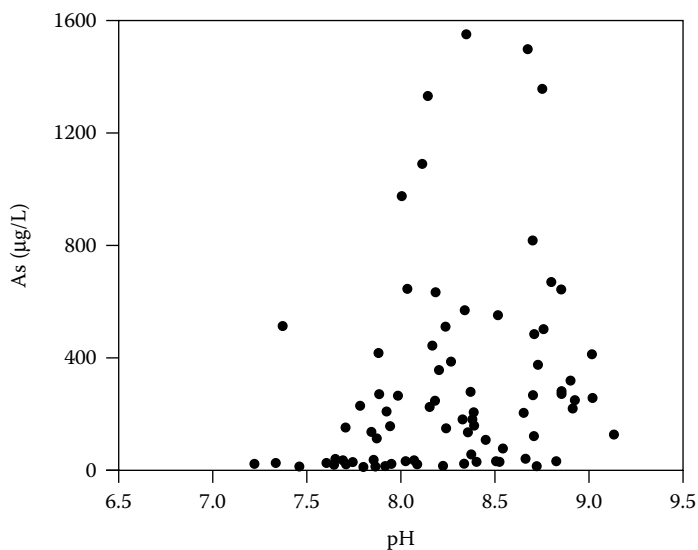


FIGURE 5.8 Relationship between As concentration and pH of groundwaters in Datong Basin, Northern China.

It is interesting to observe that most of the high As and F groundwater are soda waters, which refer to waters with $\text{Na}/(\text{Cl} + \text{SO}_4)(\text{meq})$ ratios greater than 1 [14] (Figure 5.7). The occurrence of soda water is regarded as one stage of interaction of water with aluminosilicate minerals, when the groundwater is saturated with calcite. Generally speaking, saturation usually occurs when the salinity of water is more than 0.6 g/L and pH is more than 7.4 [201]. After saturation, Ca and Mg in solution encounter geochemical barriers of calcite and montmorillonite that inhibit further enrichment of Ca and Mg in the aqueous phase and facilitate Na concentration, under conditions of retarded subsurface flow and enhanced salinity and alkalinity of groundwater. Hydrolysis of aluminosilicate minerals and evapotranspiration have been proposed to be responsible for the genesis of soda waters in regions with similar conditions [14].

As shown in Table 5.5, soda waters at Datong and Hetao basins are weakly alkaline to alkaline. As concentration in groundwaters is affected by many factors, with pH and redox conditions being the most important. Under the aerobic and acidic to near-neutral conditions typical of many natural environments, As is strongly adsorbed by (hydro)oxide minerals as the arsenate ion. Adsorption protects many natural environments from widespread As toxicity problems [6]. As pH increases, As desorbs from the oxide surfaces, thereby increasing its concentration in solution. It can be seen from Figure 5.8 that As concentration is positively correlated with pH at Datong Basin, with a substantial increase above pH 8.

ACKNOWLEDGMENTS

Our research work on As hydrogeochemistry in the past 10 years has been financially supported by National Natural Science Foundation of China (Grant Nos 49832005, 40425001, and 40830748), Ministry of Science and Technology of China (2008DFA20950), and Ministry of Education of China (111 project).

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6 Nanotechnology Application in Metal Ion Adsorption

Xiangke Wang and Changlun Chen

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6.1 INTRODUCTION

With the development of science and technology, the application of nanomaterials and nanotechnology in environmental pollution management has been intensively interesting in the last decade. Materials in the nanosized range are considered the best candidates in the removal of organic and inorganic pollutants from the environment because of their unique physicochemical properties such as large surface area, high reactivity, and high adsorption capacity. In all kinds of nanomaterials, carbon nanomaterials, including active carbon, carbon nanotubes (CNTs), and fullerenes, are studied extensively in terms of potential applications in catalyst supports, environmental remediation, etc. Their adsorption may also affect the fate, transformation, and transfer of toxic substances in the environment. Therefore, an understanding of the adsorption and desorption behavior of toxic substances is critical in evaluating environmental and health impacts.

CNTs [1] include single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs), depending on the number of layers. The monomer structure of fullerene is a closed graphite ball, whereas CNTs are rolled-up graphite sheets forming a coaxial tube (Figure 6.1) [2].

The pollution of water resources due to the indiscriminate disposal of metal ions has been causing worldwide concern. Wastewater from many industries, such as metallurgical, tannery, chemical manufacturing, mining, and battery manufacturing industries, contains one or more toxic metal ions. It is necessary to remove these metal ions from the wastewaters before releasing into the environment, because there is a possibility of toxic metal ions entering into the food chain through waste

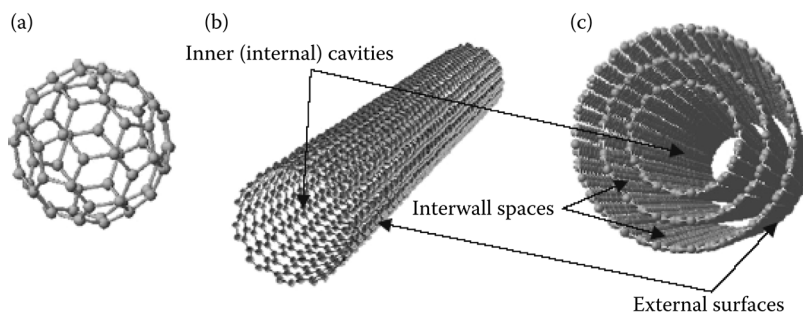


FIGURE 6.1 Schematic structures of fullerene (a), SWCNTs (b), and MWCNTs (c), showing inner cavities, interwall spaces, and external surfaces. Fullerene (C_{60}) has only an external surfaces. (From Yang, K. and Xing, B.S., *Environ. Pollut.*, 145, 529–537, 2007. With permission.)

discharges into water bodies. Adsorption is one of the conventional methods being used to remove metal ions. CNTs are considered as promising materials for use as adsorbents in adsorption technology. There are a number of recent publications on the sorption of various metal ions (i.e., Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , $Cr(VI)$, etc.) from aqueous solution by raw and surface-oxidized CNTs, which discuss their sorption capacities, mechanisms, process parameters, desorption, and further research works [3–14]. They showed that metal ion sorption equilibrium data are commonly correlated with the Langmuir and/or the Freundlich equations, as well as an increase of maximum sorption capacity with application of the oxidized CNTs. An increase in the removal of metal ions with increasing solution pH was also demonstrated, and reached a maximum at $pH > 8$ for most metal ions. Generally, the adsorption of metal ions on oxidized CNTs is a little higher than that of metal ions on raw CNTs. During the oxidization process, many functional groups (such as $-COOH$, $-CH$, and $-COH$) are introduced to the surfaces of oxidized CNTs. In the removal of $Cr(VI)$ from aqueous solutions, the adsorption of $Cr(VI)$ decreased with increasing pH values. At low pH values, part of the $Cr(VI)$ removal was attributed to the reduction of $Cr(VI)$ to $Cr(III)$ on the surfaces of oxidized CNTs [15,16].

Assessing the risks imposed by the use of nanomaterials in commercial products and environmental applications requires a better understanding of their mobility, bioavailability, and toxicity. For nanomaterials to comprise a risk, there must be both a potential for exposure and a hazard that results after exposure. The important processes and pathways of nanoparticles (NPs) in the environment are depicted in Figure 6.2. Release of NPs may come from point sources such as production facilities, landfills, or wastewater treatment plants, or from nonpoint sources such as wear from materials containing NPs. Accidental release of NPs during production or transport is also possible. In addition to the unintentional release there are also NPs released intentionally into the environment. Whether the particles are released directly into water/soil or the atmosphere, they all end up in soil or water, either directly or indirectly, for instance, via sewage treatment plants, waste handling, or aerial deposition. In the environment, the formation of aggregates and therefore of larger particles that are trapped or eliminated through sedimentation affects the concentrations of free NPs (Figure 6.3). Humans can be influenced either directly by NPs through exposure to air, soil, or water or indirectly by consuming plants or animals that have accumulated NPs. Aggregated or adsorbed NPs will be less mobile, but uptake by sediment-dwelling animals or filter feeders is still possible [17].

In the removal of heavy metal ions from the natural environment, many conventional methods have been used, including oxidation, reduction, precipitation, membrane filtration, ion exchange, sorption, etc. Among the above methods, the promising process for the removal of metal ions from water and wastewater is sorption. In this chapter, we will discuss the application of nanomaterials, especially carbon nanomaterials, in the removal of heavy metal ions from wastewater.

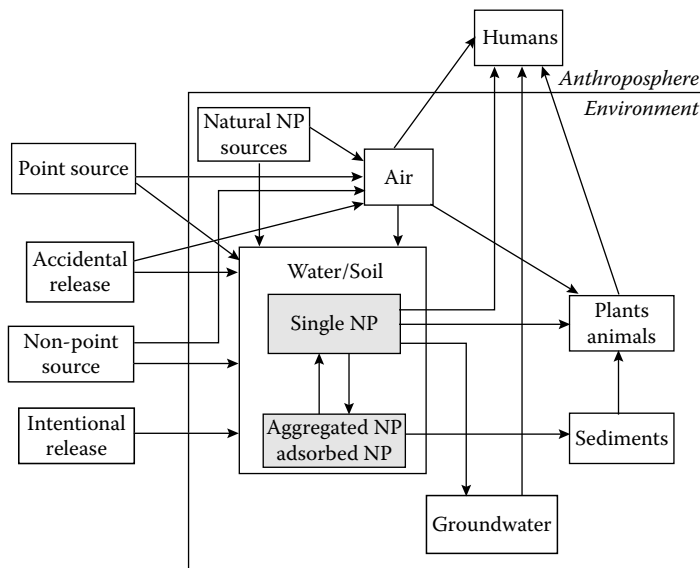


FIGURE 6.2 NP pathways from the anthroposphere into the environment, reactions in the environment, and exposure of humans. (From Nowack, B., and Bucheli, T.D., *Environ. Pollut.*, 150, 5, 2007. With permission.)

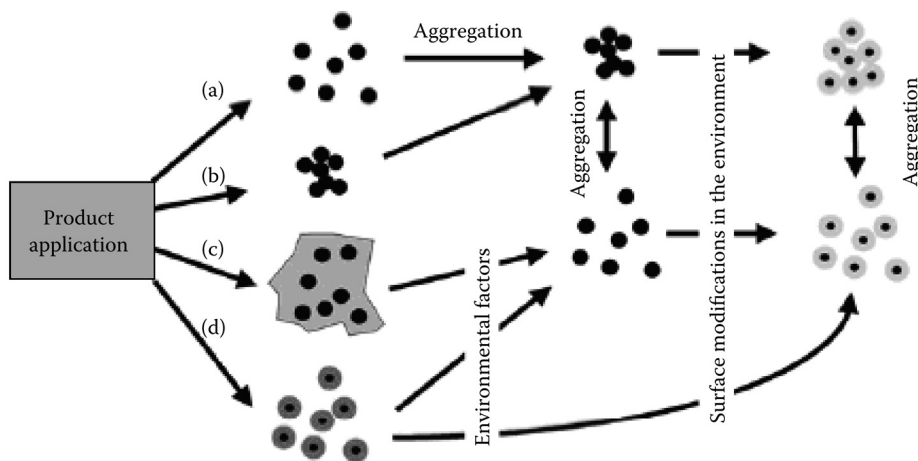


FIGURE 6.3 Release of NPs from products and (intended or unintended) applications: (a) release of free NPs, (b) release of aggregates of NPs, (c) release of NPs embedded in a matrix, and (d) release of functionalized NPs. Environmental factors (e.g., light, microorganisms) result in the formation of free NPs that can undergo aggregation reactions. Moreover, surface modifications (e.g., coating with natural compounds) can affect the aggregation behavior of NPs. (From Nowack, B., and Bucheli, T.D., *Environ. Pollut.*, 150, 5, 2007. With permission.)

6.2 CHARACTERIZATION OF NANOMATERIALS

The raw CNT is a long cylinder made of a hexagonal honeycomb lattice of carbon, bound by two pieces of fullerenes at the ends. The fullerene structure at the end of the raw tube can be removed during treatment with nitric acid or other acids [18]. Generally, 3 mol/L HNO_3 is used to remove the cap of the tubes and to generate some functional groups at the ends and on the defective sites of CNTs.

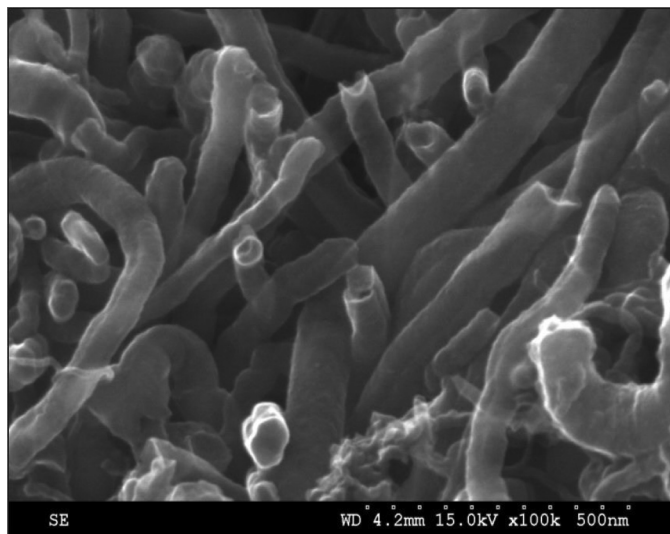


FIGURE 6.4 SEM image of oxidized MWCNTs.

CNTs and HNO_3 are mixed and ultrasonically stirred for a period of time, and then rinsed with distilled water to remove the acid in the system until the pH of the solution reaches about neutral. Removal of the cap from the end of the nanotube makes it possible for water molecules or metal ions to diffuse into the inner channel of the tube [19,20]. The morphological structures of the nanomaterial can be determined by scan electron microscopy (SEM). SEM analysis (Figure 6.4) shows that the cap of CNTs is removed after the oxidation, whereas the hollow structure of CNTs can be observed by transmission electron microscopy (TEM) (Figure 6.5).

The surface properties and the functional groups on the surfaces of oxidized MWCNTs can be characterized by Fourier transform infrared (FTIR) spectra analysis. Generally, the FTIR measurement is mounted on a KBr pellet at room temperature. Figure 6.6 shows an FTIR analysis of oxidized

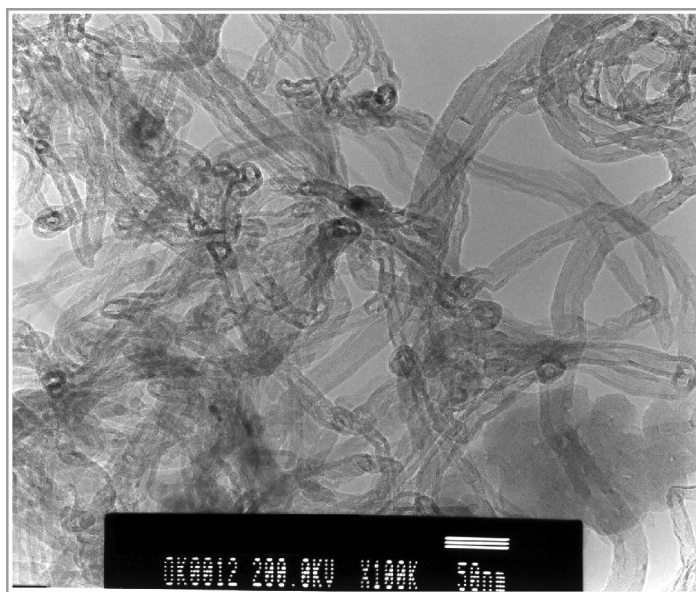


FIGURE 6.5 TEM image of oxidized MWCNTs.

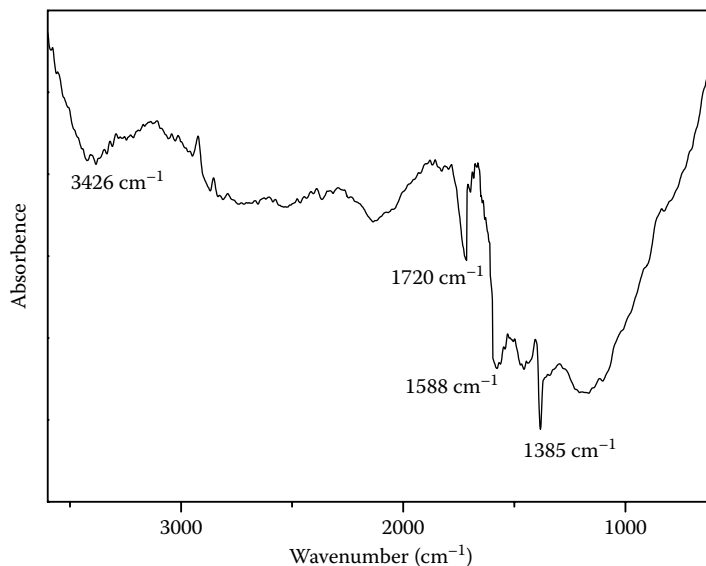


FIGURE 6.6 FTIR of oxidized MWCNTs. (From Chen, C.L. et al., *J. Colloid Interface Sci.*, 323, 33–41, 2008. With permission.)

MWCNTs and indicates that this acid treatment generates functional groups on the surfaces of oxidized MWCNTs as a hydroxyl group ($-\text{COOH}$, 3426 cm^{-1}) and a carboxyl group ($-\text{OH}$, 1720 cm^{-1}), and the bands of ~ 1600 and $\sim 1380\text{ cm}^{-1}$ correspond to asymmetric and symmetric $-\text{COO}^-$ stretching [21,22]. FTIR analysis indicates that many functional groups are generated after the oxidation treatment, and these functional groups are helpful in bonding metal ions from solution to oxidized MWCNTs.

X-ray photoelectron spectroscopy (XPS) can be used to analyze functional groups and an existing form of an element. Figure 6.7a through c shows the XPS survey spectrum, C1s and O1s high-resolution XPS spectra (using an x-ray photoelectron spectrometer, Kratos Axis Ultra DLD) of acidified MWCNTs by concentrated nitric acid [23]. The binding energies obtained in the XPS analysis were corrected by referencing the C1s line to 284.6 eV . Several peaks attributable to carbon and oxygen are present in the survey spectra of acid oxidized MWCNTs (Figure 6.7a). There is no N peak in the spectra, which indicates that no N was introduced into the acidified MWCNTs after MWCNTs were treated with concentrated nitric acid. The high-resolution C1s spectrum of acidified MWCNTs has been resolved into four individual component peaks located at 284.7 , 285.3 , 286.8 , and 289.1 eV , respectively. These peaks represent graphic carbon ($284.7 \pm 0.1\text{ eV}$), carbon linked to hydroxyl groups ($285.3 \pm 0.2\text{ eV}$), carbon in carbonyl groups ($286.9 \pm 0.1\text{ eV}$), and carboxyl groups ($289.1 \pm 0.1\text{ eV}$) according to the curve-fitting procedures (shown in Figure 6.7b) [24–26].

The high-resolution O1s spectrum of acidified MWCNTs can be fitted to two peaks (shown in Figure 6.7c). The binding energies at 531.8 and 533.4 eV can be assigned to the O in the $\text{C}=\text{O}$ and alcoholic $\text{C}-\text{O}$ groups, respectively [27]. So, incorporating the high-resolution C1s, it can be deduced that the functional groups introduced onto the surface of acidified MWCNTs are mainly hydroxyl, carbonyl, and carboxyl groups. The amounts of functional groups formed on acidified MWCNTs, including hydroxyl, carbonyl, and carboxyl, were determined by Boehm's titration method and the results are shown in Table 6.1. In Table 6.1, the amounts of hydroxyl and carboxyl first increase and then decrease, but the amounts of carbonyl change irregularly during the treatment time. During the initial stage of the acidified treatment, the defective sites and the ends of MWCNTs are easily oxidized to alcohol and aldehyde, which cause the increase of hydroxyl and carbonyl groups. The alcohol and aldehyde can be further oxidized into acid, which causes the increase of carboxyl. With increasing time, the oxidation rate of MWCNTs to alcohol and aldehyde

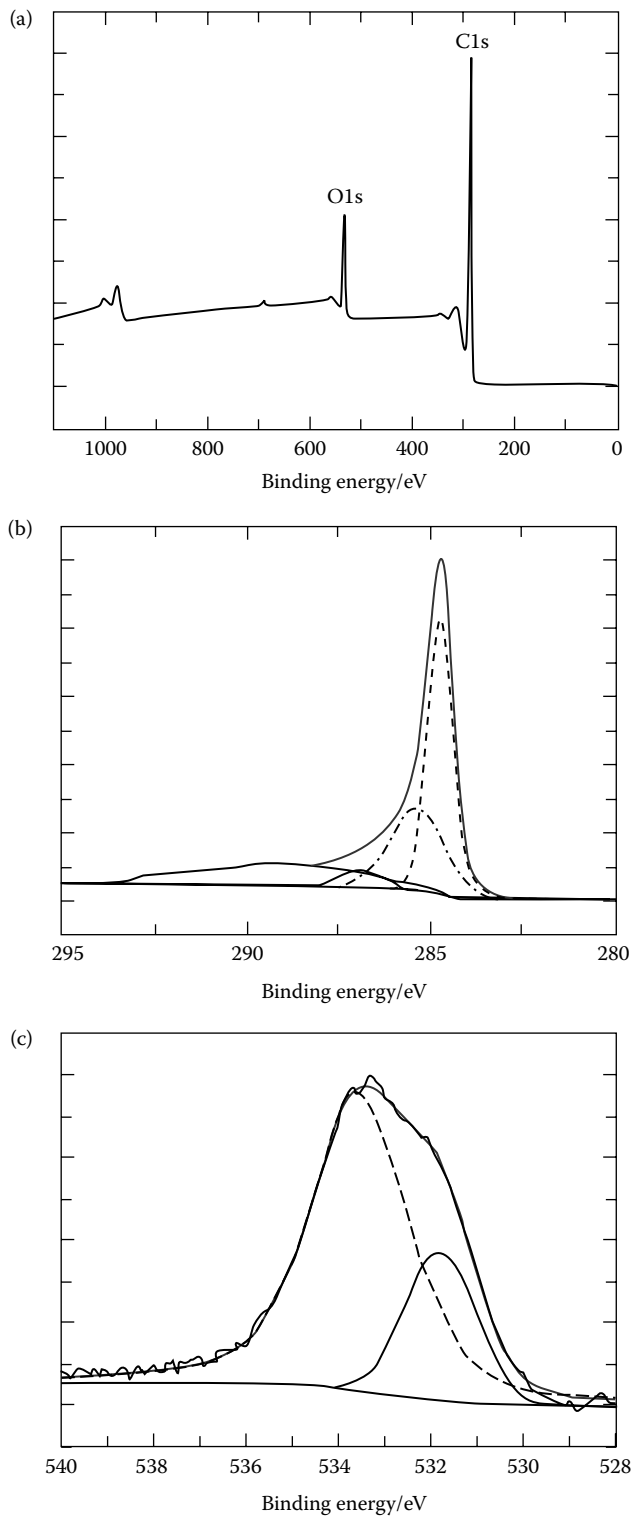


FIGURE 6.7 XPS survey (a), C1s (b), and O1s (c) high-resolution spectra of acidified MWCNTs. (From Wang, H. et al., *J. Colloid Interface Sci.*, 316, 277–283, 2007. With permission.)

TABLE 6.1
Amount of Functional Groups on MWCNTs after Different Acidification Treatment Time

Acidification Time (h)	Amount of Hydroxyl (mmol/g)	Amount of Carbonyl (mmol/g)	Amount of Carboxyl (mmol/g)	Amount of All the Groups (mmol/g/wt%)
0	— ^a	—	—	—/—
1	0.44	0.59	0.58	1.61/5.01
2	0.61	0.19	1.04	1.84/6.25
6	0.99	0.46	1.37	2.82/9.13
10	0.77	1.34	0.95	3.06/9.34
Annealed MWCNTs ^b	0.01	0.31	—	0.32/0.89

Source: Wang, H. et al., *J. Colloid Interface Sci.*, 316, 277–283, 2007. With permission.

^a — represents nondetectable.

^b The 6 h-acidified MWCNTs with 800°C annealed for 2 h in an argon flow.

slows down and the alcohol and aldehyde continue to be oxidized to acid, which causes the decrease of alcohol and aldehyde. Although alcohol and aldehyde are still oxidized to acid, because the formed acid was finally oxidized to carbon dioxide and the production rate is less than the consumption rate, the amount of carboxyl decreases. Due to the different abilities of MWCNTs being oxidized to alcohol, aldehyde, and acid, the amount of functional groups changes differently and even the carbonyl changes irregularly.

6.3 APPLICATION OF NANOMATERIALS IN THE REMOVAL OF METAL IONS

6.3.1 REMOVAL OF HEAVY METAL IONS

6.3.1.1 Removal of Cr(VI)

Chromium exists in the environment mainly in two states: trivalent Cr(III) and hexavalent Cr(VI). Cr(III) is an essential element in humans and is much less toxic than Cr(VI). Cr(VI) is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions. Cr(VI) is one of the extremely toxic heavy metals found in various industrial waters and can cause health problems such as liver damage, pulmonary congestion, vomiting, and severe diarrhea [28,29]. Due to the severe toxicity of Cr(VI), the EU Directive, WHO, and the U.S. EPA have set the maximum contaminant concentration of Cr(VI) in domestic water supplies at 0.05 mg/L [15,30].

In the study of Cr(VI) removal from wastewater, pH is one of the most important parameters controlling the sorption process. The effect of pH on the removal of Cr(VI) is investigated by testing three values of ionic strengths (i.e., 0.1, 0.01, and 0.001 M NaClO_4) and two contact times (i.e., 65 and 165 h). Figure 6.8 shows that the maximum adsorption of Cr(VI) occurs at the pH range below 2, and then the removal of Cr(VI) decreases with increasing pH values, and Cr(VI) is not adsorbed on oxidized MWCNTs at $\text{pH} > 6$ [31]. The adsorption of Cr(VI) from an aqueous solution to oxidized MWCNTs is independent of ionic strength, and dependent on pH values. The ionic strength can influence the double-layer thickness and interface potential, thereby affecting the binding of adsorbed species. Outer-sphere complexes are expected to be more susceptible to ionic strength variations than inner-sphere complexes, since the background electrolyte ions are placed in the same plane for outer-sphere complexes. In general, the sorption mechanism of surface complexation is significantly affected by pH, whereas the sorption mechanism of ion exchange is influenced by ionic strength. The strong pH-dependent and ionic strength-independent adsorption of Cr(VI) to oxidized MWCNTs suggests that the adsorption of Cr(VI) is mainly dominated by surface complexation rather than ion exchange. It is well known that Cr(VI) exists mainly as the species of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ in solution at $\text{pH} < 6$, and as CrO_4^{2-} species at $\text{pH} > 6$ [28,29]. The functional groups, such as $-\text{OH}$ and $-\text{COOH}$,

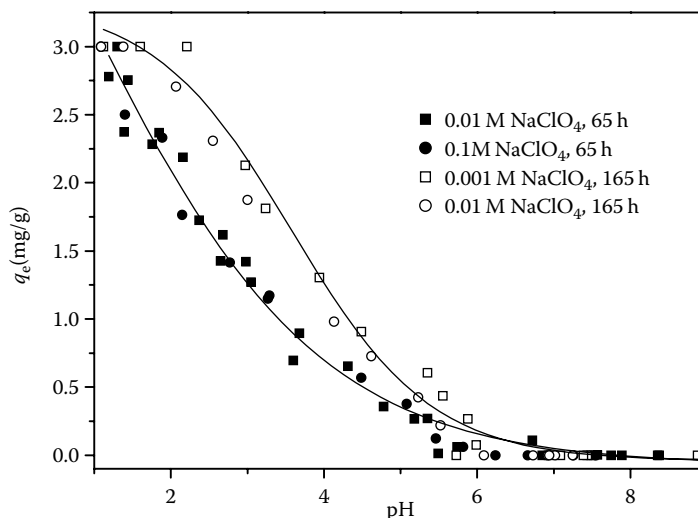
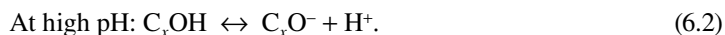
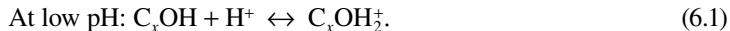
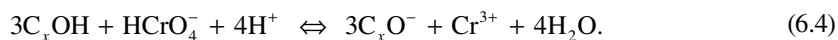
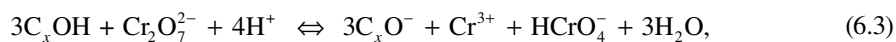


FIGURE 6.8 Removal of Cr(VI) from solution to oxidized MWCNTs as a function of pH values at different ionic strengths and contact times. $m/V = 0.1$ g/L, $C[\text{Cr(VI)}]_{\text{initial}} = 3.0$ mg/L, $T = 20 \pm 2^\circ\text{C}$. (From Hu, J. et al., *J. Hazard. Mater.*, 162, 1542, 2009. With permission.)

on the surface of the oxidized MWCNTs, are supposed that oxidized MWCNTs are the carbonaceous material as C_xOH , where C_x = carbon. It is necessary to note that the hydroxylated surface groups vary at different pH values because of the protonation/deprotonation processes:



The negatively charged Cr(VI) is easily adsorbed on oxidized MWCNTs at low pH values, and difficult to adsorb at high pH values. At high pH values, the higher the valence of adsorbed anions, the more negative the surface becomes, thus inhibiting the further adsorption of anions. Two types of chemical treatments are currently used for Cr(VI) removal: the first type removes Cr(VI) anions directly, whereas the second type relies on the reduction of Cr(VI) to Cr(III). It is known [15,16] that Cr(VI) is reduced to Cr(III) in the presence of a reducing substrate (C_xOH) on the occurrence of redox reactions between the surface groups and the Cr(VI) at low pH values [14]:



The total concentrations of Cr(VI) and Cr(III) were analyzed in solution and it was found that Cr was mainly in the trivalent form at $\text{pH} < 3$ (Figure 6.9) [15]. The presence of functional groups (such as C–H, –OH, and –COOH) on the surface of oxidized MWCNTs ensures the capture of metallic cations by surface complexation and cation exchange mechanisms. The adsorption of Cr(VI) anions is complicated, but it can be related to surface complexation reactions with protonated sites or by electrostatic attraction with electrophilic surface sites. Cr(VI) anions are adsorbed by the protonated groups and the electrophilic surface groups of MWCNTs, and then part of Cr(VI) is reduced to Cr(III) cations, which are partly released back into the solution. Cr(III) cations are captured by sorption and ion exchange on the weak acid surface groups or on the basal plane sites on MWCNTs [29,32].

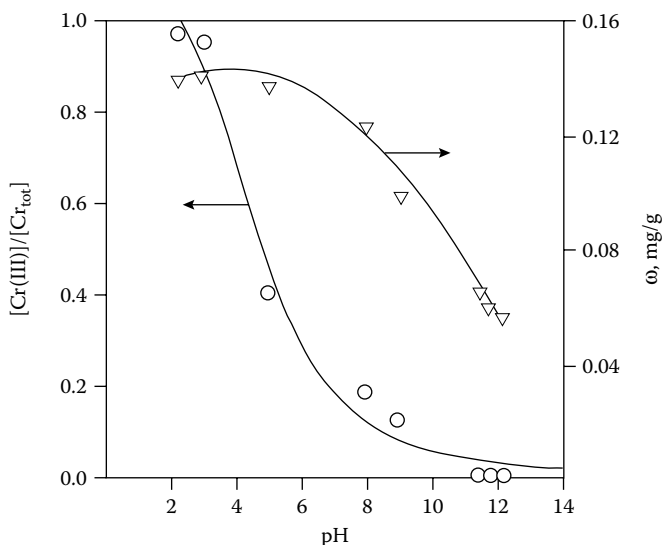


FIGURE 6.9 Total chromium adsorption capacity on activated carbon and trivalent chromium percentage for aqueous solution with initial concentration of Cr(VI) 25 mg/L at different equilibrium pH levels. (From Di Natale, F. et al., *J. Hazard. Mater.*, 145, 381–390, 2007. With permission.)

The characteristics and the concentration of ionic species in solution obviously represent the driving force for adsorption phenomena. Hence, speciation analysis of the equilibrium solution is the first step in understanding experimental data. Trivalent and hexavalent chromium speciations are calculated by using chromium mass balance and electric neutrality equations coupled with equations representative of chemical equilibria [33]. Trivalent and hexavalent chromium speciations are shown in Figure 6.10 for the case of a total chromium concentration of 0.5 mM (~25 mg/L). Speciation analyses show that at pH greater than 7 Cr(VI) is mainly present as CrO_4^{2-} , whereas at pH lower than 3 trivalent chromium is mainly represented by Cr^{3+} [15].

The adsorptions of Cr(VI) on raw and oxidized MWCNTs are shown in Figure 6.11 as a comparison. After the oxidation treatment, the functional groups at oxidized MWCNT surfaces obviously increase and thereby enhance the adsorption of Cr(VI). Figure 6.11 shows that the removal percentage of Cr(VI) on raw MWCNTs is lower than that of Cr(VI) on oxidized MWCNTs under the same experimental conditions, which is also evidence of the presence of oxygen-containing functional groups on the external and internal surfaces of oxidized MWCNTs. Carboxylate groups have also been introduced onto the surfaces of CNTs by reaction with strong oxidizing agents, and hemispherical caps on the nanotubes have been removed. These functional groups are active in forming complexes with Cr(VI) on the surfaces of oxidized MWCNTs.

To further understand the removal mechanism of Cr(VI) on MWCNTs, the sample after reaction with Cr(VI) at pH 2.85 was analyzed with XPS. The XPS spectrum (Figure 6.12) shows two $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$ peaks that are, respectively, centered at 577.5 and 587.2 eV, which are consistent with Cr(III) and Cr(VI), respectively [29,34]. XPS analysis indicates that Cr is adsorbed on MWCNTs as Cr(III) and Cr(VI), which also suggests that some adsorbed Cr(VI) anions are reduced to Cr(III) on the surfaces of MWCNTs.

6.3.1.2 Removal of Bivalent Cations

6.3.1.2.1 Removal of Ni(II)

Nickel is a toxic metal ion that is present in wastewater. More than 40% of the nickel produced is used in steel factories and nickel batteries and in the production of some alloys, which causes an increased Ni(II) burden on the ecosystem and deterioration of water quality. Wastewater dissolved

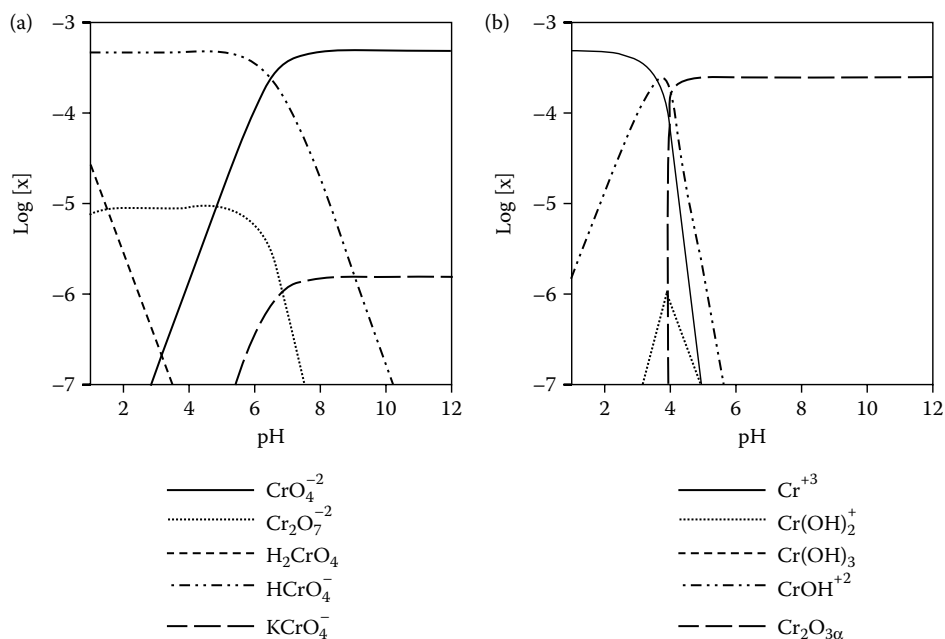


FIGURE 6.10 Speciation of hexavalent (a) and trivalent (b) chromium as a function of pH for a total chromium concentration of 0.5 mM obtained from chemical equilibrium analysis. (From Di Natale, F., et al., *J. Hazard. Mater.*, 145, 381–390, 2007. With permission.) (Values of the thermodynamics constants for ion complexation are taken from Stumm, W. and Morgan, J.J., *Aquatic Chemistry*, 3rd Edition, John Wiley and Sons, New York, 1996.)

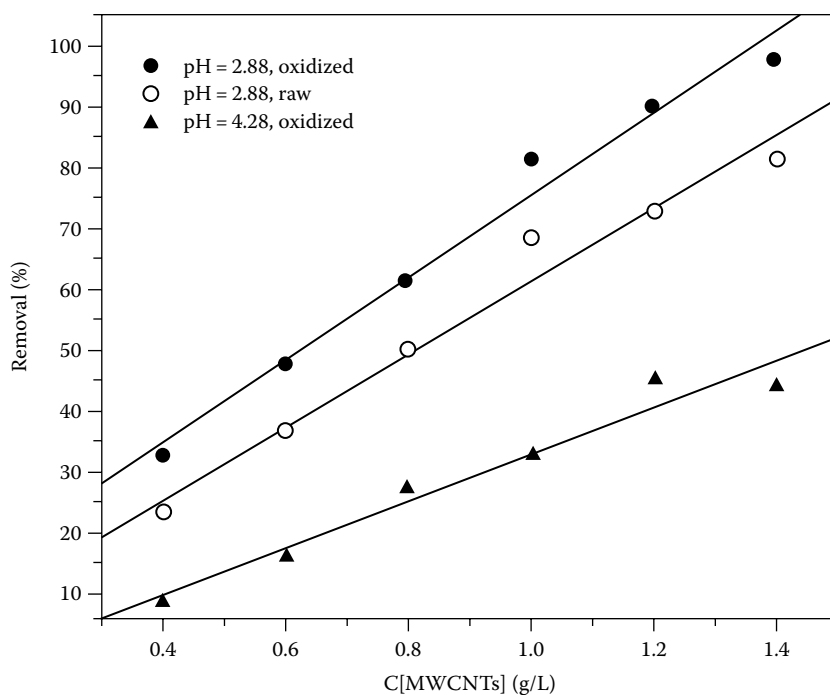


FIGURE 6.11 Removal of Cr(VI) as a function of MWCNT content. $C[\text{Cr(VI)}]_{\text{initial}} = 3.0 \text{ mg/L}$, $I = 0.01 \text{ M NaClO}_4$, $T = 20 \pm 2^\circ\text{C}$, contact time = 165 h. (From Hu, J. et al., *J. Hazard. Mater.*, 162, 1542, 2009. With permission.)

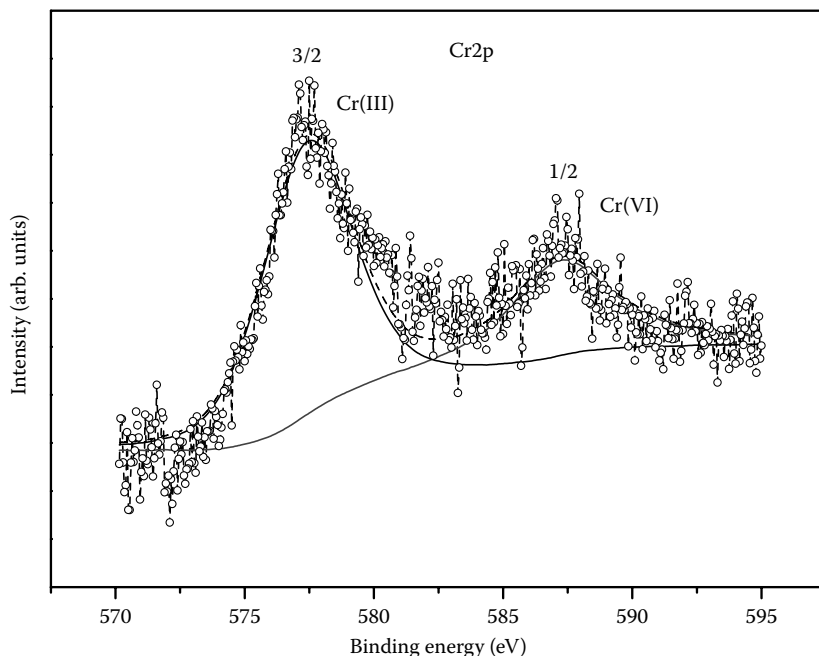


FIGURE 6.12 XPS spectrum of oxidized MWCNT sample after Cr(VI) sorption at pH 2.85. The solid lines represent the Cr(III) and Cr(VI) components. The dash line is the fit envelope, and the solid circles show the data. (From Hu, J. et al., *J. Hazard. Mater.*, 162, 1542, 2009. With permission.)

or dispersed with Ni(II) is harmful, and causes vomiting, chest pain, and shortness of breath. Various technologies exist for removing Ni(II), which include filtration, surface complexation, chemical precipitation, ion exchange, adsorption using activated carbon, electrode position, and membrane process. Adsorption is considered to be one of the most attractive processes for Ni(II) removal from solution, since adsorbents are generally easy to handle and can be used for various situations without large apparatuses.

Because of the highly porous and hollow structure, large specific surface area, light mass density, and strong adsorption ability, CNTs are considered to be the promising material in the removal of organic or inorganic pollutants. The application of CNTs in the removal of Ni(II) was investigated and the results indicated that CNTs are efficient in the removal of Ni(II) from an aqueous solution [3,12]. In the application of CNTs to remove Ni(II), the adsorption velocity is quite important because it is necessary for the use of CNTs on a large scale. Figure 6.13 shows the effect of contact time and initial Ni(II) concentration on Ni(II) adsorption on oxidized MWCNTs. Equilibrium was reached within 40 min for all concentrations of Ni(II) used in the study. This result is very interesting because equilibrium time is one of the parameters for economical wastewater treatment plant applications. The implication is that oxidized MWCNTs could be suitable for a continuous-flow system.

In Figure 6.13, the pseudo-second-order rate model was expressed as

$$\frac{t}{q_t} = \frac{1}{2K' \cdot q_e^2} + \frac{t}{q_e}, \quad (6.5)$$

where K' (g/mg/min) is the pseudo-second-order rate constant of adsorption, q_t (mg/g of dry weight) is the amount of Ni(II) adsorbed on the surface of the adsorbent at time t (min), and q_e (mg/g of dry weight) is the equilibrium adsorption capacity. Equation 6.5 was used to simulate the experimental

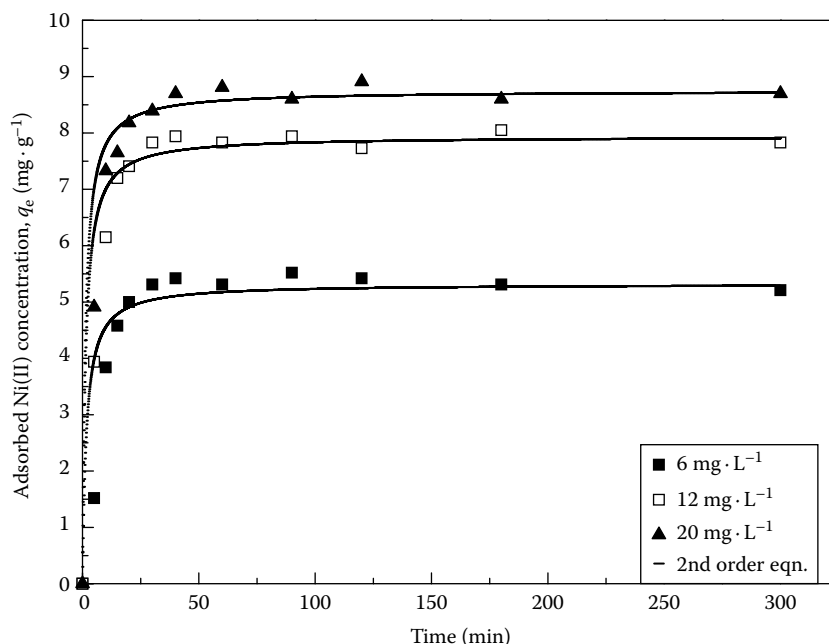


FIGURE 6.13 Effect of contact time on Ni(II) adsorption rate for various initial Ni(II) concentrations onto oxidized MWCNTs: experimental data and pseudo-second-order rate model fit ($\text{pH} = 6.55 \pm 0.02$, $I = 0.01 \text{ M KNO}_3$, $m/V = 0.75 \text{ g/L}$, $T = 291 \pm 1 \text{ K}$). (From Chen, C.L. and Wang, X.K., *Ind. Eng. Chem. Res.*, 45, 9144–9149, 2006. With permission.)

data, and the results indicated that the experimental data were modeled by the pseudo-second-order rate equation very well.

Information about the effect of temperature on the removal of metal ions is important to understand the mechanism. Figure 6.14 shows that the distribution coefficients, K_d (mL/g), increase with an increase in temperature. Bikerman [35] attributed this phenomenon to a negative temperature coefficient of solubility of solutes or a steep simultaneous decrease of real adsorption of solvent. The values of enthalpy, ΔH° , and entropy, ΔS° , were calculated from the slope and intercept of the plot of $\ln K_d$ versus $1/T$ (Figure 6.15) by using the equation

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (6.6)$$

The Gibbs free energy, ΔG° , of specific adsorption was calculated from the equation

$$\Delta G^\circ = H^\circ - T\Delta S^\circ, \quad (6.7)$$

where R (8.3145 J/mol/K) is the ideal gas constant and T (K) is the temperature. Relevant data calculated from Equations 6.6 and 6.7 are tabulated in Table 6.2. It is evident that the values of ΔH° are positive, that is, endothermic. One possible interpretation of the endothermicity of the enthalpy of adsorption is that ions such as Ni(II) are well solvated in water. For these ions to adsorb, they are to some extent denuded of their hydration sheath, and this dehydration process of ions needs energy. It is assumed that this energy of dehydration exceeds the exothermicity of ions attaching to the surface. The removal of water molecules from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of the enthalpy of adsorption to a

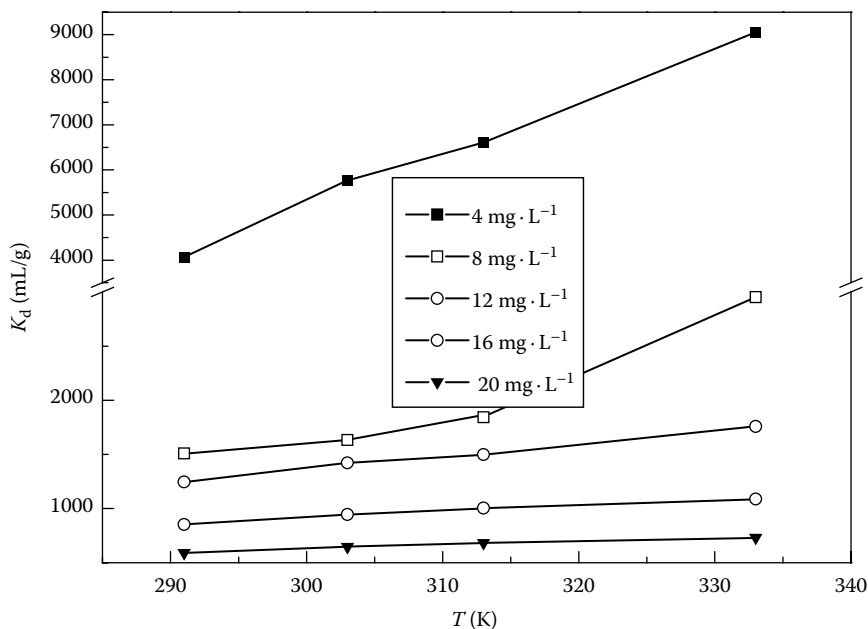


FIGURE 6.14 Plot of distribution coefficient K_d versus temperature for Ni(II) adsorption onto oxidized MWCNTs ($\text{pH} = 6.55 \pm 0.02$, $I = 0.01 \text{ M KNO}_3$, $m/V = 0.75 \text{ g/L}$). (From Chen, C.L. and Wang, X.K., *Ind. Eng. Chem. Res.*, 45, 9144–9149, 2006. With permission.)

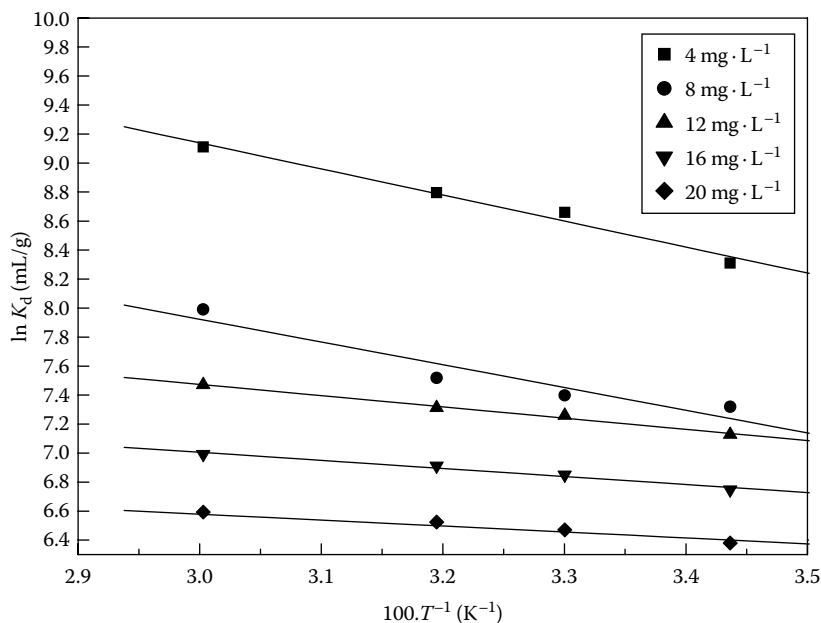


FIGURE 6.15 Semilogarithmic plot of distribution coefficient K_d versus reciprocal temperature for various concentrations of Ni(II) adsorption onto MWCNTs ($\text{pH} = 6.55 \pm 0.02$, $I = 0.01 \text{ M KNO}_3$, $m/V = 0.75 \text{ g/L}$). (From Chen, C.L. and Wang, X.K., *Ind. Eng. Chem. Res.*, 45, 9144–9149, 2006. With permission.)

TABLE 6.2
Thermodynamic Parameters for Ni(II) Adsorption onto Oxidized MWCNTs

$C_0(\text{Ni(II)})$ (mg/L)	ΔH° (J/mol)	ΔS° (J/mol/K)	$-\Delta G^\circ$ (kJ/mol)			
			$T = 292 \text{ K}$	$T = 303 \text{ K}$	$T = 313 \text{ K}$	$T = 333 \text{ K}$
4	14.93	120.75	35.12	36.57	37.78	40.19
8	13.04	104.99	30.54	31.80	32.85	34.95
12	6.45	81.47	23.70	24.68	25.50	27.12
16	4.62	72.09	20.97	21.84	22.56	24.00
20	4.07	67.09	19.52	20.32	20.99	22.34

Source: Chen, C.L. and Wang, X.K., *Ind. Eng. Chem. Res.*, 45, 9144–9149, 2006. With permission.

considerable extent. The Gibbs free energy change (ΔG°) is negative (as expected) for a spontaneous process under the conditions applied. The decrease in ΔG° with an increase in temperature indicates more efficient adsorption at higher temperatures. At higher temperatures, ions are readily desolvated, and therefore their adsorption becomes more favorable. The positive values of entropy change (ΔS°) reflect the affinity of oxidized MWCNTs toward Ni(II) ions in aqueous solutions and may suggest some structure changes in the adsorbents [36,37].

However, in the natural environment, both organic and inorganic pollutants are present in wastewater. A knowledge of the influence of organic pollutants on the adsorption of metal ions is helpful in understanding the application of nanomaterials in environmental pollution cleaning. Generally, surfactants are used extensively in household products, detergents, oil recovery, paint technology, flotation, and water treatment. Considerable amounts of surfactants are released to the environment, causing serious pollution problems in rivers, lakes, and oceans. The accumulation of surfactants can form large foam masses, affect aquatic organisms, and interfere in the removal processes of insoluble and soluble substances [38,39]. For all these reasons, many environmental and public health regulatory authorities have fixed stringent limits for anionic detergent as standard 0.5 mg/L for drinking water and relaxable up to 1.0 mg/L for other purposes [40]. At low concentrations, surfactants exist solely as monomers; above a critical aqueous concentration, which is specific for each surfactant, called the critical micelle concentration (CMC), aggregation of surfactant monomers occurs and hydrophobic interactions between the hydrocarbon chains of surfactant molecules are balanced by hydration and the electrostatic repulsive effects of the hydrophilic groups. It is recognized that surfactant properties strongly depend on counterion species. Anionic surfactant molecules, which are negatively charged, can bind to positively charged metal ions. Once the adsorption of surfactant molecules on particle surfaces is established, self-organization of the surfactant into micelles (aggregative structures of surfactants) is expected to occur above the CMC [41,42].

The adsorption isotherms of nickel on oxidized MWCNTs are shown in Figure 6.16. To gain a better understanding of the mechanism and to quantify the adsorption data, the Langmuir [$C_s = abC_e / (1 + bC_e)$] and Freundlich ($C_s = K_f C_e^{1/n}$) isotherm models are used to simulate the adsorption of nickel on MWCNTs. Herein, a is the maximum adsorption capacity, b is the Langmuir adsorption constant, and K_f and $1/n$ are the Freundlich constants. The Langmuir and Freundlich constants obtained by fitting the adsorption equilibrium data are listed in Table 6.3. The values of the correlation coefficient (R^2) derived from the Langmuir model are closer to 1 than those derived from the Freundlich model, which indicates that the adsorption of nickel on MWCNTs is better simulated by the Langmuir model than by the Freundlich model. It can also be seen that the adsorption isotherms of nickel in the presence of sodium dodecylbenzene sulfonate (SDBS) are much higher than those of nickel in the absence of SDBS. The maximum adsorption capacity of nickel adsorption on SDBS-bound MWCNTs is higher than that of nickel adsorption on bare MWCNTs, which also

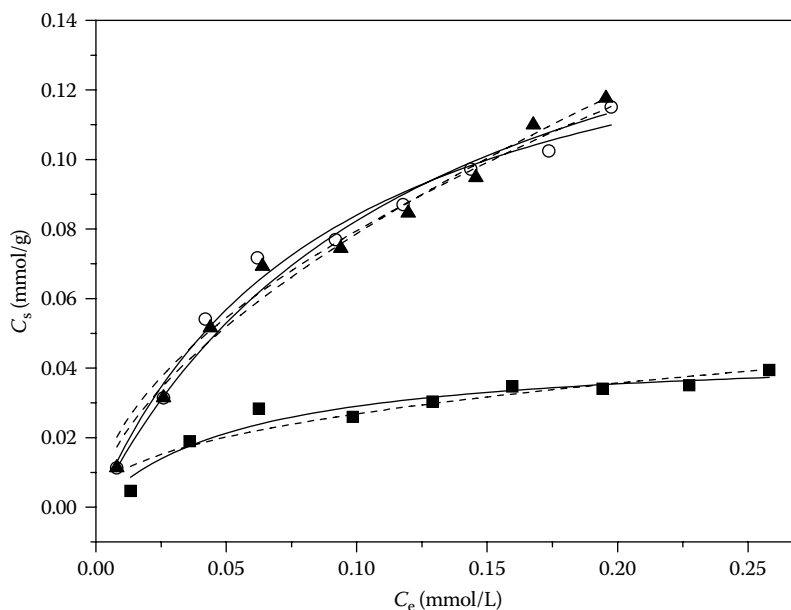


FIGURE 6.16 Adsorption isotherms of nickel to MWCNTs in the presence of SDBS. pH = 5.5 ± 0.1 , $T = 20 \pm 2^\circ\text{C}$, $I = 0.01 \text{ mol/L NaClO}_4$, $m/V = 0.8 \text{ g (MWCNTs)/L}$, $C(\text{SDBS})_{\text{initial}} = 0.98 \text{ mmol/L}$. Solid line: Langmuir model; dashed line: Freundlich model; (■) MWCNTs + nickel; (○) MWCNTs and SDBS are pre-equilibrated for 2 days before the addition of nickel (batch 1); (▲) nickel and SDBS are pre-equilibrated for 2 days before the addition of MWCNTs (batch 2). (From Tan, X.L. et al., *Carbon*, 46, 1741, 2008. With permission.)

indicates that SDBS–MWCNT hybrids have a stronger affinity for nickel adsorption than bare MWCNTs.

The adsorption isotherms of SDBS on oxidized MWCNTs are shown in Figure 6.17. The adsorption of SDBS is not affected by the addition of nickel in ternary systems. The linear adsorption isotherms of SDBS for different additional sequences suggest that the adsorption of SDBS on MWCNTs is far from saturation. The adsorption isotherms of SDBS to river sediment and to soils have also been shown to be near-linear [43,44]. The adsorption of SDBS to MWCNTs is far from saturation. MWCNTs are very suitable in the removal of SDBS from aqueous solutions.

To give a clear illustration of SDBS and nickel adsorption on MWCNTs, a diagram of adsorption mechanism is given in Figure 6.18. It is commonly believed that the chemical interaction between the metal ions and the surface functional groups of MWCNTs is the major adsorption mechanism in the absence of organic materials. In the absence of a surfactant, protons in the carboxylic and phenolic groups of MWCNTs can exchange with the metal ions in the aqueous phase. The adsorption of metal ions on

TABLE 6.3
Parameters of Adsorption Models for Nickel on Oxidized MWCNTs

System	Langmuir Model			Freundlich Model		
	a (mmol/g)	b (L/mmol)	R^2	K_f (mmol/g)	$1/n$	R^2
MWCNTs + nickel	0.0456	17.56	0.9373	0.0692	2.43	0.8849
Batch 1	0.1608	10.94	0.9850	0.2784	1.84	0.9700
Batch 2	0.1852	8.012	0.9823	0.3132	1.67	0.9821

Source: Chen, C.L. and Wang, X.K., *Ind. Eng. Chem. Res.*, 45, 9144–9149, 2006. With permission.

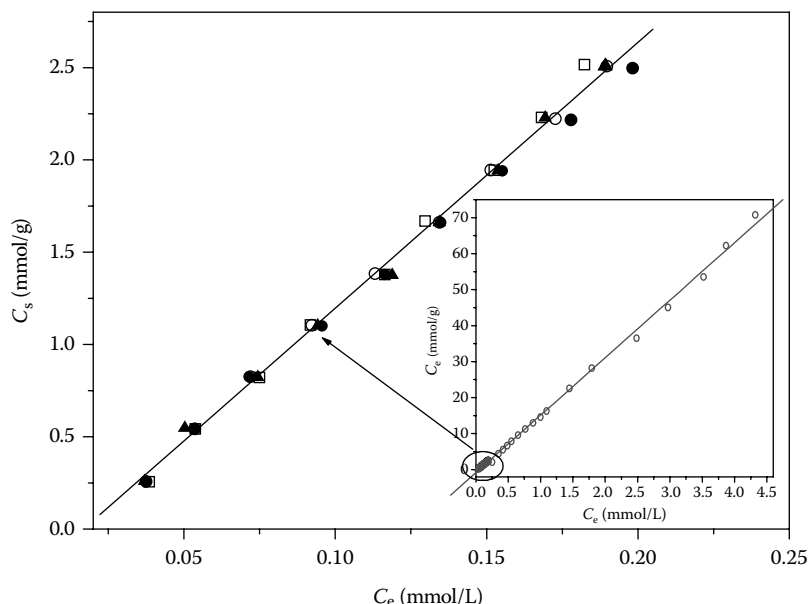


FIGURE 6.17 Adsorption isotherms of SDBS to MWCNTs in the presence of nickel. $\text{pH} = 5.5 \pm 0.1$; $T = 20 \pm 2^\circ\text{C}$; $I = 0.01 \text{ mol/L NaClO}_4$; $m/V = 0.8 \text{ g (MWCNTs)/L}$; $C(\text{nickel})_{\text{initial}} = 0.15 \text{ mmol/L}$; ($\square$) MWCNTs + SDBS; ($\circ$) MWCNTs and SDBS are pre-equilibrated for 2 days before the addition of nickel; ($\blacktriangle$) nickel and SDBS are pre-equilibrated for 2 days before the addition of MWCNTs; ($\bullet$) nickel, SDBS, and MWCNTs are added in solution simultaneously. (From Tan, X.L. et al., *Carbon*, 46, 1741, 2008. With permission.)

oxidized MWCNTs is mainly attributed to surface complexation, ion exchange, and electrostatic attraction. In the presence of a surfactant, MWCNT surfaces become hydrophilic due to the hydrophilic heads of the surfactant oriented toward the bulk solution. Surfactant monomers accumulate at the MWCNT–water interfaces and increase the contact angle between MWCNTs and nickel. SDBS molecules adsorbed on the surfaces of MWCNTs cause an attraction between the anionic head groups and the positively charged cations, and thereby promote the adsorption of nickel to MWCNTs.

6.3.1.2.2 Removal of Pb(II)

Lead in the natural environment arises from both natural and anthropogenic sources, and is detrimental to humans and living things. Long-term drinking water containing a high level of lead will cause serious disorders, such as anemia, kidney disease, and mental retardation [13]. The enrichment and bioavailability of Pb(II) by plants and crops can transfer Pb(II) from the natural environment to humans. Metal ions are nonbiodegradable, and therefore must be removed from water to eliminate the potential danger to humans and the environment. Many conventional methods have been used to remove metal ions from aqueous solutions, including oxidation, reduction, precipitation, membrane filtration, ion exchange, and sorption. Of these methods, a promising one for the removal of metal ions from water and wastewater is sorption.

Figure 6.19 shows the adsorption of Pb(II) on oxidized MWCNTs in the presence of 0.01 M NaClO_4 , KClO_4 , NaCl , and NaNO_3 , respectively, as a function of pH values. The pH of the solution plays an important role in the sorption characteristics of Pb(II) to oxidized MWCNTs. The removal of Pb(II) increases very quickly from about 10% to 90% at pH 6–7, remains constant with increasing pH values at pH 7–10, and then decreases steeply at pH > 10. It is known that lead species are present as Pb^{2+} , $\text{Pb}(\text{OH})^+$, $\text{Pb}(\text{OH})_2^0$, and $\text{Pb}(\text{OH})_3^-$ at different pH values (Table 6.4 and Figure 6.20). At pH < 6 the predominant lead species is Pb^{2+} , and its removal is mainly accomplished by sorption reaction.

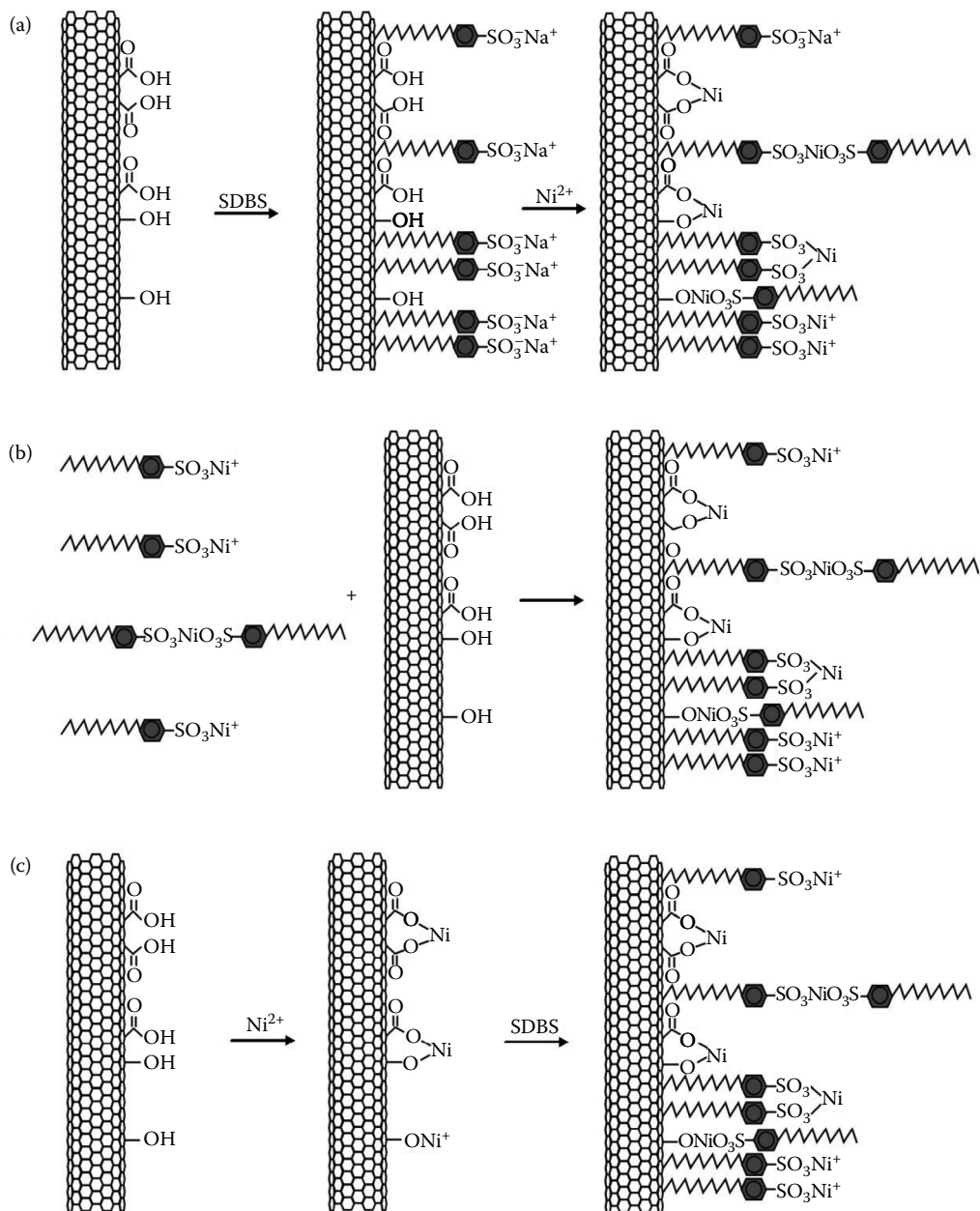


FIGURE 6.18 Diagram of the major mechanism for adsorption of nickel and SDBS on MWCNTs in the presence of SDBS/nickel. (From Tan, X.L. et al., *Carbon*, 46, 1741, 2008. With permission.)

The low Pb^{2+} sorption that takes place at low pH can be attributed partly to the competition between the H^+ and Pb^{2+} ions on the surface sites. At the pH range 7–10, the removal of Pb remains constant and reaches a maximum. The main species at pH 7–10 are $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_2^0$, and thus the removal of Pb is possibly accomplished by simultaneous precipitation of $\text{Pb}(\text{OH})_2^0$ and sorption of $\text{Pb}(\text{OH})^+$. At the pH range 10–12, the predominant lead species are $\text{Pb}(\text{OH})_2^0$ and $\text{Pb}(\text{OH})_3^-$. The decrease in Pb(II) sorption to oxidized MWCNTs at pH 10–12 can be attributed in part to competition between OH^- and $\text{Pb}(\text{OH})_3^-$; the negative $\text{Pb}(\text{OH})_3^-$ is difficult to be adsorbed on the negative surface charged oxidized MWCNTs

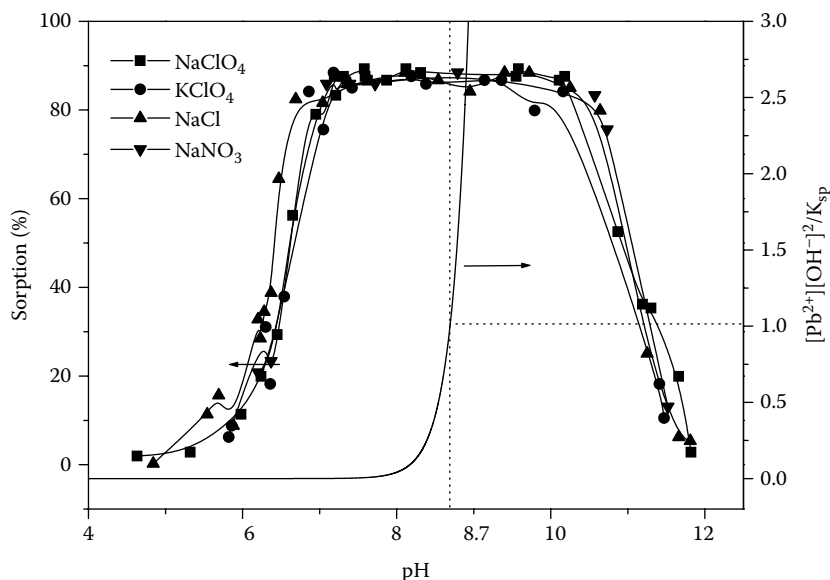


FIGURE 6.19 Variations in sorption of Pb(II) to oxidized MWCNTs as a function of equilibrium pH and foreign ions. $C[\text{Pb(II)}]_{\text{initial}} = 4.83 \times 10^{-5} \text{ mol/L}$, $m/V = 1.0 \text{ g/L}$, $I = 0.01 \text{ M}$, $T = 293 \text{ K}$, $K_{\text{sp}} = 1.2 \times 10^{-15}$. (From Xu, D. et al., *J. Hazard. Mater.*, 154, 407–416, 2008. With permission.)

at high pH values [5]. The precipitation constant of $\text{Pb(OH)}_{2(s)}$ is 1.2×10^{-15} , and the precipitation curve of lead at a concentration of $4.83 \times 10^{-5} \text{ mol/L}$ is also shown in Figure 6.19. Lead begins to form a precipitate at pH 8.7 if no lead is adsorbed on the oxidized MWCNTs. However, ~90% of the lead is adsorbed on oxidized MWCNTs at pH 7, and thereby it is impossible to form a precipitate because of the very low concentration of lead remaining in solution. Therefore, the abrupt sorption of Pb(II) on oxidized MWCNTs at pH 6–7 is not attributed to the precipitation of Pb(OH)_2 . The precipitation of Pb(OH)_2 does not play any role in the removal of Pb(II) from solution to oxidized MWCNTs at the whole pH range. The species of Pb(II) in solution at different pH values is most important for the removal of Pb(II) from an aqueous solution to oxidized MWCNTs.

Figure 6.19 also shows that the removal of Pb(II) from an aqueous solution to oxidized MWCNTs is not influenced by the background electrolyte foreign cations and anions. Heavy metal ions in solution will compete for interactions with the surface functional groups of oxidized MWCNTs, and Pb(II) ions have a higher affinity to the surfaces of oxidized MWCNTs than alkali metal ions; therefore, the competition of alkali ions on Pb(II) uptake to oxidized MWCNTs is almost negligible. Although the radii of hydration of $\text{K}^+ = 2.32 \text{ \AA}$ and $\text{Na}^+ = 2.76 \text{ \AA}$ [47] are different, the difference in the radii

TABLE 6.4
Equilibrium Constants (log K) for Pb(II) Hydrolysis Reactions

Equilibrium	log K
	$I = 0.01 \text{ M}, T = 298 \text{ K}$
$\text{Pb}^{2+} + \text{H}_2\text{O} = \text{Pb(OH)}^+ + \text{H}^+$	6.48
$\text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{Pb(OH)}_2 + 2\text{H}^+$	11.16
$\text{Pb}^{2+} + 3\text{H}_2\text{O} = \text{Pb(OH)}_3^- + 3\text{H}^+$	14.16

Source: Weng, C.H., *J. Colloid Interface Sci.*, 272, 262–270, 2004. With permission.

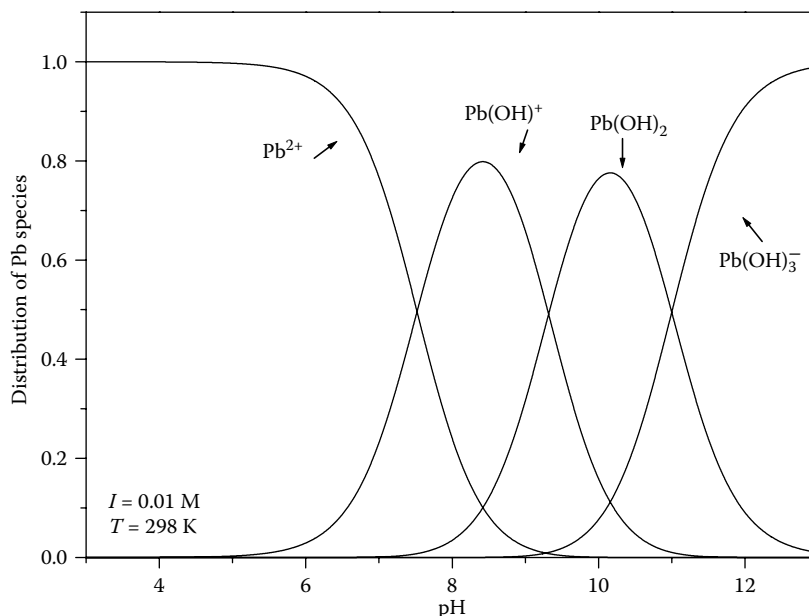


FIGURE 6.20 Distribution of Pb(II) species as a function of pH based on the equilibrium constants. (From Xu, D. et al., *J. Hazard. Mater.*, 154, 407–416, 2008. With permission.)

of hydration on bivalent Pb(II) sorption is still very weak. The inorganic acid radicals radium order is $\text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^-$; the negatively charged anions may form complexes with the oxygen-containing functional groups on the surfaces of oxidized MWCNTs. However, the effect of Cl^- , NO_3^- , and ClO_4^- on Pb(II) sorption to oxidized MWCNTs is still very weak, which suggests that surface complexes are formed on oxidized MWCNT surfaces. The effect of foreign ions on Pb(II) removal from solution to oxidized MWCNTs can be negligible.

The initial concentration of Pb(II) and solid oxidized MWCNT content (i.e., m/V) are the same for all data provided in Figure 6.19. The removal of Pb(II) is different at different pH values. The amounts of Pb(II) adsorbed on a solid (q) and remaining in solution (C_{eq}) will change with changing pH. To illustrate the variation and relationship of pH, C_{eq} , and q , experimental data of Pb(II) sorption at pH 5–10 in 0.01 M NaClO_4 and in 0.01 M KClO_4 , respectively, are plotted again as three-dimensional (3-D) plots of pH, C_{eq} , and q in Figure 6.21. On the pH– q plane, the lines are very similar to that of pH–sorption % (in Figure 6.19); on the pH– C_{eq} plane, the concentration of Pb(II) remaining in solution decreases with increasing pH. The projection on the pH– C_{eq} plane is just the inverted image of the projection on the pH– q plane; on the C_{eq} – q plane, the projection is a straight line containing all experimental data. The slope and the intercept calculated from the C_{eq} – q line are -1.0 and 4.83×10^{-5} , respectively, which are in good agreement with the values of $V/m = 1.0$ (L/g) and $C_0 V/m = 4.83 \times 10^{-5}$ (mol/L · L/g) (i.e., the values calculated from $V/m = 1.0$ L/g and $C_0 = 4.83 \times 10^{-5}$ mol/L). The complexity of the sorption edge relative to the sorption isotherm is demonstrated. The 3-D plots show the relationship of pH, C_{eq} , and q very clearly; that is, all the data of C_{eq} – q lie in a straight line with slope $-V/m$ and intercept $C_0 V/m$ for the same initial concentration of Pb(II) and the same solid content.

Figure 6.22 shows that the Pb^{2+} sorption rates increase dramatically in the first 10 min for various initial concentrations, and reach equilibrium gradually at 20, 50, and 60 min, corresponding to Pb^{2+} initial concentrations of 10, 20, and 30 mg/L, respectively. The pseudo-second-order rate equation, $t/q_t = 1/(2K' \cdot q_c^2) + t/q_c$, was evaluated based on the experimental data. A linear plot feature of t/q_t versus t (Figure 6.23) was achieved and the K' values calculated from the slopes and intercepts are summarized in Table 6.5. The correlation coefficients of the pseudo-second-order rate model for the

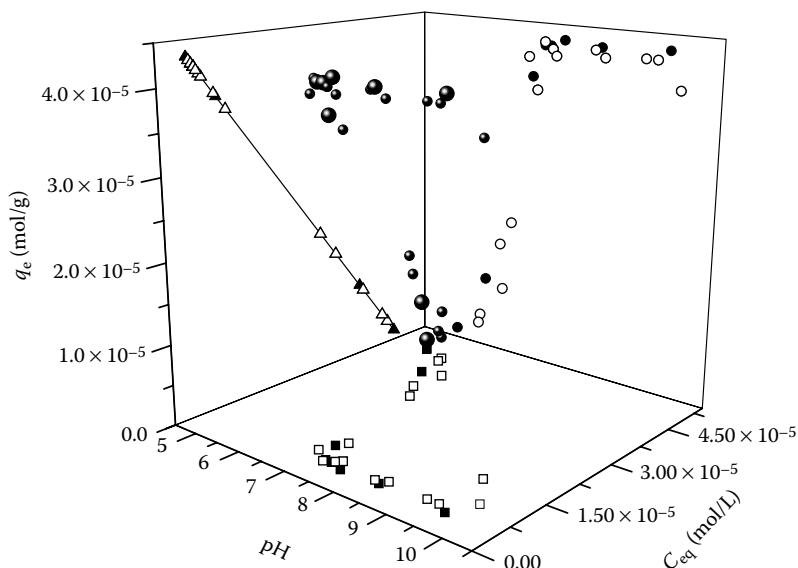


FIGURE 6.21 3-D plots of pH, C_{eq} , and q of Pb(II) sorption to oxidized MWCNTs. $C[\text{Pb(II)}]_{\text{initial}} = 4.83 \times 10^{-5}$ mol/L, $m/V = 1.0$ g/L, $T = 293$ K. Solid points: $I = 0.01$ M NaClO_4 ; open points: $I = 0.01$ M KClO_4 . (From Xu, D. et al., *J. Hazard. Mater.*, 154, 407–416, 2008. With permission.)

linear plots are very close to 1, thus suggesting that kinetic adsorption can be described by the pseudo-second-order rate equation [10].

Figure 6.24 shows the sorption isotherms of Pb^{2+} on CNTs at 280, 298, and 321 K. The Pb^{2+} sorption capacity increases with an increase in temperature. Figure 6.25 shows linearized Freundlich isotherms for Pb^{2+} sorption on CNTs at different temperatures, and Freundlich parameters are listed in Table 6.6. The results indicate that the Freundlich isotherm model fits the Pb^{2+} sorption well. The thermodynamic parameters of Pb^{2+} sorption on CNTs are listed in Table 6.7. A positive standard enthalpy change suggests that the interaction of Pb^{2+} sorbed on CNTs is endothermic, which is supported by the

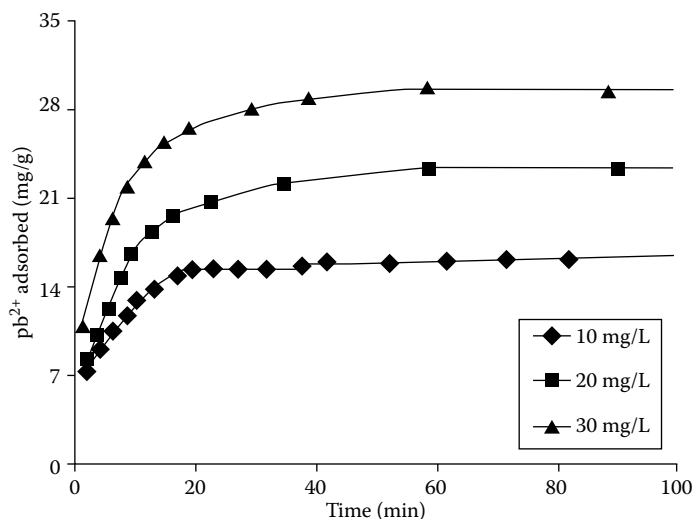


FIGURE 6.22 Effect of contact time on Pb^{2+} sorption rate for different concentrations ($\text{pH} = 5.0$, $T = 298$ K). (From Li, Y. et al., *Water Res.*, 39, 605–609, 2005. With permission.)

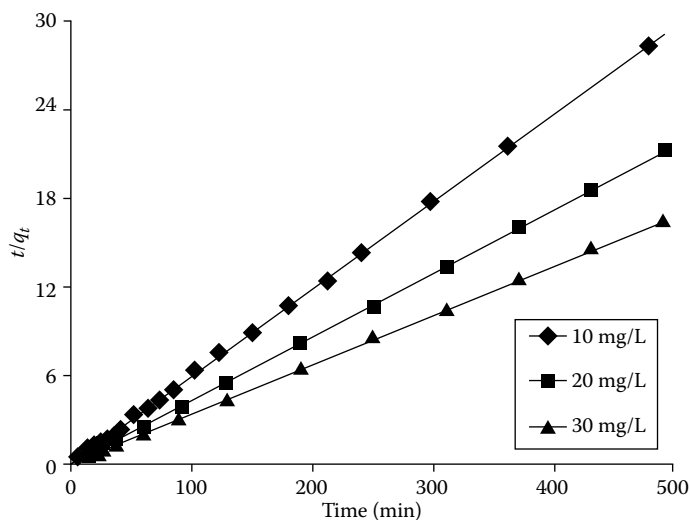


FIGURE 6.23 Test of pseudo-second-order rate equation for sorption of different concentrations of Pb^{2+} on CNTs (pH = 5.0, $T = 298\text{ K}$). (From Li, Y. et al., *Water Res.*, 39, 605–609, 2005. With permission.)

increasing sorption of Pb^{2+} with increase in temperature; a negative sorption standard free energy change and a positive standard entropy change indicate that the sorption reaction is a spontaneous process. The positive standard entropy change may be due to the release of a water molecule produced by the ion exchange reaction between the sorbate and the functional groups on the surfaces of CNTs.

To achieve molecular level information of $\text{Pb}(\text{II})$ sorption on oxidized MWCNTs at different pH values, the XPS technique is performed to identify the local structures of $\text{Pb}(\text{II})$ sorption on oxidized MWCNTs. Typical XPS spectra obtained after $\text{Pb}(\text{II})$ sorption on oxidized MWCNTs at pH 6.05 and 8.86 are shown in Figure 6.26a through c. Figure 6.26a shows the high-resolution XPS C1s spectra. The peak of typical graphitic carbon at 284.7 eV represents the C1s binding energy of MWCNTs. There is no difference in the C1s spectra of the two samples, which suggests that the species of carbon is not influenced by pH values. Figure 6.26b shows the high-resolution XPS O1s spectra of the sample around 532.5 eV. With reference to the XPS studies of CNTs, the experimental data show the functional groups present on the surface of MWCNTs: carboxyl oxygen [$-\text{O}-\text{C}=\text{O}(\text{H})$, 533.6 eV] and carbonyl oxygen [$=\text{C}=\text{O}$, 530.7 eV] [17]. Figure 6.26b shows that there is a significant difference between the oxygen peaks at pH 6.05 and 8.86. $\text{Pb}(\text{II})$ sorption is accompanied by a change in oxygen binding, providing evidence that the oxygen-containing functional groups on the surface of oxidized

TABLE 6.5
Kinetic Parameters of Pb^{2+} Sorbed on CNTs at Different Initial Pb^{2+} Concentrations

Initial Pb^{2+} Concentration (mg/L)	Pseudo-Second-Order		
	q_e	K'	R^2
10	17.09	0.0092	0.9989
20	23.41	0.0116	0.9999
30	30.32	0.0053	0.9987

Source: Li, Y., Di, Z., Ding, J., Wu, D., Luan, Z., and Zhu, Y., *Water Res.*, 39, 605–609, 2005. With permission.

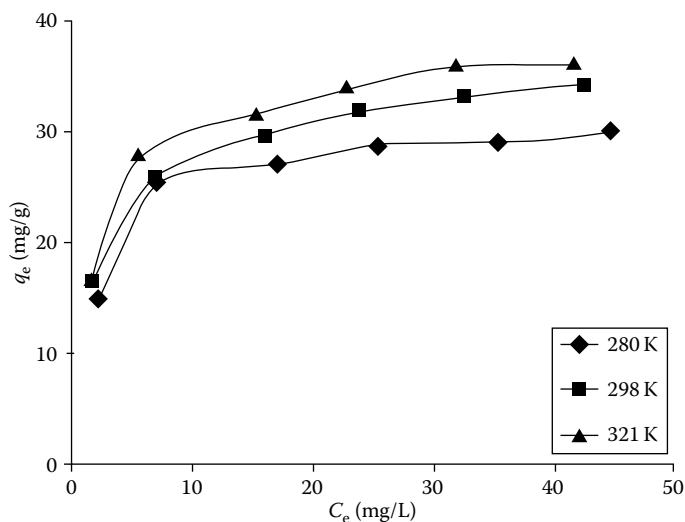


FIGURE 6.24 Sorption isotherms of Pb^{2+} onto CNTs at different temperatures. (From Li, Y. et al., *Water Res.*, 39, 605–609, 2005. With permission.)

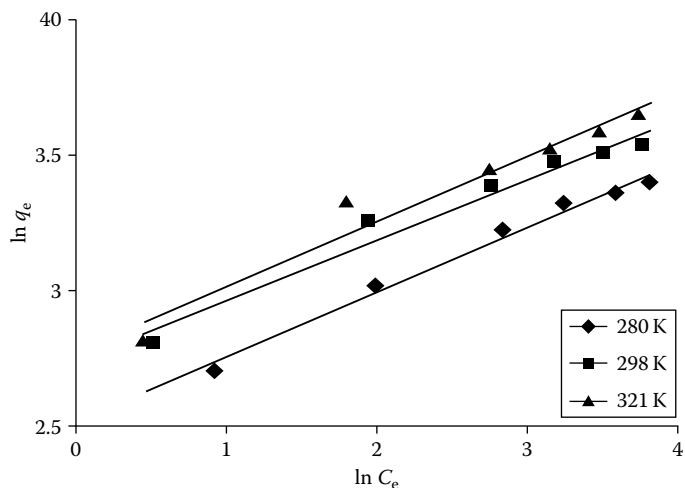


FIGURE 6.25 Linearized Freundlich isotherms for Pb^{2+} adsorption by CNTs at different temperatures. (From Li, Y. et al., *Water Res.*, 39, 605–609, 2005. With permission.)

TABLE 6.6

Parameters of Freundlich Adsorption Isotherm Models for Pb^{2+} on CNTs

Temperature (K)	K_F	N	R^2
280	12.4100	4.5269	0.9869
298	15.5646	4.4802	0.9659
321	16.1448	4.3440	0.9755

Source: Li, Y. et al., *Water Res.*, 39, 605–609, 2005. With permission.

TABLE 6.7
Values of Various Thermodynamic Parameters for Adsorption of Pb²⁺ on CNTs

Temperature (K)	Thermodynamic Constants		
	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS° (J/mol K)
280	-1.329	0.441	6.321
298	-1.453	0.441	6.356
321	-1.588	0.441	6.321

Source: Li, Y. et al., *Water Res.*, 39, 605–609, 2005. With permission.

MWCNTs take part in Pb(II) sorption. The oxygen peak is shifted by 0.55 eV between pH 8.86 and 6.05. This shift is due to the fact that Pb(OH)₂ pellets begin to form and cover the adsorbent surface at pH 8.86. The characteristic low-binding energy XPS feature is present in the Pb4f XPS signal at pH 6.05 and 8.86 (Figure 6.26c). This XPS feature is associated with an MWCNT–OPb complex at pH 6.05 and MWCNT–Pb(OH)₂ pellet formation at pH 8.86. Figure 6.26c shows that doublets characteristic of Pb at pH 6.05 appear at 139.0 eV (assigned to Pb4f_{7/2}) and 143.85 eV (assigned to Pb4f_{5/2}), and doublets characteristic of Pb at pH 8.86 appear at 138.6 eV (assigned to Pb4f_{7/2}) and 143.45 eV (assigned to Pb4f_{5/2}). The peaks observed at 139.0 and 138.6 eV agree with the 139.0 and 138.4 eV values reported for PbC₂O₄ and Pb(OH)₂, respectively [48]. This indicates further complexation of Pb onto oxidized MWCNTs at pH 6.05 and precipitation of Pb occurs at high pH.

6.3.1.2.3 Removal of Cd(II)

Cadmium is considered to be one of the most toxic metals, and causes severe health problems to animals and humans [49,50]. The tolerance limits of metals for drinking water are different, depending on the standards in different countries: for example, in the United States, these values are 0.005 mg/L for Cd, 0.1 mg/L for Cr, 1.3 mg/L for Cu, 0.002 mg/L for Hg, and 0.01 mg/L for As and Pb [51]. Cadmium could be introduced into water bodies through wastewaters from metal plating, cadmium–nickel battery industries, phosphate fertilizers, mining residues, and pigments [52].

The removal of Cd(II) from an aqueous solution using activated carbon, CNTs, and other sorbents has been studied extensively. Generally, the adsorption of Cd(II) is strongly dependent on pH values. Because many metal ions are present in solution, the simultaneous removal of these ions from solution to nanomaterials is inevitable. As mentioned earlier, the species of metal ions in solution is essential in understanding the physicochemical behavior in the natural environment, and therefore it is helpful in evaluating the adsorption of metal ions on nanomaterials. The relative species of different metal ions in aqueous solution as a function of pH is shown in Figure 6.27, which, under ambient conditions, shows that the species of metal ions is strongly dependent on pH values and is obviously influenced by the presence of CO₂.

6.3.1.2.4 Removal of Cu(II)

Copper is one of the most widespread heavy metal contaminants of the environment. It is essential to human life and health but, like all heavy metals, is potentially toxic. The major sources of copper in industrial effluents are metal cleaning and electroplating. Figure 6.28 presents the adsorption isotherms of Cu²⁺ on CNTs at pH 6, as a relationship between the amount of Cu²⁺ adsorbed per unit mass of CNTs (q_e) and the equilibrium concentration in solution (C_e) at different temperatures. The adsorption capacities increased with concentration, reaching a plateau, which represents the maximum adsorption capacity. Table 6.8 summarizes the coefficients of the Langmuir and Freundlich isotherms for different temperatures and CNTs. Comparing the R^2 values given in Table 6.8 indicates that the Langmuir isotherm better fits the experimental data on the adsorption of Cu²⁺ onto CNTs than does the Freundlich isotherm. The validity of the Langmuir isotherm suggests that the

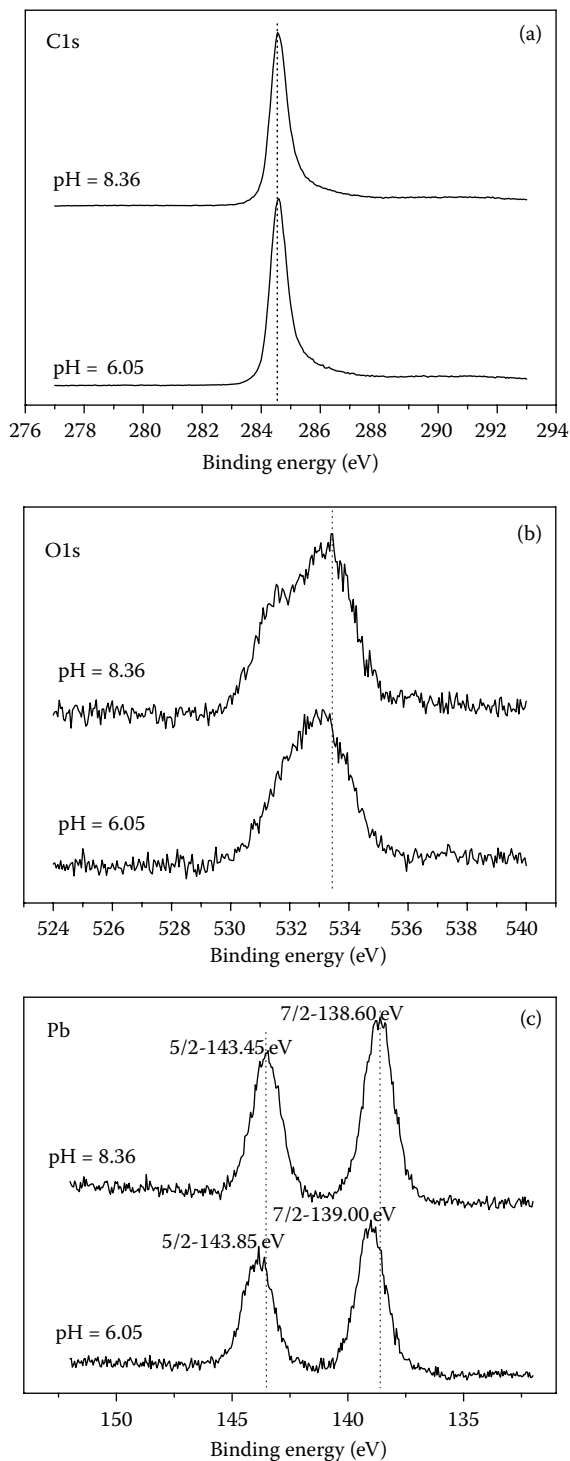


FIGURE 6.26 XPS spectra for free-dried samples of Pb(II) adsorbed on MWCNTs: (a) C1s; (b) O1s; and (c) Pb4f. (From Xu, D. et al., *J. Hazard. Mater.*, 154, 407–416, 2008. With permission.)

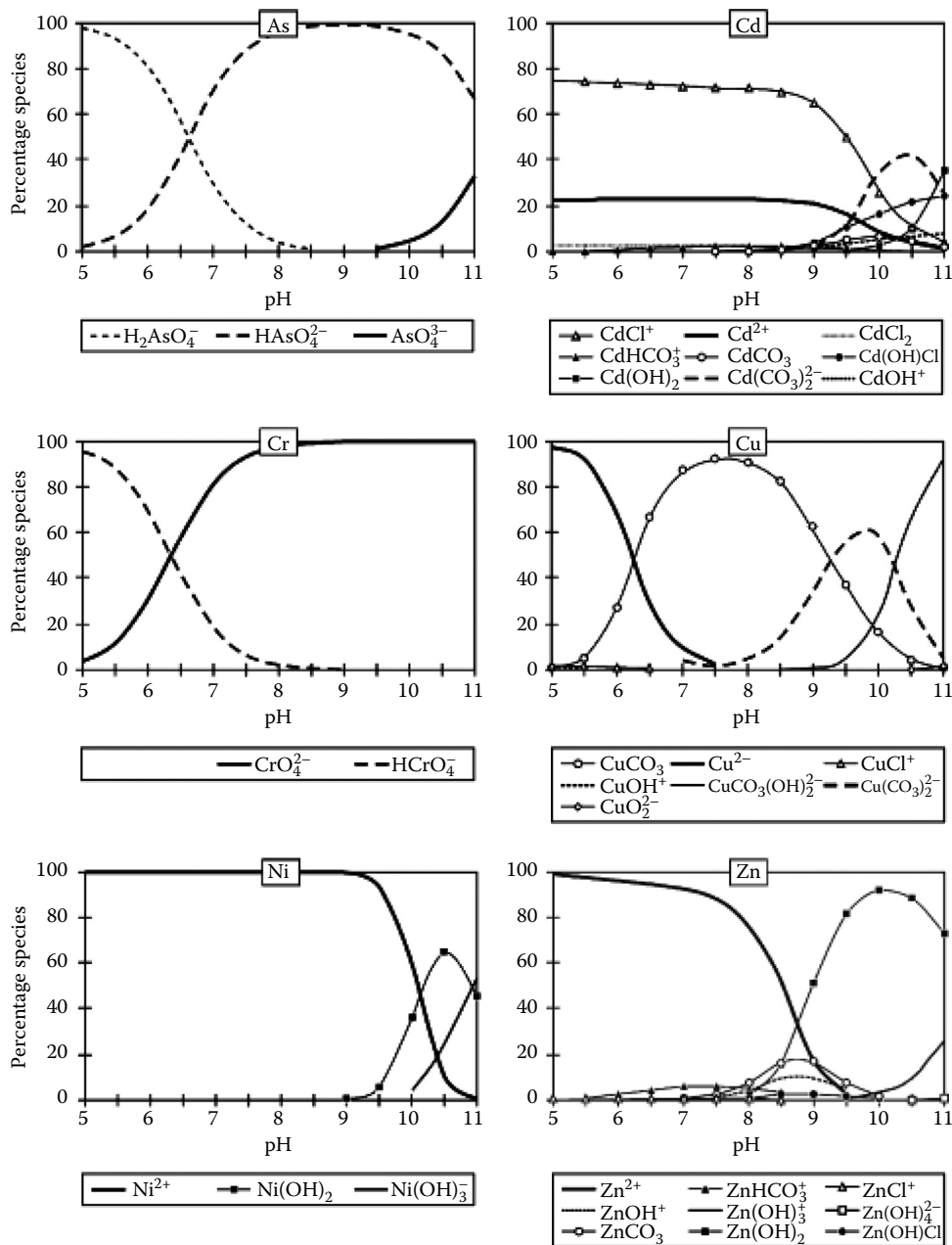


FIGURE 6.27 Speciation of As, Cd, Cr, Cu, Ni, and Zn in water obtained using the PHREEQ-C model with ionic strength of 0.01 M NaCl and 0.003 M NaHCO_3 buffer. (From Genc-Fuhrman, H., Mikkelsen, P.S., and Ledin, A., *Water Res.*, 41, 591–602, 2007. With permission.)

adsorption is a monolayer process and the adsorptions of all molecules have equal activation energies. The Langmuir constant, K_L , increased with temperature, indicating that the adsorption of Cu^{2+} onto CNTs increased with temperature. The results implied that the affinity of the binding sites for Cu^{2+} increased with temperature. Moreover, K_L values for various CNTs followed the order NaOCl-modified CNTs > HNO_3 -modified CNTs > as-produced CNTs, suggesting that the affinity of the binding sites for Cu^{2+} also followed this order.

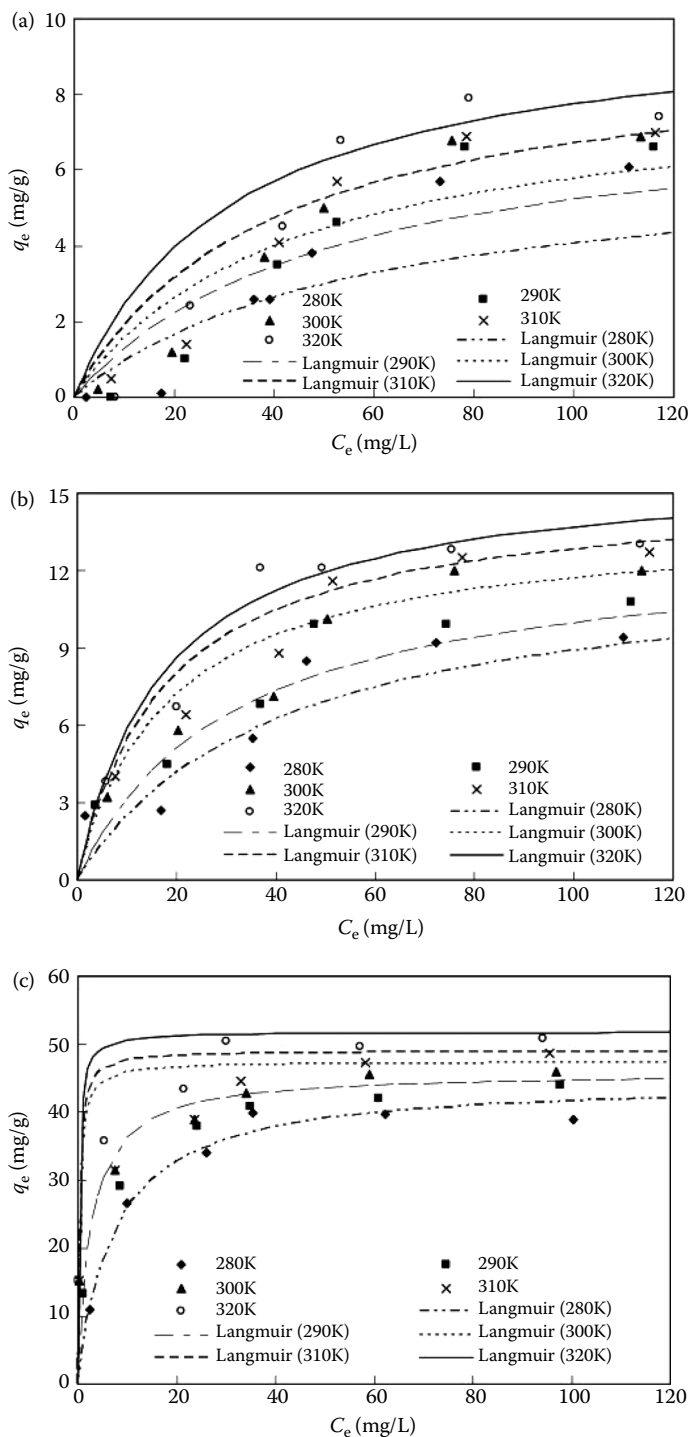


FIGURE 6.28 Effects of temperature for (a) as-produced CNTs, (b) HNO_3 -modified CNTs, and (c) NaOCl-modified CNTs (pH 6, ionic strength = 0.01 M, CNTs = 0.5 g/L, and contact time = 24 h). (From Wu, C.H., *J. Colloid Interface Sci.*, 311, 338–346, 2007. With permission.)

TABLE 6.8
Coefficients of Langmuir and Freundlich Isotherms

Temperature	Langmuir Isotherm			Freundlich Isotherm		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F	n	R^2
As-produced CNTs						
280 K	0.0175	6.39	0.887	0.190	1.317	0.903
290 K	0.0198	7.87	0.910	0.374	1.600	0.862
300 K	0.0234	8.25	0.842	0.498	1.739	0.863
310 K	0.0255	9.34	0.801	0.753	2.058	0.798
320 K	0.0320	10.17	0.645	1.035	2.291	0.611
HNO ₃ -modified CNTs						
280 K	0.0250	12.46	0.901	0.455	1.451	0.858
290 K	0.0321	13.10	0.925	1.608	2.404	0.937
300 K	0.0542	13.87	0.960	1.542	2.330	0.986
310 K	0.0565	15.11	0.972	3.098	3.238	0.698
320 K	0.0584	16.04	0.945	2.784	2.841	0.699
NaOCl-modified CNTs						
280 K	0.1386	44.64	0.998	9.897	2.893	0.870
290 K	0.3854	45.87	0.997	14.160	3.610	0.937
300 K	2.9515	47.39	0.974	21.020	5.331	0.989
310 K	3.3800	49.02	0.952	22.300	5.540	0.951
320 K	4.1925	51.81	0.933	29.540	7.716	0.872

Source: Wu, C.H., *J. Colloid Interface Sci.*, 311, 338–346, 2007. With permission.

The Freundlich isotherm does not describe the saturation behavior of the adsorbent. With regard to the coefficients of the Freundlich model, the Freundlich constant K_F increased with temperature, revealing that the adsorption capacity increased with temperature. Like K_F , the Freundlich constant n increased with temperature. Since the n values obtained from the isotherms all exceeded unity, Cu²⁺ adsorption is favorably adsorbed onto as-produced and modified CNTs at all temperatures. The highest value of n , 7.716 at 320 K for NaOCl-modified CNTs, represents favorable adsorption at high temperature. Both the Langmuir and the Freundlich isotherms suggest that increasing the temperature increased adsorption capacity, suggesting that the adsorption is endothermic.

Table 6.9 presents the thermodynamic parameters at various temperatures for different CNTs. Positive ΔH° values indicate that the adsorption of Cu²⁺ onto CNTs is endothermic, which is supported by an increase in the adsorption of Cu²⁺ with temperature. The increasing adsorption capacity of the adsorbent with temperature is attributable to the enlargement of pores and/or the activation of the adsorbent surface [54]. Furthermore, the positive ΔS° revealed that the degrees of freedom increased at the solid–liquid interface during the adsorption of Cu²⁺ onto CNTs. The ΔG° values were negative at all of the tested temperatures (280–320 K), verifying that the adsorption of Cu²⁺ onto CNTs was spontaneous and thermodynamically favorable. Restated, a more negative ΔG° implies a greater driving force of adsorption, resulting in higher adsorption capacity. As the temperature increased from 280 to 320 K, ΔG° became highly negative, suggesting that adsorption was more spontaneous at high temperatures. Additionally, adsorption by modified CNTs was more spontaneous than that by as-produced CNTs. Hence, the ΔG° results implied that the adsorption affinity of Cu²⁺ onto modified CNTs was stronger than that onto as-produced CNTs.

6.3.1.2.5 Removal of Zn(II)

Figure 6.29a and b shows the effect of pH on the sorption of Zn²⁺ onto oxidized SWCNTs and MWCNTs, respectively [5,6]. With a C_0 of 10 mg/L, the sorption of Zn²⁺ onto CNTs increased with

TABLE 6.9
Thermodynamic Parameters of CNTs at Various Temperatures

<i>T</i> (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
As-produced CNTs			
280	-16.34	10.84	96.89
290	-17.23		
300	-18.24		
310	-19.07		
320	-20.29		
HNO ₃ -modified CNTs			
280	-17.17	17.08	122.88
290	-18.38		
300	-20.33		
310	-21.12		
320	-21.89		
NaOCl-modified CNTs			
280	-21.16	67.77	319.76
290	-24.38		
300	-30.30		
310	-31.66		
320	-33.26		

Source: Wu, C.H., *J. Colloid Interface Sci.*, 311, 338–346, 2007. With permission.

an increase in pH in the range of 1–8, fluctuated very little and reached a maximum in the pH range of 8–11, and decreased at a pH of 12. It is known that zinc species can be present in deionized water as Zn^{2+} , $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2^0$, $\text{Zn}(\text{OH})_3^-$, and $\text{Zn}(\text{OH})_4^{2-}$ [55]. At pH < 8, the predominant zinc species is always Zn^{2+} , and its removal is mainly accomplished by adsorption reaction. Therefore, the low Zn^{2+} sorption that took place at low pH can be attributed in part to competition between H^+ and Zn^{2+} ions on the same sites [56,57]. Furthermore, the zeta potential of CNTs becomes more negative with increasing pH, which causes electrostatic attraction and thus results in the adsorption of more Zn^{2+} onto CNTs. In the pH range of 8–11, the removal of Zn remained constant and reached a maximum. The main species are $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2^0$, and $\text{Zn}(\text{OH})_3^-$, and thus the removal of Zn is possibly accomplished by the simultaneous precipitation of $\text{Zn}(\text{OH})_2(\text{s})$ and sorption of $\text{Zn}(\text{OH})^+$ and $\text{Zn}(\text{OH})_3^-$. At a pH of 12, the predominant zinc species are the negative species $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$. Therefore, the decrease in Zn removal that took place at a pH of 12 can be attributed in part to competition among OH^- , $\text{Zn}(\text{OH})_3^-$, and $\text{Zn}(\text{OH})_4^{2-}$ ions on the same sites. With a C_0 of 80 mg/L, the sorption of Zn^{2+} onto CNTs increased with the increase in pH in the pH range of 1–7. Above a pH of 7, a large amount of $\text{Zn}(\text{OH})_2(\text{s})$ was formed and suspended in the solutions.

Figure 6.30a and b shows the effect of temperature on the sorption rate of Zn^{2+} by SWCNTs and MWCNTs, respectively. The initial Zn^{2+} concentration is 60 mg/L. For all the experiments, the sorption of Zn^{2+} increased quickly with time and then slowly reached equilibrium in 60 min, irrespective of temperature. Similar results have been reported for the sorption of Zn^{2+} onto activated carbon [58]. However, the times required to uptake 50% of the maximum sorption capacity (t_{50}) at 5°C, 15°C, 25°C, 35°C, and 45°C are 3.34, 2.90, 2.75, 2.38, and 2.28 min for SWCNTs and 5.04, 4.59, 4.28, 4.12, and 3.84 min for MWCNTs. It appears that the half-sorption capacity would be reached faster at a higher temperature. The equilibrium capacities of Zn^{2+} at 5°C, 15°C, 25°C, 35°C, and 45°C are 31.2, 35.6, 36.8, 39.6, and 41.4 mg/g for SWCNTs and 25.5, 27.5, 27.8, 28.5, and 29.5 mg/g

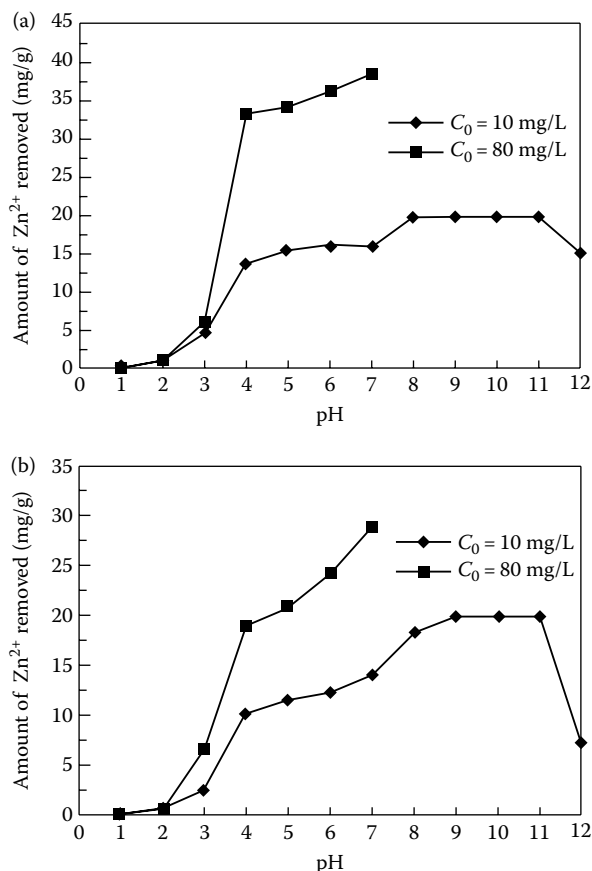


FIGURE 6.29 Effect of pH on the sorption of Zn²⁺ with purified CNTs: (a) SWCNTs and (b) MWCNTs. (From Lu, C. and Chiu, H., *Chem. Eng. Sci.*, 61, 1138–1145, 2006. With permission.)

for MWCNTs. The solution pH dropped to 0.5 and 0.25 pH units during the sorption of Zn²⁺ onto SWCNTs and MWCNTs, respectively. This could be explained by the release of H⁺ ions from the surface site of CNTs, where Zn²⁺ ions are adsorbed and thus lead to a decrease in solution pH. As the temperature increased from 15°C to 25°C, the equilibrium pH value slightly dropped by 0.06 and 0.05 pH units for the SWCNTs and MWCNTs, respectively. This was because, as more Zn²⁺ ions are adsorbed onto CNTs at higher temperatures, more H⁺ ions are desorbed from the surface site of CNTs into the solution, which therefore results in a lower equilibrium pH.

The Zn²⁺ adsorption isotherms data are fitted using the Langmuir and Freundlich models. The Langmuir and Freundlich constants were obtained from fitting the isotherm model to the adsorption equilibrium data and are listed in Table 6.10. For Zn²⁺ adsorption onto SWCNTs, the *R*² values of the Langmuir model are higher than those of the Freundlich model. For Zn²⁺ adsorption onto MWCNTs, the *R*² values of both models are very close. The constants *a* and *K_f*, which represent Zn²⁺ adsorption capacity, are greater for SWCNTs than for MWCNTs and increase with a rise in temperature. The constant *b*, which reflects the free energy of adsorption, presents generally the same trend. The slope 1/*n*, which is related to the intensity of adsorption, is greater for SWCNTs, indicating the more favorable sorption of Zn²⁺ onto SWCNTs. The Langmuir isotherms of Zn²⁺ adsorption onto SWCNTs and MWCNTs at various temperatures are presented in Figure 31a and b, respectively. It is obvious that the Zn²⁺ adsorption capacity of CNTs increased with a rise in temperature, and high capacity was observed at 35°C and 45°C. The isotherm curves of 15°C and 25°C are relatively close, probably

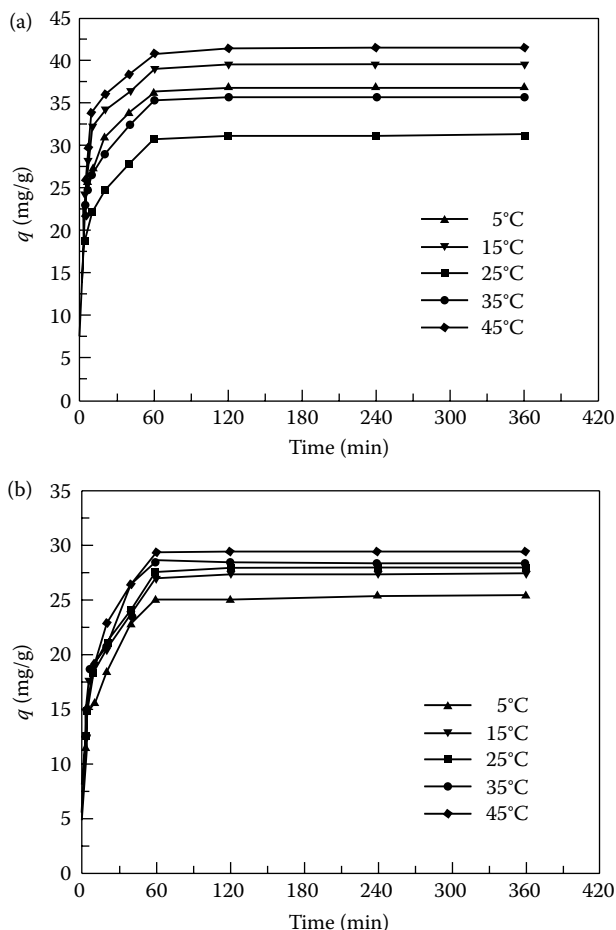


FIGURE 6.30 Effect of temperature on the sorption rate of Zn^{2+} by CNTs: (a) SWCNTs and (b) MWCNTs. (From Lu, C. et al., *Ind. Eng. Chem. Res.*, 45, 2850–2855, 2006. With permission.)

TABLE 6.10
Constants of Langmuir and Freundlich Models of Zn^{2+} Adsorption by CNTs at Various Temperatures

CNTs	Temperature (°C)	Langmuir Model			Freundlich Model		
		a	b	R^2	K_f	$1/n$	R^2
SWCNTs	5	37.03	0.132	0.997	9.97	0.303	0.979
	15	40.65	0.159	0.997	12.01	0.288	0.984
	25	41.84	0.161	0.996	12.37	0.289	0.984
	35	45.45	0.164	0.998	1175	0.305	0.976
	45	46.94	0.178	0.997	13.58	0.302	0.971
MWCNTs	5	30.30	0.101	0.983	8.23	0.283	0.979
	15	31.74	0.124	0.987	10.43	0.242	0.983
	25	33.33	0.118	0.982	10.62	0.248	0.984
	35	33.78	0.129	0.979	12.15	0.219	0.972
	45	34.36	0.149	0.985	12.87	0.215	0.984

Source: Lu, C. et al., *Ind. Eng. Chem. Res.*, 45, 2850–2855, 2006. With permission.

Notes: Units: a = mg/g; b = L/mg, K_f = (mg/g) (L/mg) $^{1/n}$; n = dimensionless; and R = dimensionless.

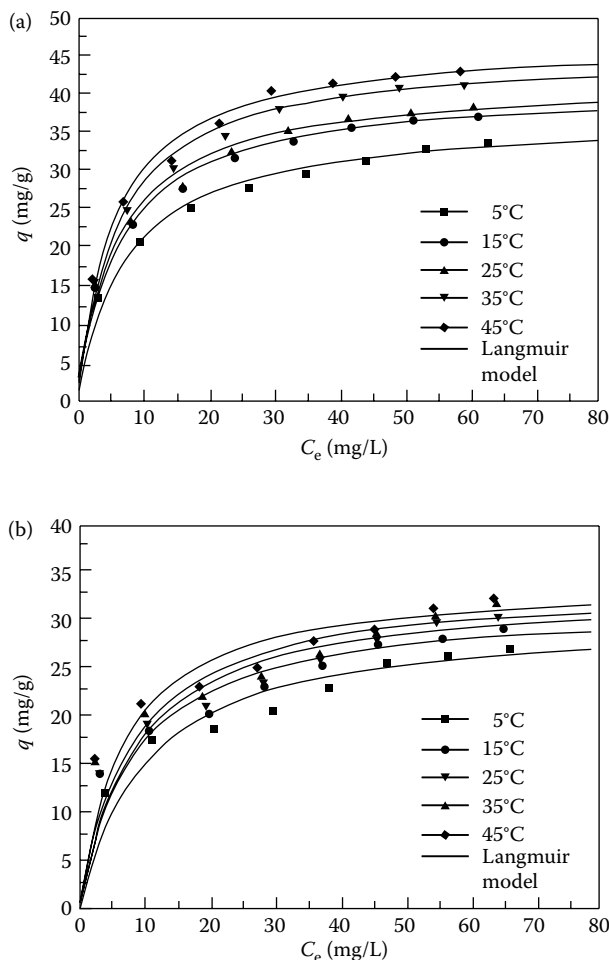


FIGURE 6.31 Langmuir isotherms of Zn^{2+} sorption by CNTs at various temperatures: (a) SWCNTs and (b) MWCNTs. (From Lu, C. et al., *Ind. Eng. Chem. Res.*, 45, 2850–2855, 2006. With permission.)

because of the experimental deviation in the determination of the amount of adsorbed Zn^{2+} . Zn^{2+} adsorption capacity of SWCNTs is greater than that of MWCNTs, which could be explained from the BET measurements, which show that the surface area of SWCNTs ($423 \text{ m}^2/\text{g}$) available for liquid-phase mass transfer is higher than that of MWCNTs ($297 \text{ m}^2/\text{g}$). As the temperature increased from 5°C to 45°C , the maximum Zn^{2+} sorption capacity of SWCNTs and MWCNTs calculated by the Langmuir model increased from 37.03 to 46.94 mg/g and from 30.3 to 34.36 mg/g , respectively. These values are much greater than that of commercially available PAC (13.5 mg/g ; San Ying Enterprises Co., Taipei, Taiwan) measured at 25°C in this study. This suggests that both MWCNTs and SWCNTs are efficient adsorbents for the removal of Zn^{2+} from an aqueous solution.

Figure 6.32 shows the Zn^{2+} recoveries of CNTs under various pH values of the regeneration solution ranging from 1 to 5. Zn^{2+} recovery is defined as the percentage ratio of the Zn^{2+} adsorption capacity of regenerated sorbents to that of virgin sorbents. The Zn^{2+} recovery of SWCNTs and MWCNTs, reached 91.1% and 90.7% at a solution pH of 1 and decreased to 62.28% and 43.26% at a solution pH of 5. This could be explained by the fact that the surface charge of CNTs becomes more negative with an increase in the pH value of the solution, which causes more electrostatic attractions between the Zn^{2+} ions and the surface of CNTs and thus results in lower Zn^{2+} recovery.

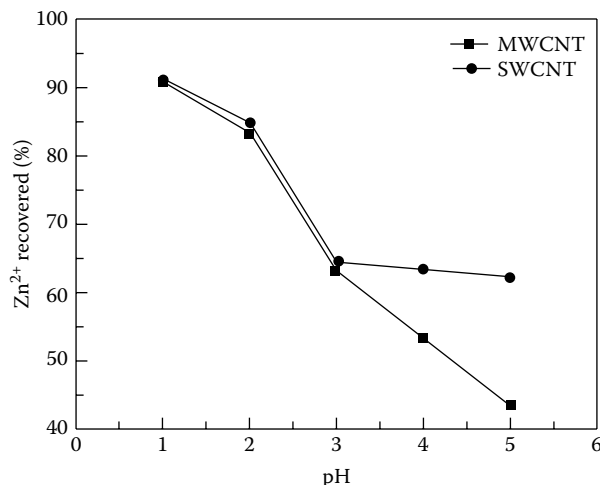


FIGURE 6.32 Effect of pH of the solution on the Zn^{2+} recovery of CNTs. (From Lu, C. et al., *Ind. Eng. Chem. Res.*, 45, 2850–2855, 2006. With permission.)

Figure 6.33 shows the Zn^{2+} sorption capacities of SWCNTs, MWCNTs, and PAC, whereas Figure 6.34 displays the Zn^{2+} recoveries of SWCNTs, MWCNTs, and PAC under various regeneration cycles (RCs) of 0, 1, 5, and 10. As the RC increased, the amount of adsorbed Zn^{2+} and the Zn^{2+} recovery of SWCNTs and MWCNTs slightly decreased but those of PAC sharply decreased. This could be explained by the fact that CNTs have no porous structure like PAC, in which Zn^{2+} ions have to move from the inner surface to the exterior surface of the pores on PAC, which makes desorption of Zn^{2+} ions from the surface site of CNTs much easier. The amounts of adsorbed Zn^{2+} under RCs of 0, 1, 5, and 10, respectively, are 34.1, 30.9, 28.8, and 27.25 mg/g for SWCNTs; 26.8, 24.2, 22.4, and 20.59 mg/g for MWCNTs; and 11.8, 4.8, 2.18, and 1.55 mg/g for PAC.

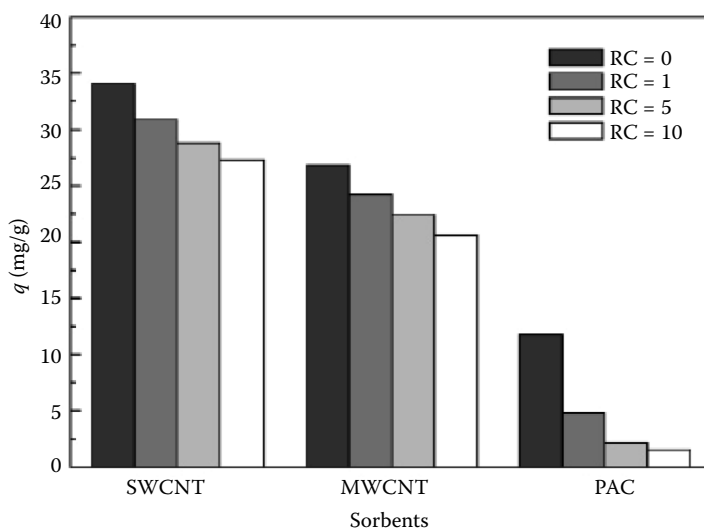


FIGURE 6.33 Zn^{2+} sorption capacities of CNTs and PAC under various RCs of 0, 1, 5, and 10. (From Lu, C. et al., *Ind. Eng. Chem. Res.*, 45, 2850–2855, 2006. With permission.)

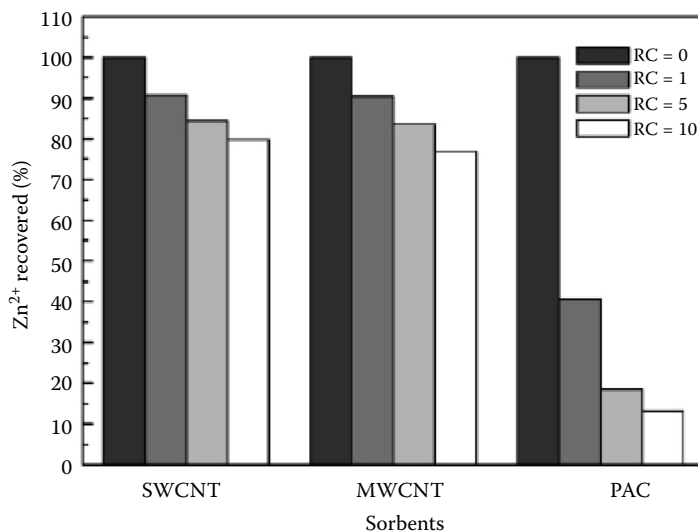


FIGURE 6.34 Zn²⁺ recoveries of CNTs and PAC under various RCs of 0, 1, 5, and 10. (From Lu, C. et al., *Ind. Eng. Chem. Res.*, 45, 2850–2855, 2006. With permission.)

The Zn²⁺ recoveries under RCs of 1, 5, and 10, respectively, are 90.61%, 84.46%, and 79.91% for SWCNTs; 90.30%, 83.58%, and 76.83% for MWCNTs; and 40.68%, 18.47%, and 13.10% for PAC. It is evident that the Zn²⁺ ions would be easily removed from the surface sites of SWCNTs and MWCNTs by a 0.1-mol/L HNO₃ solution and the adsorption capacity is maintained after 10 cycles of the adsorption–desorption process. This indicates that SWCNTs and MWCNTs can be reused through many cycles of water treatment and regeneration for Zn²⁺ removal from an aqueous solution. The cost for the replacement of sorbents is, thus, greatly reduced. This is the key factor for whether a novel but expensive adsorbent can be accepted by the field or not. It is expected that the unit cost of CNTs can be further reduced in the future so that CNTs can possibly be cost-effective sorbents.

Table 6.11 lists comparisons of CNT characterizations and their sorption capacities of various divalent metal ions (Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺). It is evident that the metal ion sorption capacity of CNTs does not have a direct correlation with their specific surface area, pore specific volume, and mean pore diameter but strongly depends on their surface total acidity. The metal ion sorption capacity of CNTs increased as a rise in the amount of surface total acidity (including carboxyls, lactones, and phenols) present on the surface site of CNTs. This reflects that the sorption of metal ions onto CNTs is by the chemisorption process rather than the physisorption process. Oxidized CNTs have more surface total basicities, which are responsible for the sorption of anions from aqueous solutions, than raw CNTs.

Competitive sorption is important in water and wastewater treatment because most metal ions to be sorbed exist in solution with other sorbable metal ions. Figure 6.35 shows the effect of CNT dosage on the competitive sorption of Pb²⁺, Cu²⁺, and Cd²⁺ by CNTs. The sorption capacities of all three heavy metal ions increase with increasing CNT dosages. The sorption percentages of Pb²⁺, Cu²⁺, and Cd²⁺ are 56.1%, 23.7%, and 1.3%, respectively, at a CNT dosage of 0.05 g. The former two reach almost 100% sorption at a CNT dosage of 0.3 g/L. The increase of Cd²⁺ sorption percentage was slow at first and attained 75.4% at a CNT dosage of 0.3 g/L. At that point, Pb²⁺ and Cu²⁺ ions are almost adsorbed completely and there are more vacant active sorption sites used for Cd²⁺ sorption. In other words, the affinities of CNTs for Pb²⁺, Cu²⁺, and Cd²⁺ follow the order Pb²⁺ > Cu²⁺ > Cd²⁺.

The simultaneous removal of Cd, Cu, Ni, and Zn using the sorbents are shown in Figure 6.36 on a double logarithmic scale. The amount of heavy metal removal increased with increasing initial heavy metal concentration. The simultaneous sorption of heavy metal ions depends not only on the

TABLE 6.11
Comparisons of CNT Characterizations and Maximum Sorption Capacities of Various Divalent Metal Ions

Metal Ions	Sorbents	SA	PV	MPD	STA	STB	q_m
Ni^{2+}	SWCNTs	577	1.15	7.98	0.54	0.23	9.22
	SWCNTs (NaOCl)	397	0.46	4.62	4.42	0.35	47.85
	MWCNTs	448	1.10	8.26	0.44	0.19	7.53
	MWCNTs (NaOCl)	307	0.39	5.21	3.06	0.31	38.46
Pb^{2+}	CNTs (HNO_3)						
	Xylene-Fe	47	0.18	3.40	1.63		14.80
	Benzene-Fe	62	0.26	2.4–3.2	1.65		11.20
	Propylene-Ni	154	0.58	3.60	4.04		59.80
Zn^{2+}	Methane-Ni	145	0.54	3.60	4.31		82.60
	SWCNTs	590	1.12	7.60			11.23
	SWCNTs (NaOCl)	423	0.43	4.12			43.66
	MWCNTs	435	0.91	8.35			10.21
Cd^{2+}	MWCNTs (NaOCl)	297	0.38	5.17			32.68
	As-grown CNTs	122	0.28	3.60			1.10
	CNTs (H_2O_2)	130	0.36	3.60	2.52		2.60
	CNTs (KMnO_4)	128	0.32	3.60	3.36		11.00
	CNTs (HNO_3)	154	0.58	3.60	4.04		5.10

Source: Lu, C. and Liu, C., *J. Chem. Technol. Biotechnol.*, 81, 1932, 2006; Li, Y.H. et al., *Carbon*, 41, 1057, 2003; Lu, C. and Chiu, H., *Chem. Eng. Sci.*, 61, 1138, 2006; Li, Y.H. et al., *Diamond Relat. Mater.*, 15, 90, 2006.

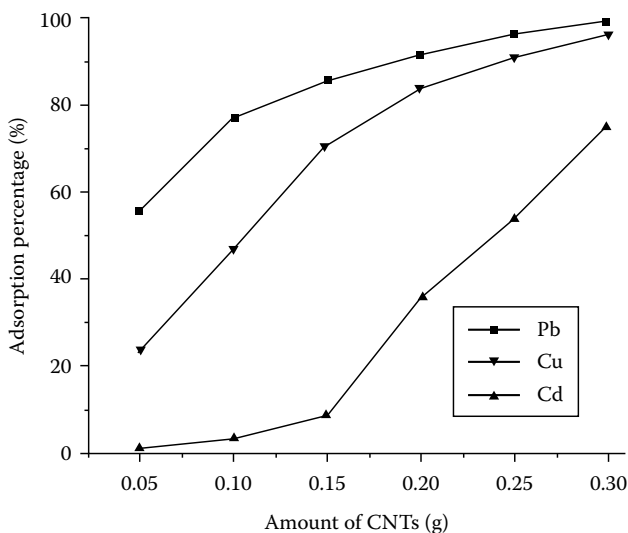


FIGURE 6.35 Effect of CNT dosage on the competitive sorption of Pb^{2+} , Cu^{2+} , and Cd^{2+} ions onto CNTs at room temperature and initial ion concentration of 30 mg/L. (From Li, Y. et al., *Carbon*, 41, 2787–2792, 2003. With permission.)

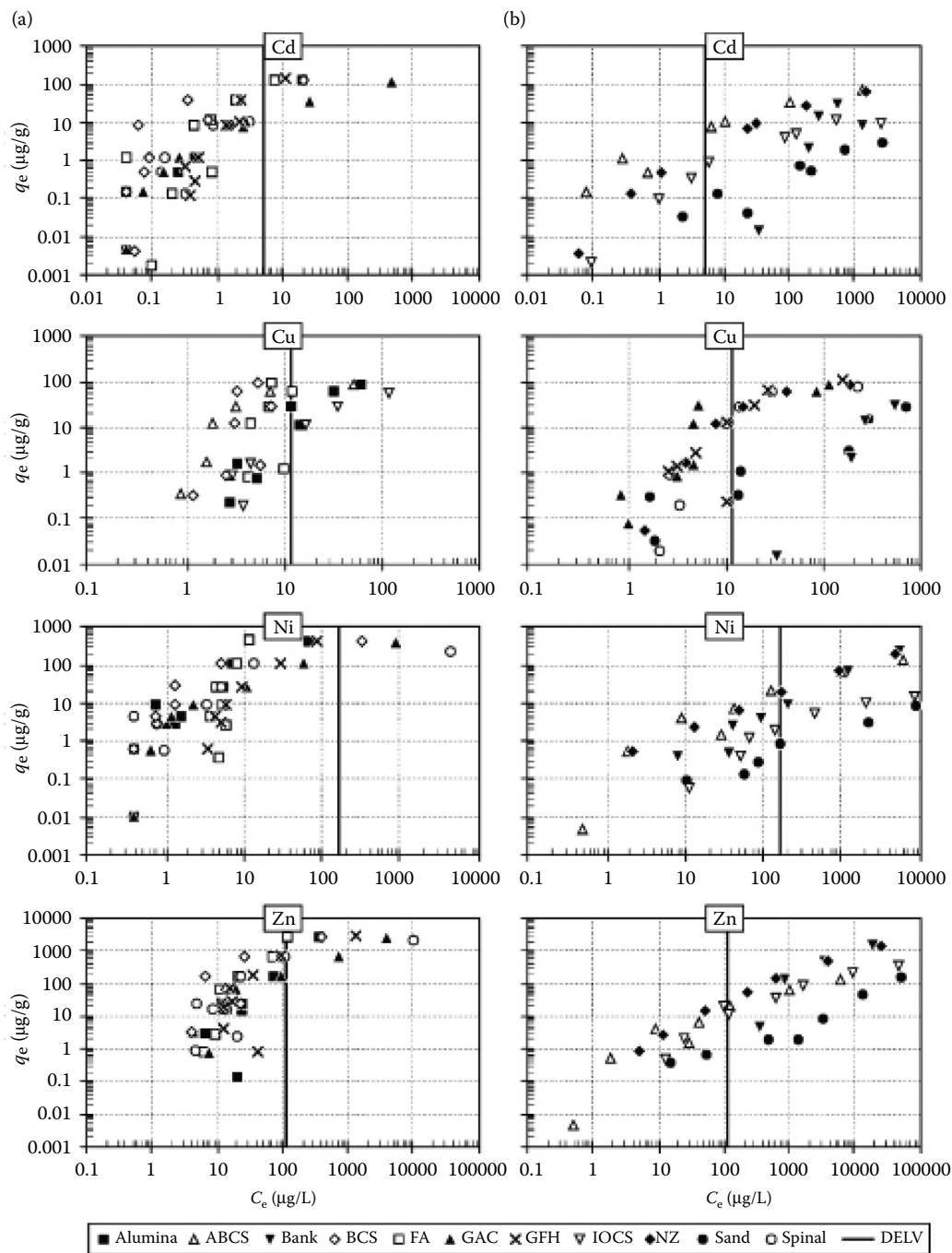


FIGURE 6.36 Cd, Cu, Ni, and Zn removal using (a) sorbents with high heavy metal removal efficiency and (b) sorbents with moderate or low heavy metal removal efficiency, with a starting pH of 6.5, a sorbent dosage of 20 g/L, an ionic strength of 0.01 M NaCl, and 0.003 M NaHCO₃ buffer. DELV is Danish emission limit values for fresh surface waters. (From Genc-Fuhrman, H. et al., *Water Res.*, 41, 591–602, 2007. With permission.)

sorbent properties, but also on the heavy metal ions' properties. Generally, the similar species and similar radii of metal ions have very similar physicochemical behaviors.

6.3.2 KINETIC SORPTION AND DESORPTION OF $^{152+154}\text{Eu(III)}$

With the development of nuclear power, large volumes of high-level radioactive nuclear waste are being produced. The removal of long-lived radionuclides from nuclear waste solutions is an important environmental concern in nuclear waste management.

Figure 6.37 shows the adsorption of Eu(III) as a function of Eu(III) concentration at two different ionic strengths, 0.1 and 0.01 M NaClO_4 . The ideal linear adsorption isotherms suggest that the adsorption of $^{152+154}\text{Eu(III)}$ on MWCNTs is far from saturation, although the concentration of MWCNTs is quite low (0.5 g nanotubes/L solution) and the initial $^{152+154}\text{Eu(III)}$ concentration is quite high (the maximum initial concentration 2.8×10^{-5} mol/L). The high adsorption capacity of MWCNTs indicates that MWCNTs are very suitable material for the preconcentration of lanthanides/actinides from large volumes of aqueous solutions.

To study the reversibility–irreversibility of Eu(III) adsorption on MWCNTs, kinetic desorption analysis of Eu(III) from MWCNTs was investigated after different contact times of Eu(III) with MWCNTs (0.5 g/L MWCNTs, initial Eu(III) concentration 1.2×10^{-5} mol/L, pH 6.3 ± 0.2 , and in 0.1 M NaClO_4). A purified filter membrane coated with a resin containing imminodiacetic acid groups (Chelating Extraction Disk, 3M Empore) was added to the solution after previous equilibration with the electrolyte, and the pH was adjusted to 6.3 (Figure 6.38b) and 3.2 (Figure 6.38c). A fast reaction was found for the adsorption of Eu(III) to the resin in the absence of nanotubes (Figure 6.38a). More than 99.99% of the Eu(III) can form very strong complexes with the chelating resin. Adsorption of Eu(III) on the chelating resin was about 100% for 1.2×10^{-5} mol/L Eu(III). Chelating resin can form strong complexes with Eu(III), and therefore can be used to investigate the

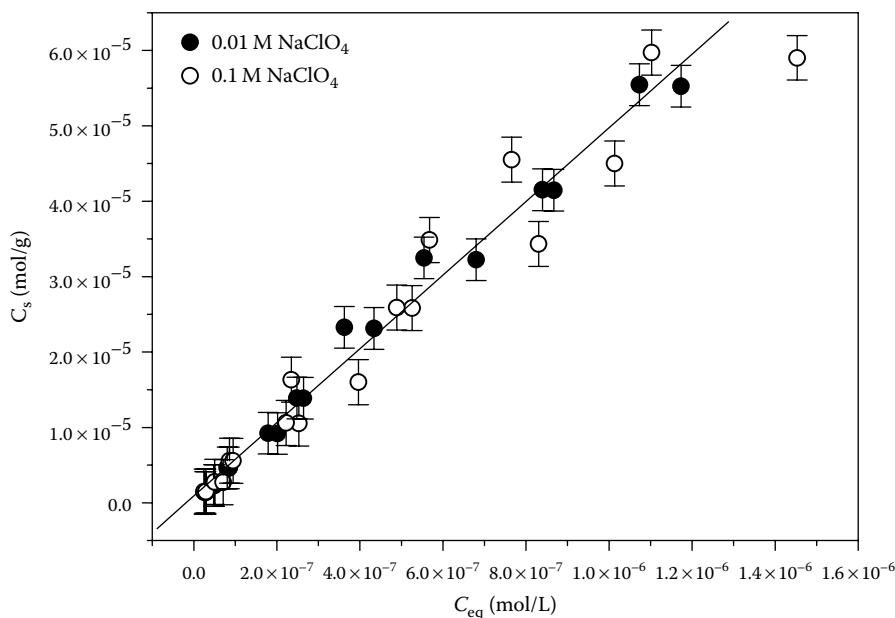


FIGURE 6.37 Sorption isotherms of Eu(III) on MWCNTs as a function of ionic strength and Eu(III) solution concentrations. 25°C, pH = 6.3 ± 0.2 , $t = 4$ days, 0.5 g MWCNTs/L solution. (From Tan, X.L. et al., *Radiochim. Acta*, 96, 23–29, 2008. With permission.)

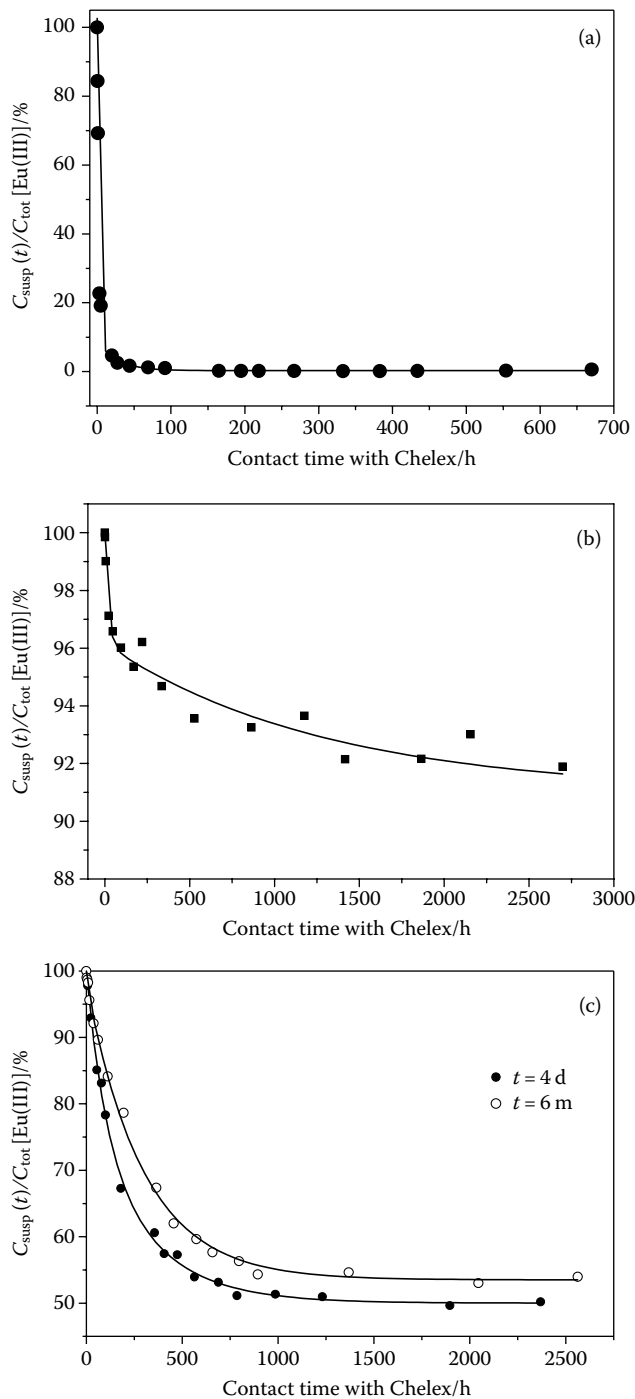
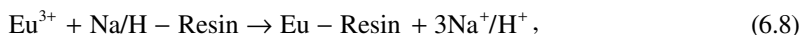
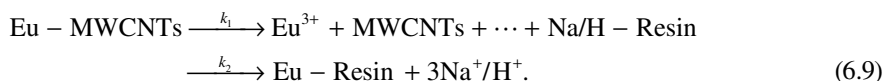


FIGURE 6.38 Fractions of $^{152+154}\text{Eu(III)}$ species in nanotube suspensions as a function of contact time with a chelating resin in 0.1 M NaClO_4 . (a) Free $^{152+154}\text{Eu(III)}$ solution, pH 5.0 ± 0.2 ; (b) presence of CNTs, pH 6.3 ± 0.2 , $t = 4$ days; (c) presence of CNTs, pH 3.2 ± 0.1 , the pH of the solution before the addition of chelating resin was 6.3 ± 0.2 , and then the pH was adjusted to 3.2 ± 0.1 after the addition of chelating resin. (From Tan, X.L. et al., *Radiochim. Acta*, 96, 23–29, 2008. With permission.)

kinetic desorption of Eu(III) from MWCNTs. The adsorption/complexation reaction of Eu(III) with the chelating resin in the absence of MWCNTs according to [20,59],



is rather fast. The desorption reaction of Eu(III) from MWCNTs is observed in the following equation:



After the chelating resin is added to the MWCNT suspension, the free Eu(III) ion in solution is firstly adsorbed by chelating resin and then the adsorbed Eu(III) on the MWCNT surface is desorbed from MWCNTs and quickly adsorbed by chelating resin. Equation 6.9 is the reaction of Eu(III) from MWCNTs to chelating resin. In Equation 6.9, k_2 is rather fast, whereas k_1 is very slow compared to the reaction of free Eu(III) with chelating resin.

To quantify the differences in Eu(III) desorption behavior, we described the kinetic desorption of Eu(III) from MWCNTs using a pseudo-first-order kinetics [20,59]. At least two different Eu(III) complexation species, showing “fast” and “slow” desorption kinetics, are used to simulate the kinetic desorption data:

$$\frac{C_{\text{susp}}(t)}{C_{\text{tot}}} = \frac{C_{\text{final}}}{C_{\text{tot}}} + A_1 \cdot \exp\left(\frac{-t}{\tau_1}\right) + A_2 \cdot \exp\left(\frac{-t}{\tau_2}\right), \quad (6.10)$$

where $C_{\text{susp}}(t)$ is the concentration of $^{152+154}\text{Eu(III)}$ in the MWCNT suspension at time t (h); C_{final} is the final concentration of $^{152+154}\text{Eu(III)}$ in the MWCNT suspension after equilibration with the chelating resin, which is considered as the portion of the irreversible Eu(III) adsorption on MWCNTs; and C_{tot} is the initial $^{152+154}\text{Eu(III)}$ concentration in the system ($t = 0$). Generally, the fraction of A_1 is considered as a “weak” binding fraction, and the fraction of A_2 is considered as a “strong” binding fraction. The adsorbed Eu(III) on “weak” sites can be “fast” desorbed from MWCNTs with a time constant τ_1 (%), whereas that adsorbed on “strong” sites can be “slow” desorbed from MWCNTs with a time constant τ_1 (%). τ_1 and τ_2 are desorption time constants (h).

The different systems were studied in the kinetic desorption of Eu(III) from MWCNTs and named as follows: aging time $t = 4$ days, pH was adjusted to 6.3 ± 0.2 in the desorption study (Figure 6.38b); aging time $t = 4$ days, pH was adjusted to 3.2 ± 0.1 in the desorption study (Figure 6.38c, solid points); and aging time $t = 6$ months, pH was adjusted to 3.2 ± 0.1 in the desorption study (Figure 6.38c, open points). In the presence of MWCNTs, the initial Eu(III) concentration first drops rapidly at the initial time and then decreases very slowly. The rapid decrease at the beginning is related to the free Eu(III) not complexed with the MWCNTs in solution. The kinetic parameters obtained by fitting the experimental data to Equation 6.10 are listed in Table 6.12. The slow desorption kinetic of Eu(III) is attributed to the very slow desorption kinetics of Eu(III) from the MWCNTs. Even after more than 100 days of contact with the chelating resin, $(91.0 \pm 0.5)\%$ (pH 6.3 ± 0.2), $(50.0 \pm 0.4)\%$ ($t = 4$ days, pH 3.2 ± 0.1), and $(53.5 \pm 0.5)\%$ ($t = 6$ m, pH 3.2 ± 0.1) of Eu(III) still remains bound to MWCNTs. The experimental results indicate that Eu(III) forms kinetically stabilized complexes with MWCNTs and is not easily desorbed from MWCNTs. This finding clearly proves the existence of strong chemical binding of Eu(III) with nanotubes, and europium cannot easily release from the surface of CNTs to solution.

Figure 6.38c shows that for the two different aging times (4 days and 6 months), the final concentration of Eu(III) remaining on MWCNTs (C_{final}) for 6 months is higher than that for 4 days. This indicates that Eu(III) is bound to MWCNTs in at least two forms, and the irreversible fractions

TABLE 6.12**Kinetic Parameters Obtained for Desorption Experiments by Fitting Experimental Data to the Kinetic Equation 6.10**

System	$C_{\text{final}}/C_{\text{tot}}$ (%)	τ_1 (h)	A_1 (%)	τ_2 (h)	A_2 (%)
Eu-Resin	0.3 ± 0.8	27.6 ± 7.3	8.1 ± 0.4	2.0 ± 0.3	94.2 ± 0.2
Eu-MWCNTs-Resin (pH = 6.3, $t = 4$ days)	91.0 ± 0.5	20 ± 8	3.8 ± 0.5	1296 ± 210	5.1 ± 0.4
Eu-MWCNTs-Resin (pH = 3.2, $t = 4$ days)	50.0 ± 0.4	99 ± 34	22.4 ± 1.3	312 ± 72	27.5 ± 1.4
Eu-MWCNTs-Resin (pH = 3.2, $t = 6$ months)	53.5 ± 0.5	10 ± 13	1.8 ± 1.0	297 ± 10	44.7 ± 0.9

Source: Tan, X.L. et al., *Radiochim. Acta*, 96, 23–29, 2008. With permission.

increase with increasing aging time. The results are very similar to water conduction through the channels of CNTs [60]. The microstructure of adsorbed Eu(III) on the surface of MWCNTs perhaps changes with increasing aging time, the fractions of Eu(III) in the center channels of CNTs increase with increasing aging time, and the Eu(III) remaining in the channels of CNTs is irreversible to be desorbed from CNTs. This is a reasonable interpretation of the different final fractions of Eu(III) remaining on MWCNTs for 4 days and 6 months of aging time.

The fractions of A_1 are $(22.4 \pm 1.3)\%$ and $(1.8 \pm 1.0)\%$ for 4 days and 6 months of aging time, respectively; those of A_2 are $(27.5 \pm 1.4)\%$ and $(44.7 \pm 0.9)\%$ for 4 days and 6 months of aging time, respectively. The fraction of Eu(III) on “weak” sites decreases, whereas that of Eu(III) on “strong” sites increases with increasing aging time. This indicates that the surface-adsorbed Eu(III) on MWCNTs can be changed from “weak” to “strong” sites with increasing aging time. The results indicate the two changes of the microstructure on the surface and Eu(III) fraction with aging time.

The kinetic results suggest that metal ions adsorbed on MWCNTs are difficult to be desorbed from the CNTs at similar conditions to the sorption experiments. However, if the material is placed in solutions of low pH, the adsorbed metal ions on CNTs can be desorbed from solid surfaces. The fraction of metal ions that can be desorbed from solid surfaces is dependent on pH values, and increases with decreasing pH.

6.3.3 EFFECT OF ORGANIC MATERIAL

In the natural environment, the presence of natural organic matters (such as humic acid or fulvic acid) influences the physicochemical behavior of metal ions because of the strong complexation capacity of organic matters with metal ions. The presence of humic substances obviously influences the species of metal ions. In this study, we present the results of Eu(III) species in the natural environment in the absence and presence of humic substances as a comparison. Table 6.13 lists the relative thermodynamic constants for the calculation of Eu(III) species, and the relative species of Eu(III) are shown in Figure 6.39.

Figure 6.39 clearly shows that the species of Eu(III) in the natural environment are strongly dependent on pH values and humic substances. The sorption behavior of metal ions is affected by the species of metal ions in solution. Therefore, the presence of humic substances affects the sorption of metal ions on nanomaterials. Generally, the presence of humic substances enhances metal ion sorption at low pH values and decreases metal ion sorption at high pH values. The increase of sorption is explained by the sorption of humic substances onto the solid surface followed by the interaction of metal ions with surface-adsorbed humic substances, whereas the reduction of sorption

TABLE 6.13
Thermodynamic Constants Used for Speciation Calculations

Reaction	log K
$\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$	-13.79
$\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$	-17.43
$\text{Eu}^{3+} + \text{CO}_3^{2-} + \text{HA} \rightleftharpoons [\text{Eu}(\text{CO}_3)_2\text{HA}]$	12.4
$\text{Eu}^{3+} + 2\text{H}_2\text{O} + \text{HA} \rightleftharpoons [\text{Eu}(\text{OH})_2\text{HA}] + 2\text{H}^+$	-10.03
$\text{Eu}^{3+} + \text{H}_2\text{O} + \text{HA} \rightleftharpoons [\text{Eu}(\text{OH})\text{HA}] + \text{H}^+$	-0.96
$\text{Eu}^{3+} + \text{HA} \rightleftharpoons [\text{EuHA}]^{3+}$	6.4
$\text{Eu}^{3+} + 3\text{CO}_3^{2-} \rightleftharpoons [\text{Eu}(\text{CO}_3)_3]^{3-}$	13.53
$\text{Eu}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons [\text{Eu}(\text{CO}_3)_2]^-$	10.81
$\text{Eu}^{3+} + \text{CO}_3^{2-} \rightleftharpoons [\text{Eu}(\text{CO}_3)]^+$	6.38
$\text{Eu}^{3+} + \text{NO}_3^- \rightleftharpoons [\text{Eu}(\text{NO}_3)]^{2+}$	1.22
$\text{Eu}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons [\text{Eu}(\text{OH})_2]^+ + 2\text{H}^+$	-16.15
$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Eu}(\text{OH})]^{2+} + \text{H}^+$	-8.08

Source: Geckeis, H. et al., *Environ. Sci. Technol.*, 36, 2946–2952, 2002. With permission.

is explained by the formation of soluble HS–metal ion complexes, which stabilize the metal ions in aqueous solution. Generally, humic substances are negatively charged and are easily adsorbed on solid surfaces at low pH values because of the positive surface charge at $\text{pH} < \text{pH}_{\text{pzc}}$ (point of zero charge). At $\text{pH} > \text{pH}_{\text{pzc}}$, the sorption of humic substances on solid surfaces decreases with increasing pH because of the negative surface charge at $\text{pH} > \text{pH}_{\text{pzc}}$.

To the best of our knowledge, the simultaneous sorption of heavy metal ions and organic pollutants on CNTs is still not available. The removal of organic pollutants or heavy metal ions from aqueous solutions by using all kinds of CNTs has been extensively studied; the removal of heavy metal ions to CNTs in the presence of organic pollutants is still not reported. It is well known that organic pollutants and heavy metal ions coexist in wastewater; it is therefore inevitable that the sorption of organic pollutants and heavy metal ions should be investigated. From the results of heavy metal ion sorption on nanosized clay minerals and oxides [63–66], one can conclude that the presence of organic matter increases the sorption of heavy metal ions at low pH and decreases the sorption of heavy metal ions at high pH.

6.3.4 COMPOSITES OF CNTs AND OTHER NANOMATERIALS

6.3.4.1 MWCNT–TiO₂ Composites

MWCNTs are suitable materials in the preconcentration and solidification of heavy metal ions from large-volume solutions. In a natural environment, TiO₂–MWCNT composites are considered better than MWCNTs in the sorption of Cr(VI), and better than TiO₂ in the photocatalytic reduction of Cr(VI). The synthesis and characterization of TiO₂–MWCNT composites in view of their photocatalytic application have been reported [67–70]. TiO₂–MWCNT composites showed remarkable enhancement in photocatalytic properties compared with pure TiO₂ particles. The large sorption ability of MWCNTs and the remarkable photocatalytic reduction property of TiO₂ make TiO₂–MWCNTs a novel material for the reduction of organic and inorganic components in polluted environments.

The XRD patterns of MWCNTs, TiO₂, and treated TiO₂–MWCNTs are given in Figure 6.40. The most intense peaks of MWCNTs correspond to the (002) and (100) reflections. The peaks in

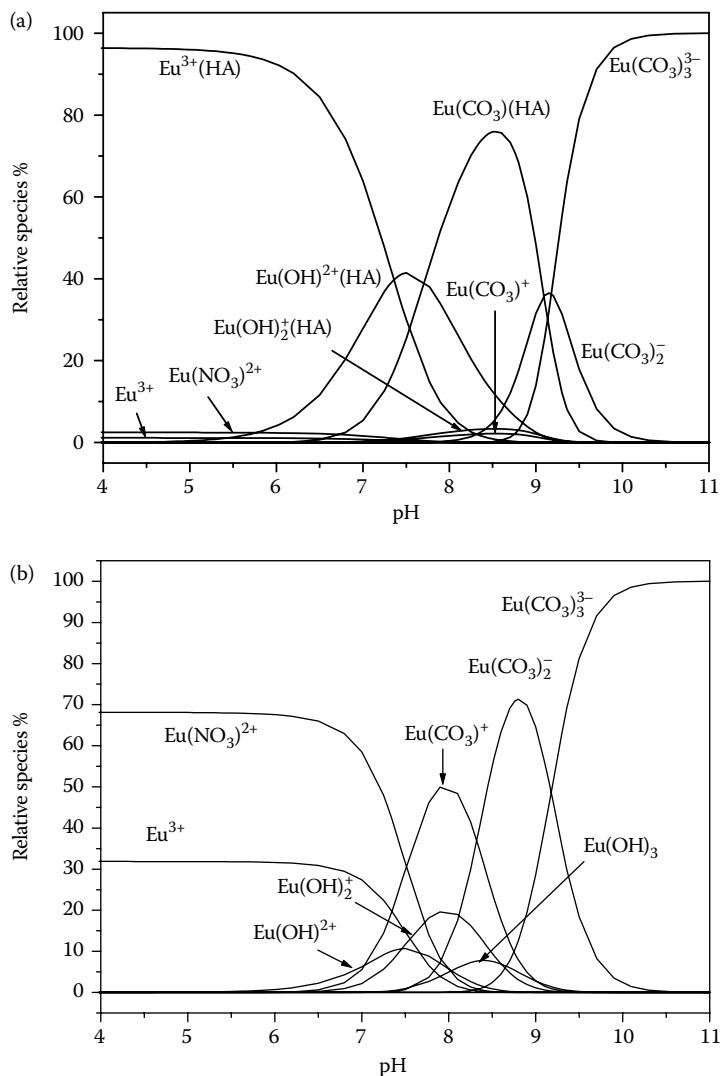


FIGURE 6.39 Relative species distribution of Eu(III) in solution in the presence of humic acid (HA) (a) and the absence of HA (b). $I = 0.1 \text{ mol/L KNO}_3$, $T = 20 \pm 1^\circ\text{C}$ under ambient conditions. (From Tan, X.L. et al., *Environ. Sci. Technol.*, 42, 6532–6537, 2008. With permission.)

TiO_2 correspond to anatase TiO_2 (JCPDS card of 894921, space group of $\text{P4}_2 \text{ mnm}^{-1}$, $a_0 = 3.777 \text{ \AA}$, $c_0 = 9.501 \text{ \AA}$). In the case of TiO_2 –MWCNT composites after thermal treatment at 450°C , it is worth noting that the (002) reflection due to MWCNTs overlaps the anatase TiO_2 (101) reflection. The treated TiO_2 –MWCNT composites seem to be quite well crystallized, and only TiO_2 in the anatase phase can be identified.

The adsorption and photocatalytic reduction of Cr(VI) on TiO_2 , MWCNTs, and TiO_2 –MWCNT composites at different Cr(VI) concentrations are shown in Figure 6.41. For comparison, the activities of TiO_2 , MWCNTs, and TiO_2 –MWCNT composites were tested under the same conditions. It shows that different samples have apparently different capacities of Cr(VI) removal. As expected, the amount of Cr(VI) ions removed by the solid phases increased with increasing Cr(VI) concentration. Due to their large specific area, MWCNTs exhibit more of a superadsorption capacity than TiO_2 and TiO_2 –MWCNTs in the dark. The photocatalytic activity of TiO_2 –MWCNT composites is a little higher than

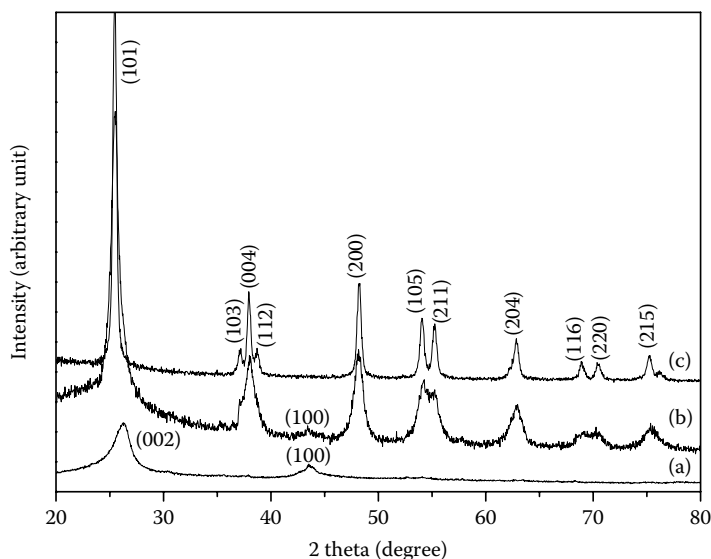


FIGURE 6.40 XRD patterns of samples: (a) MWCNTs, (b) $\text{TiO}_2/\text{MWCNTs}$, and (c) anatase TiO_2 . (From Tan, X.L., Fang, M., and Wang, X.K., *J. Nanosci. Nanotech.*, 8, 5624, 2008. With permission.)

that of pure TiO_2 under UV irradiation. Firstly, the introduction of MWCNTs into the composite catalysts remarkably induces not only a synergetic effect on Cr(VI) adsorption capacities, but also high photocatalytic reduction activity. MWCNTs can adsorb Cr(VI) from solution, centralize them on the surface of TiO_2 , and thereby favor photocatalytic activity. Secondly, MWCNTs can conduct electrons

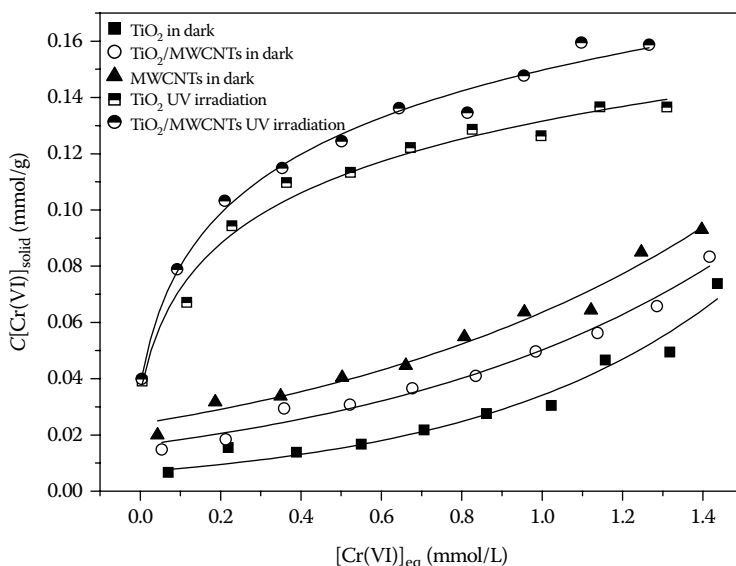


FIGURE 6.41 Effect of Cr(VI) concentration on the removal of Cr(VI) by TiO_2 , MWCNTs, and $\text{TiO}_2/\text{MWCNTs}$ in the dark and under UV irradiation. $\text{pH} = 3.0 \pm 0.1$, $C[\text{TiO}_2/\text{MWCNTs}] = 0.2 \text{ g/L}$, $C[\text{K}_2\text{SO}_4] = 7.5 \times 10^{-5} \text{ mol/L}$, irradiation time = 6 h. (From Tan, X.L., Fang, M., and Wang, X.K., *J. Nanosci. Nanotech.*, 8, 5624, 2008. With permission.)

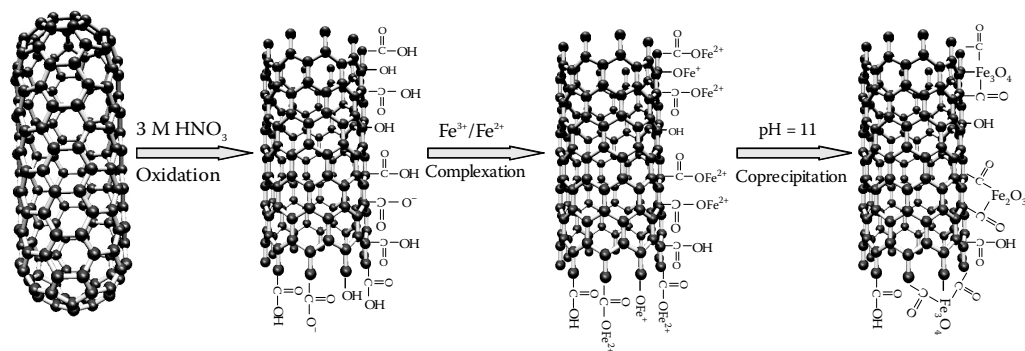


FIGURE 6.42 Preparation process of MWCNT–iron oxide magnetic composites.

and reduce electronic accumulation of TiO₂; they can decrease the recombination of electron–hole pairs. The attachment of MWCNTs to TiO₂ surfaces possibly results in increased adsorption of cations and in turn its photocatalysis rate [69,70].

Figure 6.41 clearly shows that MWCNT–TiO₂ composites have much higher sorption and photocatalytic reduction abilities than pure TiO₂ under UV irradiation. Although MWCNT–TiO₂ composites have lower sorption capacities than pure MWCNTs in the dark, the photocatalytic reduction capacity of TiO₂ makes the composites have much higher capacities in the removal of Cr(VI) under UV-irradiation conditions. The MWCNT–TiO₂ composites may not be good material in the removal of heavy metal ions as compared with MWCNTs; however, if the photocatalytic reduction ability of TiO₂ is taken into account, the preconcentration property of MWCNTs and the photocatalytic reduction property of TiO₂ make the MWCNT–TiO₂ composites very good material in the removal and reduction of some special heavy metal ions such as Cr(VI).

6.3.4.2 MWCNT–Iron Oxide Magnetic Composites

The high sorption capacity of CNTs suggests that CNTs may be a promising adsorbent for treating wastewater containing organic and inorganic pollutants. However, it is difficult to separate CNTs from an aquatic phase because of their small size. The centrifugation method needs a very high rate, and the traditional filtration method may cause the blockage of filters. Compared with centrifugation and filtration methods, the magnetic separation method is considered as a rapid and effective technique for separating magnetic particles from solutions. Magnetic separation methods, which represent a group of techniques based on the use of magnetic or magnetizable adsorbents, carriers, and cells, have been used for many applications in biochemistry, microbiology, cell biology, analytical chemistry, mining ores, and environmental technologies [72–74]. To facilitate the separation and recovery of CNTs from solution, the incorporation of magnetite with CNTs may be a promising method.

The preparation process of MWCNT–iron oxide magnetic composites is illustrated in Figure 6.42. Oxidized MWCNTs are functionalized with negative carboxylic and hydroxylic groups, which have the potential ability to bind metal ions. Positive ferrous and ferric ions are attached on oxidized MWCNTs due to the coordination reaction between ferrous and ferric ions and carboxylic and hydroxylic groups in the wet impregnation process.

We have applied synthesized MWCNT–iron oxide magnetic composites to adsorb metal ions and to separate magnetic composites from aqueous solutions by a magnetic process using a permanent magnet made of Nd–Fe–B. The results indicate that the magnetic method is as good as the centrifugation method in separating magnetic composites from aqueous solutions. As mentioned earlier, the application of magnetic composites in the removal of heavy metal ions from aqueous solutions is a very promising method. Further investigation, however, is still necessary.

6.4 CONCLUSIONS

The application of CNTs in the removal of heavy metal ions is summarized in this chapter. The special physicochemical properties of CNTs and their high sorption capacity and stability make them very suitable materials in the removal of heavy metal ions from large volumes of aqueous solutions. The organic pollutants in wastewater can also be removed easily by CNTs because of the strong interaction between CNTs and organic pollutants.

MWCNT–TiO₂ composites and MWCNT–iron oxide magnetic composites are briefly discussed at the end of the chapter. According to the application of composites in the removal of heavy metal ions from aqueous solution, the composites synthesized from MWCNTs and other oxides have special properties, and this feature enables the composites to have special applications.

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7 Biosorption of Metals onto Granular Sludge

Shu Guang Wang, Xue Fei Sun, Wen Xin Gong, and Yue Ma

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7.1 INTRODUCTION

Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries, and other metal-processing and refining operations contain considerable amounts of toxic metal ions. Of the important metals, mercury, lead, copper, nickel, cobalt, cadmium, and chromium (VI) are regarded as highly toxic [1]. Radionuclides, such as uranium, possess high toxicity and radioactivity, and exhibit a serious threat, even at small concentrations, to the health of human beings [2].

The toxic characteristics of heavy metals are as follows: (1) the toxicity can last for a long time; (2) some heavy metals can even be transformed from relevant low-toxic species into more toxic

forms in a certain environment (e.g., mercury); (3) the bioaccumulation and bioaugmentation of heavy metals by food chain can damage normal physiological activity and eventually endanger human life; (4) metals can only be transformed and changed in valence and species, but they cannot be degraded by any method including biotreatment; and (5) the toxicity of heavy metals occurs even in low concentrations of about 1.0–10 mg/L. Some strong toxic metal ions, such as Hg and Cd, are very toxic even at their trace levels of 0.001–0.1 mg/L [1,3].

Considerable researches have been carried out in developing cost-effective heavy metal removal techniques: chemical precipitation, chemical oxidation or reduction, evaporation, adsorption, ion exchange, and membrane technologies [4,5]. These techniques may be ineffective or expensive, especially when the concentrations are in the order of 1–100 mg/L [6–8]. It is important to find alternative effective, economical, and practical techniques. Biosorption is the term given to the passive sorption and/or complexation of metal ions by biomass. The mechanisms of biosorption are generally based on physico-chemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange, and metal ion chelation or complexation [9,10]. Because of low cost and good performance, biosorption is promising for removing heavy metals from aqueous solutions in recent years. A number of biomaterials have been used as biosorbents in the literature, including fungus, algal, biosludge, and microalgae [5,8,11–16]. However, most of the biosorbents currently used are in the form of suspended biomass; hence, one of the major operational problems associated is postseparation of biosorbent from the treated effluent. To overcome this drawback, a cell immobilization technique has been developed, but the immobilization procedure is often expensive and complex.

A great body of research showed that granular sludge is a microbial aggregate with compact structure and excellent settleability. Granular sludge was first described for strictly anaerobic systems in 1980 [17], and by the late 1990s, the formation and application of aerobic granules had been reported [18–20]. Anaerobic granules possessed a compact porous structure and excellent settling ability. The particulate biomass was found to possess high mechanical strength. Even under aggressive chemical environments (acidic or basic conditions), the biomass demonstrated excellent stability with no visible structural damage [21]. Although the aerobic granules were densely packed, microbial aggregates and their densities were much higher than that of conventional activated sludge. In addition, the aerobic granules were known to exhibit advantages of (1) regular, smooth, and nearly round in shape; (2) excellent settleability; (3) dense and strong microbial structure; (4) high biomass retention; (5) ability to withstand at high organic loading; and (6) tolerance to toxicity [22]. The gross morphology of anaerobic and aerobic granules is shown in [Figure 7.1](#). The schematic diagrams of the upflow anaerobic sludge blanket (UASB) and the sequencing batch reactor (SBR) reactor are shown in [Figures 7.2 and 7.3](#).

The average diameter of granular sludge is in the range 0.2–5 mm. The settling velocity ranges from 30 to 100 m/h, whereas that of suspended flocs is usually lower than 9 m/h. Advantages of compact structure and excellent settling property have been well recognized. They also exhibited good performance in heavy metals uptake and dyes uptake [23–31]. Granular sludge could be considered as a potential candidate for metal removal such as cadmium(II), copper(II), nickel(II), and zinc(II). This chapter is devoted to focus on metal removal from aqueous solutions by granular sludge based on a substantial number of references on metal biosorption and our previous work.

7.2 BIOSORPTION CAPACITY OF GRANULAR SLUDGE

7.2.1 BIOSORPTION CAPACITY

The determination of the metal uptake rate by the biosorbent is often based on the equilibrium state of sorption system. The sorption uptake is expressed in milligrams of metal sorbed per gram of the (dry) sorbent (the basis for engineering process—mass balance calculations), or mmol/g or meq/g (when stoichiometry and/or mechanism are considered) [32]. Metal ion uptake by granular sludge

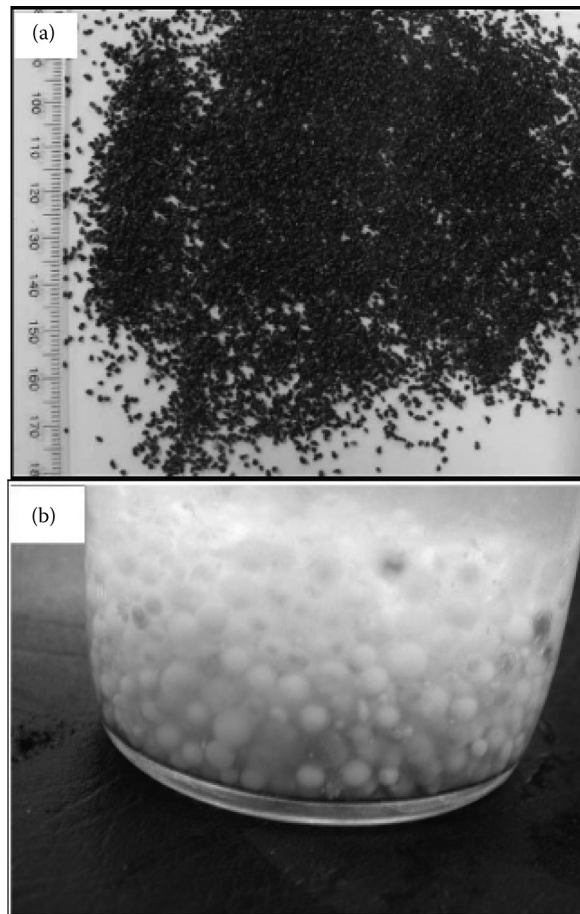


FIGURE 7.1 Gross morphology of granular sludge: (a) anaerobic granules and (b) aerobic granules.

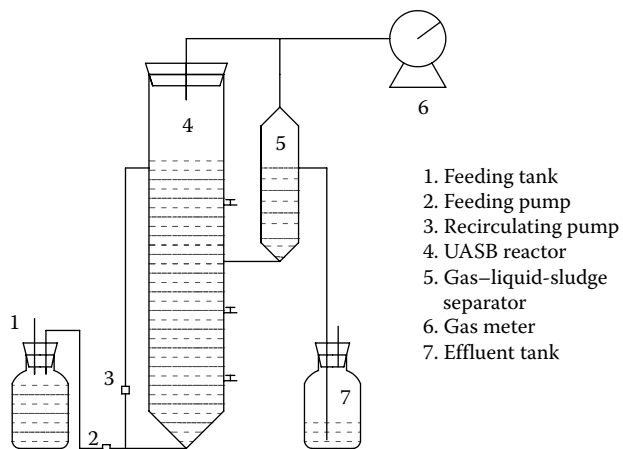
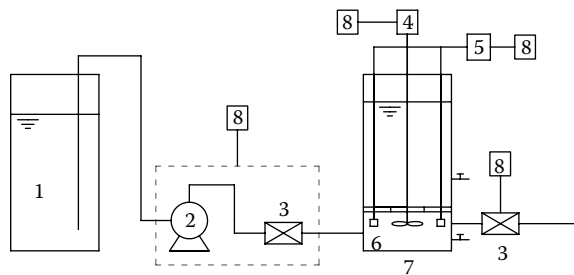


FIGURE 7.2 Schematic diagram of the UASB reactor. (Adapted from Shen, D.S. et al, *J. Hazard. Mater.*, 125, 231–236, 2005.)



1. Water tank 2. Influent pump 3. Valve 4. Stirrer
5. Air pump 6. Air diffuser 7. Reactor 8. Timer

FIGURE 7.3 Schematic diagram of the SBR reactor. (Adapted from Hu, L.L. et al., *Proc. Biochem.*, 40, 5–11, 2005.)

has been reported in a substantial number of references. Table 7.1 presents some data on the biosorptive capacities of different metal ions.

The biosorption capacity is strongly dependent on parameters such as the concentration of metals, pH, and adsorption time. The biosorption capacity of each metal is comparable with those

TABLE 7.1
Biosorption Capacity of Different Metals

Metals	Sorbent	Uptake Capacity (mg/g)	<i>T</i> (°C)	pH	References
Copper(II)	Anaerobic granules	55	—	5	[23]
	Aerobic granules	59.6	26	4	[24]
		40.65	20	5	[28]
		44.90	25	6	[50]
		246.1	26	7	[34]
Cadmium(II)	Anaerobic granules	60	—	5	[23]
	Aerobic granules	172.7	26	4	[24]
		566	26	7	[25]
		90.26	25	6	[50]
Zinc(II)	Aerobic granules	164.5	26	4	[24]
		270	26	6	[33]
		180	26	7	[34]
		62.50	20	5	[26]
Uranium(VI)	Aerobic granules	218 ± 2	30	4	[30]
Cerium(IV)	Aerobic granules	357	—	—	[53]
Lead(II)	Anaerobic granules	255	—	5	[23]
	Aerobic granules	87.72	—	—	[54]
Cobalt(II)	Anaerobic granules	12.34	—	7	[31]
		11.71	—	7	[31]
		9.40	30	7	[38]
		1.69	30	—	[55]
	Aerobic granules	55.25	20	7	[26]
Nickle(II)	Anaerobic granules	12.02	—	7	[31]
		13.33	—	7	[31]
		8.92	30	7	[38]
		26	—	5	[23]
	Aerobic granules	33.5	21	7	[36]
		17.5	25	6	[41]
		22.42	25	6	[50]

TABLE 7.2**A Comparative Study of Different Biomaterials with Granular Sludge**

Metal	Biosorptive Capacity (mg metal/g Dry Weight Biomass)	References
Zn(II)	<i>Sargassum</i> sp. (118.5) > <i>Bacillus jeotgali</i> (105.2) > Powdered waste sludge (82.0) > Aerobic granule (62.5) > <i>Ascophyllum nodosum</i> (25.6) > <i>Penicillium chrysogenum</i> (19.2) > <i>F. vesiculosus</i> (17.3) > Activated sludge (9.7) > <i>S. rimosus</i> (6.63)	[3,26]
Co(II)	PFB1 (190.0) > <i>Mortierella</i> SPS 403 (61.2) > Aerobic granule (52.4) > Anaerobic granule (12.3) > <i>Oscillatoria angustissima</i> (5.3) > <i>Myriophyllum spicatum</i> L. (2.3)	[26,31]
Pb(II)	<i>Ascophyllum nodosum</i> (271.1) > Anaerobic granule (258.7) > <i>Sargassum natans</i> (252.5) > <i>Penicillium chrysogenum</i> (122.13) > <i>Rhizopus arrhizus</i> (89.8) > Activated sludge (89.0) > Aerobic granule (87.8)	[23,53]
Cu(II)	Aerobic granule (59.6) > Anaerobic granule (55.3) > Activated sludge (49.0) > Sugar beet pulp (21.0) > <i>Rhizopus arrhizus</i> (10.2) > <i>Penicillium chrysogenum</i> (8.9)	[23,24]
Cd(II)	Aerobic granule (172.7) > <i>Ascophyllum nodosum</i> (132.2) > <i>Sargassum natans</i> (131.0) > Activated sludge (68.3) > Anaerobic granule (59.4) > <i>Penicillium chrysogenum</i> (56.0) > <i>Rhizopus arrhizus</i> (26.9)	[23,24]
Ni(II)	<i>Ascophyllum nodosum</i> (40.5) > Aerobic granule (33.5) > Anaerobic granule (25.8) > <i>Sargassum natans</i> (24.1) > Activated sludge (18.2) > Sugar beet pulp (12.9)	[23,36]

conventional suspended biosorbents [24,33,34]. As far as metal species is concerned, the investigation is narrow and not systemic. Fewer documents about metals with multivalences and complicated forms, such as arsenic and chromium, have been reported.

7.2.2 GRANULAR SLUDGE VERSUS OTHER BIOMATERIALS

Table 7.2 presents a part of comparative results of metal biosorption capacity between granular sludge and other biomaterials. By comparing the maximum sorption capacity ($q_{\max}$ of the Langmuir equation) with various types of biomass for the removal of zinc and cobalt ions, Sun et al. [26] indicated that aerobic granular sludge has a higher capacity for single- and binary-metal biosorption systems. Hawari and Mulligan [23] investigated various types of waste biomass including brown algae bacteria, fungus as well as activated sludge for biosorption of metals. They found that the metal removal capacity of anaerobic granular sludge was higher than that of granular and powder-activated carbons. Anaerobic granular sludge appeared to be more efficient in metal uptake than sugar beet pulp, activated sludge, *Penicillium chrysogenum*, and *Rhizopus arrhizus* fungus. The considerably low cost of the granular sludge, its physical characteristics, and the high uptake capacity of the heavy metals make it a very attractive biosorbent.

7.3 INFLUENTIAL FACTORS

7.3.1 INITIAL METAL CONCENTRATION

The uptake rate of the metal ion will increase with increasing the initial concentration [25,27]. At lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low; the fractional sorption thus becomes independent of the initial concentration. However, at higher concentrations, the sites available for sorption become fewer compared to the moles of solute present and hence, the removal of solute is strongly dependent on the initial solute concentration. It is always necessary to identify the maximum saturation potential of a biosorbent, for which experiments should be conducted at the highest possible initial solute concentration.

7.3.2 pH

For biosorption of heavy metal ions, pH is the most important environmental factor. The pH value of a solution strongly influences not only the site dissociation of the biomass surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, the speciation, and the biosorption availability of the heavy metals [35].

The biosorptive capacity of metal cations increases with increasing the pH of the sorption system, but not in a linear relationship (Figure 7.4). On the other hand, too high a pH value can cause precipitation of metal complexes, so it should be avoided during experiments.

Xu et al. [36] found that the amount of nickel uptake by granules tended to increase and a sharp increase in the maximum specific uptake ($q_{\max}$) was observed in pH between 3 and 6. This led them to suggest that at low pH, the cell surface-binding sites should be protonized, thereby making them unavailable for the other cations. However, with an increase in pH, there was an increase in ligands with negative charges, which resulted in increased binding of cations. Hawari and Mulligan [23] proved that the biosorption capacity of Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} is dependent on pH. For all the metal ions they studied, the optimal pH values are in the range 4.0–5.5. A further possible explanation of increasing sorption with increasing pH is that hydrolyzed species have a lower degree of hydration, that is, less energy is necessary for removal or reorientation of the hydrated water molecules upon binding. With further increase in pH (6–9), the solubility of metals decreases enough for precipitation to occur. This should be avoided during sorption experiments, as distinguishing between sorption and precipitation metal removal becomes difficult [37]. van Hullebusch [38] and Gai et al. [28] obtained a similar conclusion.

7.3.3 TEMPERATURE

The biosorption process is usually not operated at high temperature because it will increase the operational cost. Temperature seems to affect biosorption only to a lesser extent within the range from 20°C to 35°C [2]. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute [39,40]. Liu and Xu [41] found that nickel adsorption was enhanced by increasing the incubation temperature (Figure 7.5). This was based on the fact that $q_{\max}$ increased with an increase in temperature to a plateau at 55°C for 26.9 mg Ni(II) g⁻¹ and 1.29 mmol Pd(II) g⁻¹, thereby implying the need for energy in the form of heat for maximal adsorption of metal ions.

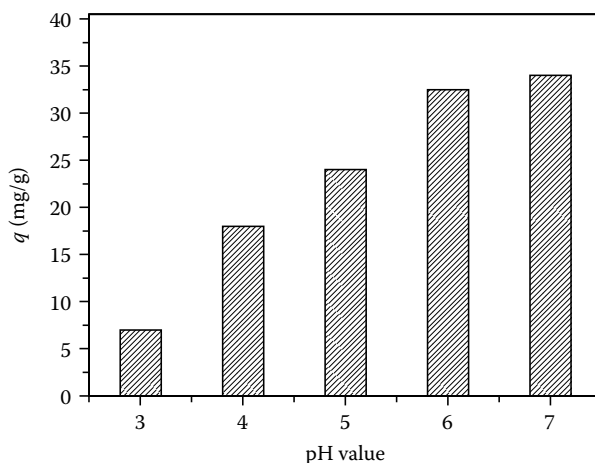


FIGURE 7.4 $q_{\max}$ at various initial pH values. (Adapted from Xu, H. et al., *Bioresour. Technol.*, 97, 359–363, 2006.)

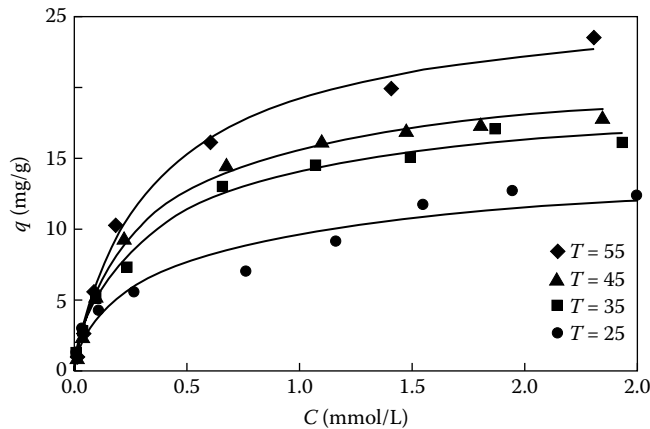


FIGURE 7.5 Biosorption isotherm of Ni^{2+} by aerobic granules at different temperatures. (Adapted from Xu, H. et al., *Bioresour. Technol.*, 97, 359–363, 2006.)

7.3.4 CONTACT TIME

The biosorption process of heavy metal by granular sludge is usually completed rapidly. The biosorption of metals such as copper, cobalt, nickel, zinc, and uranium is a rapid process and often reaches equilibrium within several hours. Table 7.3 shows the equilibrium time for different metal–sludge systems. The biosorption of Pb, Cd, Cu, and Ni with anaerobic granules reached equilibrium within 30 min [23]. In the case of Cu by aerobic granules, equilibrium was attained in 30 min [28].

Generally speaking, metal biosorption consists of two phases: a very rapid initial sorption, followed by a long period of much slower uptake. During the initial stage of sorption, a large number of vacant surface sites are available for biosorption. After some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase. Besides, the metal ions are adsorbed onto the mesopores that get almost saturated with metal ions during the initial stage of biosorption. Thereafter, the metal ions have to traverse farther and deeper into the pores, encountering much larger resistance. This results in the slowing down of the biosorption during the later period of biosorption [26].

TABLE 7.3
Equilibrium Time for the Metal–Sludge System

Metal	Biosorbents	Equilibrium Time (h)	References
Cu(II)	Aerobic granule	0.5	[28]
		0.5	[23]
Zn(II)	Aerobic granule	0.5	[26]
Pb(II)	Aerobic granule	0.5	[23]
Cd(II)	Aerobic granule	0.5	[23]
		2	[24]
		1.7	[25]
Uranium(VI)	Aerobic granules	1	[30]
Co(II)	Anaerobic granule	96	[38]
	Aerobic granule	0.5	[26]
Ni(II)	Anaerobic granule	96	[38]
	Aerobic granule	0.5	[23]

7.3.5 PRESENCE OF COMPETING IONS

Competitive sorption is important in water and wastewater treatment, because most metal ions to be sorbed exist in solution with other metal ions. Usually, the biosorption capacity of one metal ion is often interfered and reduced by co-ions, including other metal ions and anions presenting in solution; however, the gross uptake capacity of all metals in solutions remains almost unchangeable. Sun et al. [26] studied the individual and competitive sorption of Zn^{2+} and Co^{2+} ions onto aerobic granules. The sorption capacities of granules for the two metal ions are in the order of $\text{Zn}^{2+} > \text{Co}^{2+}$ and the competitive sorption of metal ions also follows the same order. The sorption capabilities of granular sludge without competition are much better than those with competition because the granule surface is utilized by competing metal ions. Hawari and Mulligan [42] observed that the single-metal sorption uptake capacity of the biomass for Pb was slightly inhibited by the presence of Cu and Cd cations (by 6%) and by the presence of nickel (by 11%). The affinity order of anaerobic biomass for the four metals was established as follows: $\text{Pb} > \text{Cu} > \text{Ni} > \text{Cd}$.

7.3.6 THERMODYNAMICS

Both energy and entropy are the key factors to be considered in any process design. In this study, the thermodynamic parameters, such as standard free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were estimated to evaluate the feasibility and endothermic nature of the adsorption process. These were calculated by using the following equations:

$$\Delta G^\circ = -RT \ln K_e, \quad (7.1)$$

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (7.2)$$

The K_e value can be obtained from the linearized form of Langmuir equation.

The thermodynamic parameters for Ni^{2+} ions onto aerobic granule, which provide useful information concerning the inherent energetic changes of the sorption process, revealed that the negative free energy change (ΔG°) suggests that the sorption process is spontaneous with a high preference of Ni^{2+} ions for aerobic granules. The value of ΔH° was estimated as 63.8 kJ/mol and 0.26 kJ/mol K for ΔS° . The enthalpy change (ΔH°) is positive, indicating the endothermic nature of the sorption process [41]. The positive entropy change (ΔS°) reflects the increased randomness at the solid–solution interface during biosorption; it also indicates that ion replacement reactions occurred.

7.4 MODELS

The assessment of a solid–liquid sorption system is usually based on two types of investigations: equilibrium batch sorption tests and dynamic continuous-flow sorption studies [43].

7.4.1 BIOSORPTION ISOTHERMS

A biosorption isotherm, the plot of uptake (q) versus the equilibrium solute concentration in the solution (C_f), is often used to evaluate the sorption performance. Isotherm curves can be evaluated by varying the initial solute concentrations, while fixing the environmental parameters, such as pH, temperature, and ionic strength. In general, the uptake increases with increase in concentration, and will reach saturation at higher concentrations. Figure 7.6 shows the outline of the general experimental procedure to obtain data points for the sorption isotherm [44].

Equilibrium isotherm models are usually classified into the empirical equations and mechanistic models, based on the mechanism of metal ion biosorption. Mechanistic models can be used not only to represent, but also to explain and predict the experimental behavior [3].

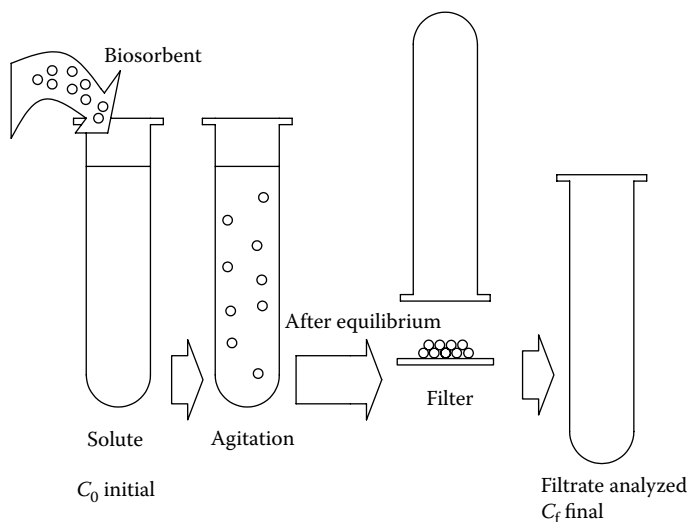


FIGURE 7.6 Outline of the experimental procedure to obtain data points for the sorption isotherm. (Adapted from Vijayaraghavan, K. and Yun, Y.S., *Biotechnol. Adv.*, 26, 266–291, 2008.)

Empirical models are simple mathematical relationships, characterized by a limited number of adjustable parameters, which give a good description of the experimental behavior over a large range of operating conditions [2]. Within the literature, the Langmuir [45] and Freundlich [46] models (two-parameter models) have been used to describe the biosorption isotherm. The models are simple, well established, have physical meaning, and are easily interpretable, which are some of the important reasons for their frequent and extensive use.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It can be expressed as

$$q = \frac{q_{\max} b C_f}{1 + b C_f} \quad (7.3)$$

This classical model incorporates two easily interpretable constants: $q_{\max}$, which corresponds to the maximum achievable uptake by a system; and b , which is related to the affinity between the sorbate and sorbent [27]. A typical Langmuir adsorption isotherm is shown in Figure 7.7. The Langmuir constant “ $q_{\max}$ ” is often used to compare the performance of biosorbents; the other constant “ b ” characterizes the initial slope of the isotherm. Thus, for a good biosorbent, a high $q_{\max}$ and a steep initial isotherm slope (i.e., high b) are generally desirable [32].

The Freundlich isotherm is given as

$$q = K_F C_f^{1/n_F} \quad (7.4)$$

The Freundlich isotherm was originally empirical in nature, but was later interpreted as the sorption to heterogeneous surfaces or to surfaces supporting sites with various affinities. It is assumed that the stronger binding sites are initially occupied, with the binding strength decreasing with increasing degree of site occupation [46]. It incorporates two constants: K_F , which corresponds to the binding capacity; and n_F , which characterizes the affinity between the sorbent and sorbate.

For the biosorption of metal ions by granular sludge, the classical Langmuir model and the Freundlich model have been employed to describe the single-metal biosorption system, and in most cases, both models fitted the experimental data very well (correlation coefficient was usually larger than 0.9). Table 7.4 presents a part of biosorption isothermal constants for the Langmuir and

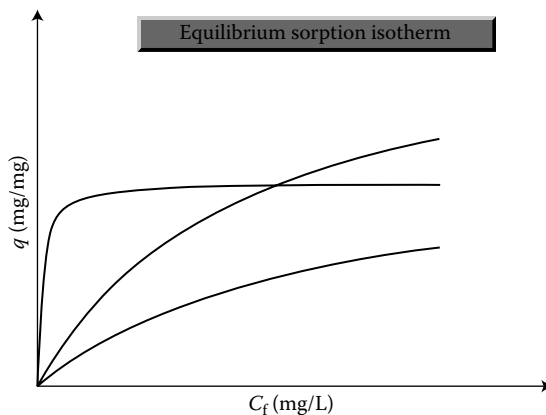


FIGURE 7.7 Biosorption–Langmuir isotherm relationship curves.

Freundlich models reported in the references. Table 7.4 shows that, in most cases, the classical Langmuir model and the Freundlich model can represent single-metal biosorption behavior.

7.4.2 BIOSORPTION KINETICS

For any practical applications, the process design, operation control, and sorption kinetics are very important [47]. Adsorption kinetics modeling explains how fast the sorption process occurs and also the factors affecting the reaction rate. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for the full-scale batch process. Also, it is important to establish the time dependence of adsorption systems under various process conditions. The nature of sorption process will depend on the physical or chemical characteristics of the adsorbent system and also on the system conditions [48,49].

The kinetic modeling of metal sorption by granular sludge has been carried out using the Lagergren pseudo-first-order (Equation 7.5) and pseudo-second-order (Equation 7.6) kinetic models:

$$\log \frac{q_e - q_t}{q_e} = \frac{-K_{1,ad}t}{2.3}, \quad (7.5)$$

TABLE 7.4
Isothermal Constants of the Langmuir and Freundlich Models for the Metal–Sludge System

Metal	Sorbent	Langmuir Model			Freundlich Model			References
		q_{max}	b	R^2	K_F	n	R^2	
Zn(II)	Aerobic granule	56.50	0.004	0.934	0.681	1.496	0.993	[26]
Co(II)	Aerobic granule	51.28	0.003	0.988	0.462	1.396	0.987	[26]
	Anaerobic granule	8.42	0.031	0.944	13.31	0.628	0.991	[38]
Cu(II)	Aerobic granule	40.65	0.043	0.988	10.06	3.83	0.965	[28]
	Anaerobic granule	60	0.024	0.95				[23]
Pb(II)								
Cd(II)	Anaerobic granule	286	0.006	0.92				[23]
	Anaerobic granule	64	0.013	0.95				[23]
Ni(II)	Anaerobic granule	25	0.03	0.97				[23]
	Anaerobic granule	7.90	0.034	0.956	16.69	0.572	0.989	[38]

TABLE 7.5

Comparison of Pseudo-First-Order and Pseudo-Second-Order Adsorption Rate Constants at Different pH and C_0 Values

C_0 (mg/L)	pH	First-Order Kinetic Model			Second-Order Kinetic Model		
		$K_{1,ads}$ (min ⁻¹)	q_e (mg/g)	R_1^2	$K_{2,ads}$ (10 ⁻³ g/mg min)	q_e (mg/g)	R_2^2
50	3	0.015	6.812	0.5735	11.28	16.56	0.9966
	4	0.0221	10.817	0.6659	6.51	22.57	0.9973
	5	0.0297	13.744	0.8295	5.62	26.67	0.9994
125	3	0.0074	4.5394	0.1086	15.70	19.31	0.9923
	4	0.0205	11.593	0.7362	8.23	31.45	0.9979
	5	0.0168	14.067	0.7019	6.51	36.23	0.9963
250	3	0.0272	8.902	0.5367	11.21	28.17	0.9992
	4	0.0205	14.138	0.7057	6.24	34.72	0.9985
	5	0.0267	14.312	0.7296	5.10	39.84	0.9994

Source: Gai, L.H. et al., *J. Chem. Technol. Biotechnol.*, 83, 806–813, 2008.

$$\frac{t}{q_t} = \frac{1}{K_{2,ad} q_e^2} + \frac{t}{q_e}, \quad (7.6)$$

where q_e is the amount of solute sorbed at equilibrium (mg/g), q_t is the amount of solute sorbed at time t (mg/g), and $K_{1,ad}$ is the first-order equilibrium rate constant (min⁻¹) and $K_{2,ad}$ is the second-order equilibrium rate constant (g/mg min) [5,27].

Gai et al. [28] investigated the kinetics of biosorption of copper(II) ions by aerobic granules at varying initial solution pH and initial concentration C_0 (Table 7.5). The results showed that correlation coefficients of the pseudo-first-order kinetic model ($R_1^2=0.54-0.83$) were low compared with those of the pseudo-second-order kinetic model ($R_2^2 > 0.99$) at each pH studied. Lagergren's first-order rate equation describes the adsorption rate based on the adsorption capacity, whereas the pseudo-second-order rate expression is used to describe chemisorption involving valency forces and ion exchange. This suggests that the biosorption of Cu(II) process may take place through ion exchange and chemisorption involving valency forces.

Sun et al. [26] reported similar results in the study of Co(II) and Zn(II) sorption kinetics by aerobic granules in a single- and a binary-metal system. In the study, the values of the initial biosorption rate decreased as follows: Co(II) > Zn(II) > Co(II) (Co–Zn) > Zn(II) (Co–Zn), indicating that aerobic granules can adsorb Co(II) alone more rapidly than Zn(II) alone from aqueous solutions.

7.5 BIOSORPTION MECHANISM

Generally speaking, biosorption is the interaction of metals in an aqueous solution and the organic interface of granular sludge. The analyses of elemental composition, x-ray diffraction (XRD), and Fourier transform infrared (FTIR) could reveal some interaction. For granular sludge, the multi-layer structure and the role of exocellular polysaccharide (EPS) in the formation and stability of granules have focused attention on biosorption. Immobilization of heavy metal ions or radionuclides can be divided into three parts: (1) adsorption to cell walls, (2) adsorption to the EPS matrix, and (3) interaction with minerals present in the granular sludge [30]. To make clear the mechanism, further characterization of energy dispersive x-ray (EDX) and x-ray photoelectron spectroscopy (XPS) has been done, and encouraging results have been obtained [26,28,50].

7.5.1 SCANNING ELECTRON MICROSCOPY/EDX

Scanning electron microscopy (SEM) is an extremely useful method for visual confirmation of surface morphology and the physical state of the surface. Figure 7.8 shows the microbial structure of the granular sludge, and it can be seen that the surface of anaerobic granular sludge is rough, uneven, and porous [29], whereas aerobic granules have a compact structure with a regular, rigid, and stable surface as well as lots of cavities. SEM coupled with energy dispersive analysis of EDX is used to determine the metal uptake mechanism on granules. Liu and Xu [41] utilized SEM equipped with EDX to analyze fresh and Ni^{2+} -contaminated aerobic granules (Figures 7.9 and 7.10).

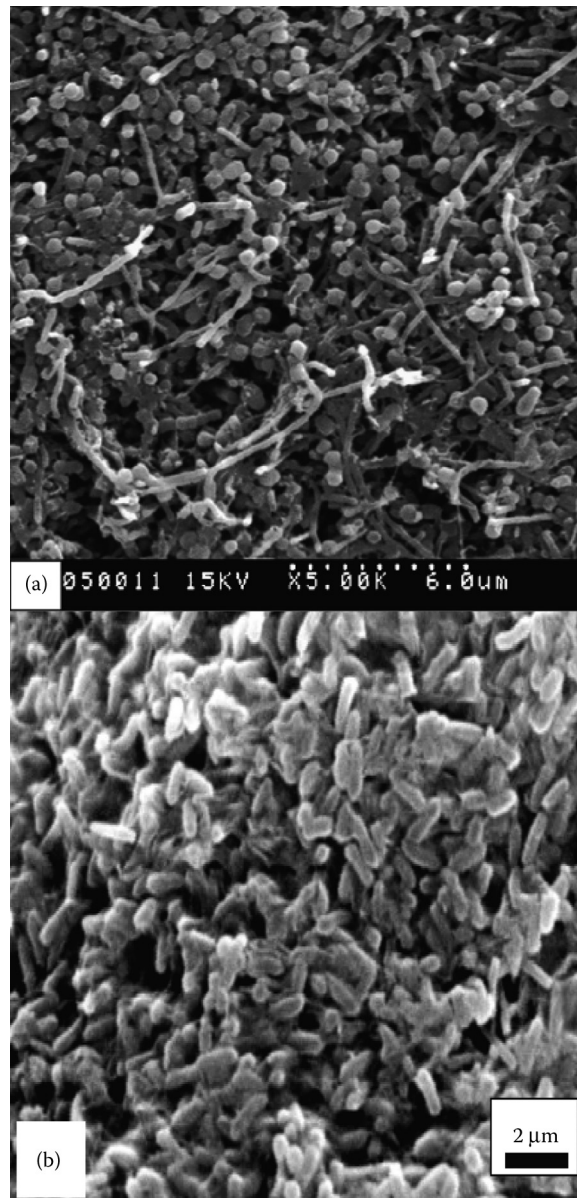


FIGURE 7.8 Typical SEM micrograph: (a) anaerobic granules and (b) aerobic granules. (Adapted from Liu, Y. et al., *Biochem. Eng. J.*, 39, 538–546, 2008.)

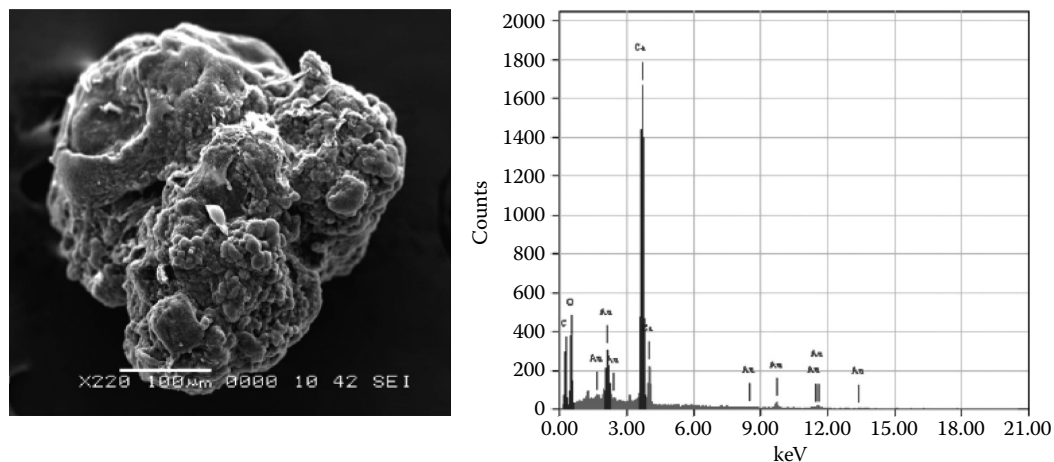


FIGURE 7.9 SEM image and EDX spectrum of fresh aerobic granules. (Adapted from Liu, Y. and Xu, H., *Biochem. Eng. J.*, 35, 174–182, 2007.)

The results proved that the adsorbed Ni^{2+} ions are uniformly distributed from the surface to the center of aerobic granules.

7.5.2 XRD

The crystal phases of aerobic granules before and after the biosorption experiments were analyzed by an x-ray powder diffraction analyzer [41,50]. According to Liu and Xu [41], chemical precipitation of Ni^{2+} would not be involved in Ni^{2+} biosorption by aerobic granules under the studied conditions. Xu and Liu [50] found a similar phenomenon; however, for Cd^{2+} - and Cu^{2+} -contaminated aerobic granules, their peak positions and ratios are different from those of fresh aerobic granules (Figures 7.11 through 7.13). The appearance of the new peaks indicates that there were different crystals precipitated in Cd^{2+} - and Cu^{2+} -contaminated aerobic granules. One of the mechanisms is believed to be chemical precipitation for the biosorption of Cu^{2+} and Cd^{2+} by aerobic granules; however, there is no evidence for the involvement of chemical precipitation in the removal of Ni^{2+} (Figure 7.14).

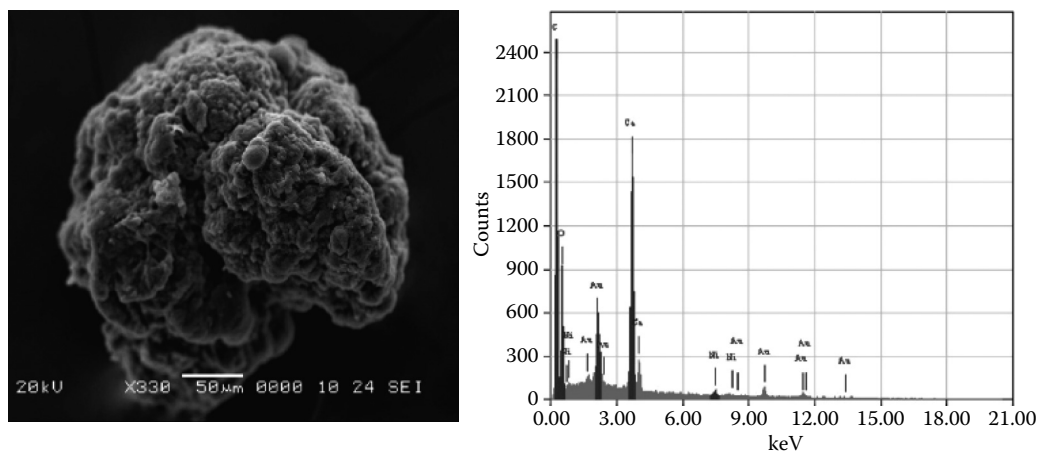


FIGURE 7.10 SEM image and EDX spectrum of the Ni^{2+} -contaminated aerobic granules. (Adapted from Liu, Y. and Xu, H., *Biochem. Eng. J.*, 35, 174–182, 2007.)

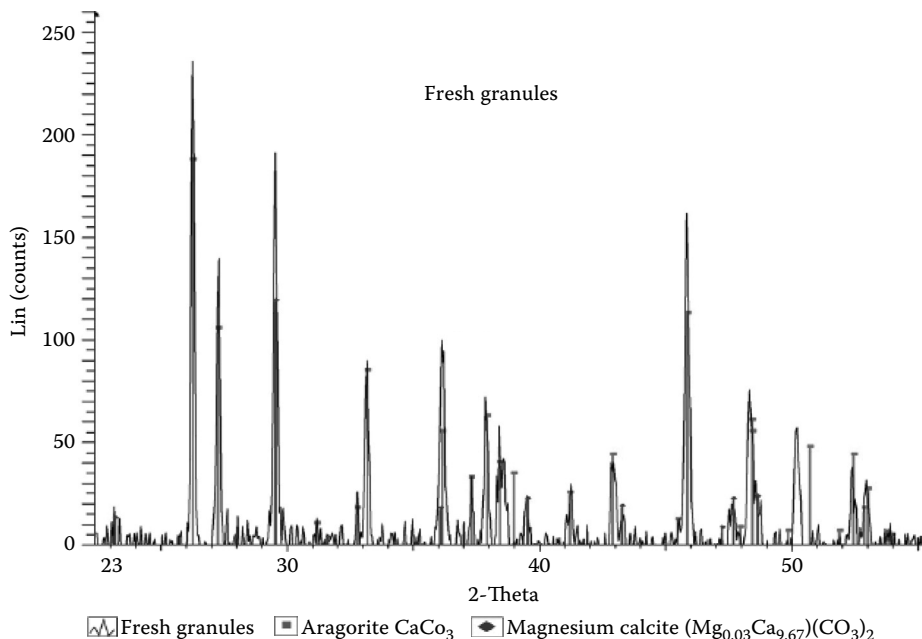


FIGURE 7.11 XRD analysis of fresh aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purif. Technol.*, 58, 400–411, 2008.)

7.5.3 FTIR/XPS

Table 7.6 lists the main functional groups corresponding to the peaks observed on FTIR spectra of fresh aerobic granules. The FTIR spectra of raw and metal-loaded granules in the range of 400–4000 cm^{-1} were taken to obtain information on the nature of possible interactions between

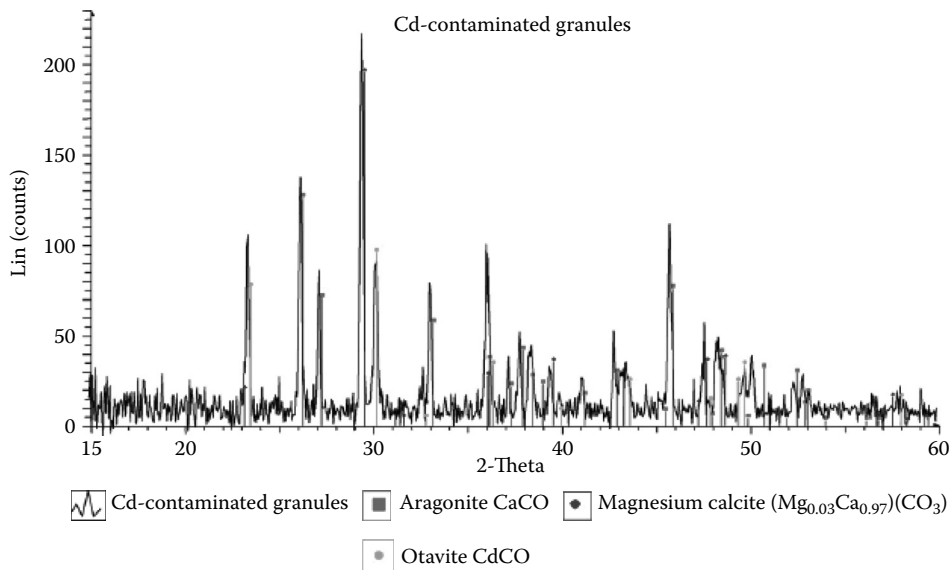


FIGURE 7.12 XRD analysis of Cd^{2+} -contaminated aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purif. Technol.*, 58, 400–411, 2008.)

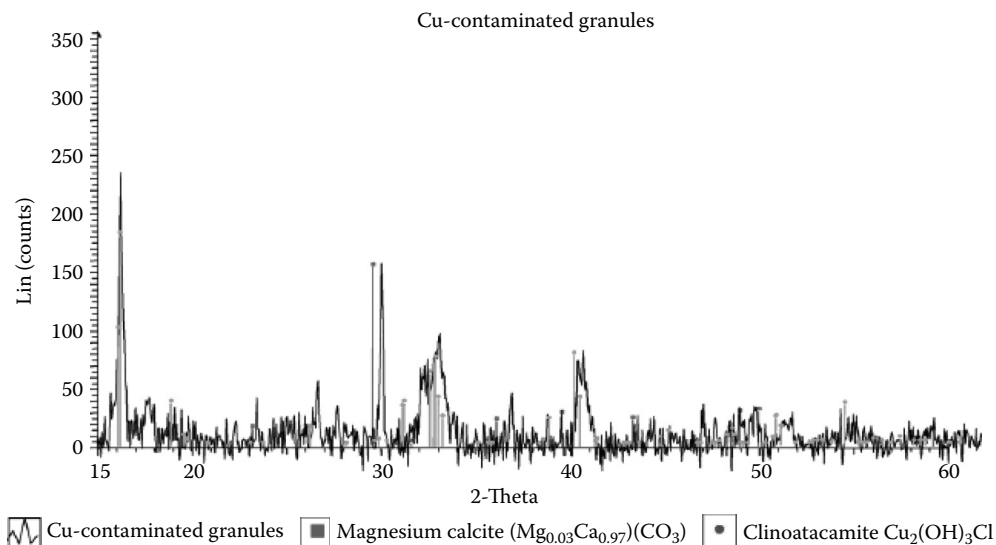


FIGURE 7.13 XRD analysis of Cu^{2+} -contaminated aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purif. Technol.*, 58, 400–411, 2008.)

the functional groups of aerobic granules and the metal ions, as presented in Figure 7.15. The peak at $1650\text{--}1660\text{ cm}^{-1}$ of granules, corresponding to the superimposition of different amide I bands (C–O stretching coupled with N–H deformation mode) from different materials (including proteins and amide-bearing materials), was significantly decreased after metal loading, indicating the complexation of metal ions with the functional groups from the protein. When the granules were loaded with the metal ions, the peaks at 1455 , 1306 , and 1249 cm^{-1} disappeared, leading to the formation of

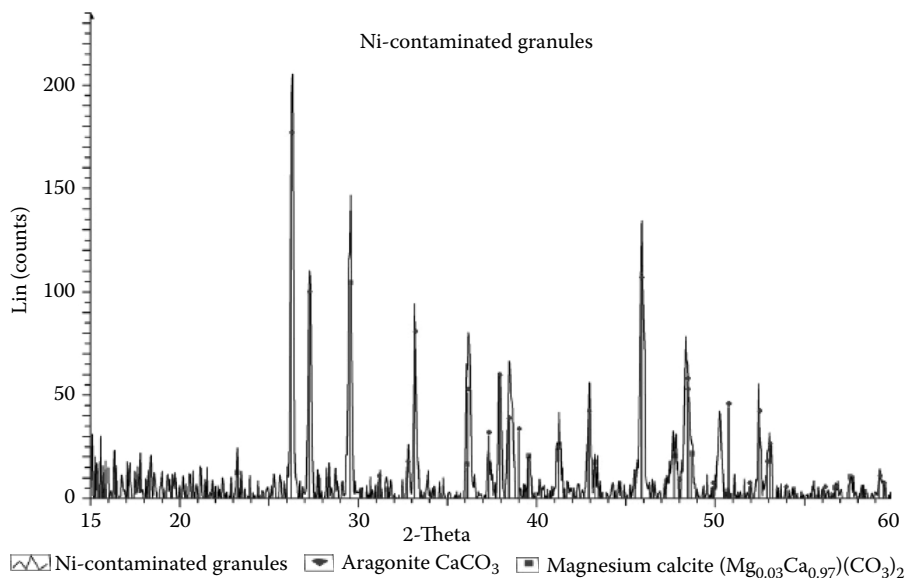


FIGURE 7.14 XRD analysis of Ni^{2+} -contaminated aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purif. Technol.*, 58, 400–411, 2008.)

TABLE 7.6
Main Functional Groups on Fresh Aerobic Granule

Wave Number (cm ⁻¹)	Vibrational Type	Functional Type
≈3200–3600	Overlapping of stretching vibration of OH and NH	OH into polymeric compounds and amine
≈2927	CH stretching (CH ₂ and CH ₃ groups)	
≈1739–1725	Stretching vibration of C=O	Membrane lipids, fatty acids, and carboxylic acids
≈1648	Stretching vibration of C=O and C–N (amide I)	Protein (peptidic bond)
≈1520–1540	N–H bending and C–N stretching in amides (amide II)	Protein (peptidic bond)
≈1370–1410	Symmetric stretching for deprotonated COO ⁻ group	
≈1240–1260	Deformation vibration of C=O	Carboxylic acids
≈1130–1160	Stretching vibration C–O–C	Polysaccharides
≈1082	Bending vibration of C–O	Polysaccharides
≈1050–1060	Stretching vibration of OH	Polysaccharides
<1000	“Fingerprint” zone	Phosphate or sulfur functional groups

Source: Sun, X.F. et al., *J. Colloid Interface Sci.*, 324, 1–8, 2008; Xu, H. and Liu, Y. *Sep. Purif. Technol.*, 58, 400–411, 2008; and Ojeda, J.J. et al., *Langmuir*, 24, 4032–4040, 2008.

a complex between the metal and the C–O–C group of polysaccharides, the CH₂ group of lipids, and the carboxyl group of the protein. Compared to the intensities of the C–O stretching of the hydroxyl group (C–O–H) from saccharides at 1053 cm⁻¹, the peak shifted to lower wave numbers 1049 and 1047 cm⁻¹ for Co(II)- and Zn(II)-loaded granules, respectively, which demonstrated that hydroxyl groups were involved in the metal biosorption [26].

Table 7.7 shows elemental composition of different kinds of aerobic granules. It also shows that fresh aerobic granules mainly comprised seven major elements, namely, C, H, O, N, S, P, and Ca. As for heavy metals, element Cd was not detected in fresh aerobic granules, whereas very small amounts of Cu, Ni, and Zn were found in fresh aerobic granules. These are simply due to the fact

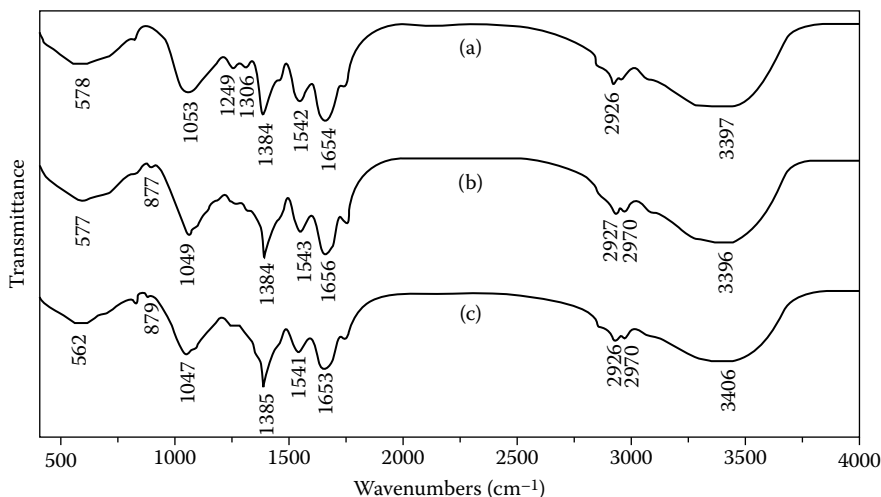


FIGURE 7.15 FTIR spectra of (a) fresh, (b) Co(II)-loaded, and (c) Zn(II)-loaded granules. (Adapted from Sun, X.F. et al., *J. Colloid Interface Sci.*, 324, 1–8, 2008.)

TABLE 7.7
Elemental Compositions of Different Kinds of Aerobic Granules
(mg/g Dry Weight of Granules)

Element	Types of AG			
	Fresh AG	Cd-AG	Cu-AG	Ni-AG
C	315.830	314.730	298.330	320.200
H	44.470	43.100	40.030	44.300
N	49.930	57.100	53.200	56.900
S	4.770	4.370	4.930	4.730
O	421.390	358.740	419.060	404.100
P	4.344	3.920	3.790	4.100
Cd	0.000	84.520	0.000	0.000
Cu	0.250	0.229	44.140	0.263
Ni	0.027	0.005	0.005	21.720
Zn	0.239	0.140	0.162	0.217
Ca	150.360	129.860	134.380	140.280
Mg	1.370	0.780	0.312	0.804
K	3.470	1.365	0.390	1.131
Others	3.550	1.141	1.270	1.255

AG, aerobic granules.

Source: Xu, H. and Liu, Y., *Sep. Purifi. Technol.*, 58, 400–411, 2008.

that Cu, Ni, and Zn were added to synthetic wastewater as the trace elements required for microbial growth. The Ca content in fresh aerobic granules was as high as 150.36 mg/g, whereas it was 1.37 and 3.47 mg/g for Mg and K, respectively. It seems that aerobic granules would contain a significant amount of light metal ions.

Moreover, Figures 7.15 through 7.18 showed the XPS survey scanning spectra of aerobic granules before and after Cd²⁺, Cu²⁺, and Ni²⁺ biosorption, respectively. The changes of binding energy (BE) of the coordination carbon atom (C1s) in aerobic granules before and after metal adsorption are

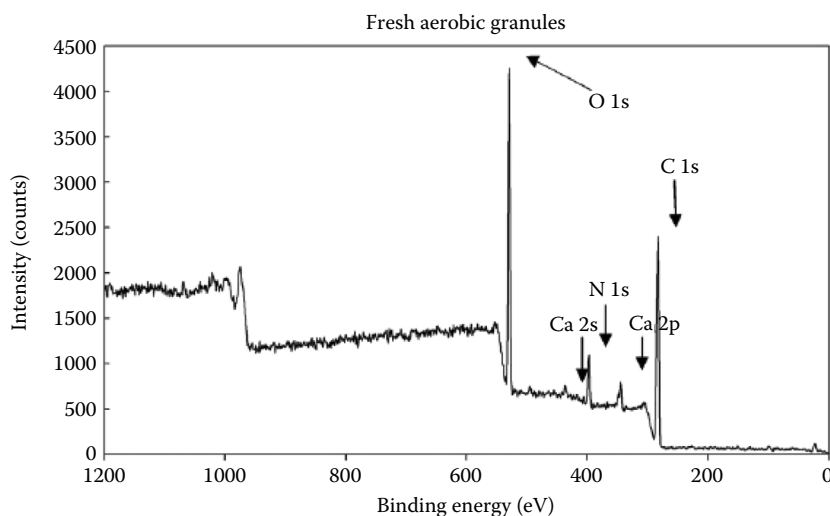


FIGURE 7.16 XPS survey scanning spectrum of fresh aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purifi. Technol.*, 58, 400–411, 2008.)

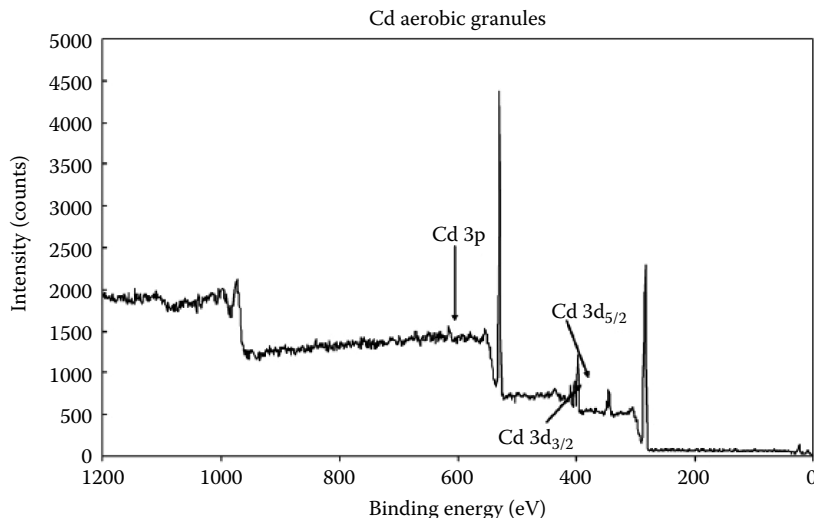


FIGURE 7.17 XPS survey scanning spectrum of Cd^{2+} -contaminated aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purifi. Technol.*, 58, 400–411, 2008.)

presented in Figure 7.19. It is clear that the C1s spectra of all the samples comprised three peaks with BE of 284.1, 285.2, and 287.2 eV, which are attributed to the carbon in C–C, C–OH, and O = C–O, respectively. The result verified that a high concentration of hydroxyl groups and carboxylate groups were present on the aerobic granule surface [26]. The analyses by FTIR and XPS showed that functional groups on aerobic granules, such as alcoholic, carboxylate, and ether, would be the main binding sites for biosorption of the studied heavy metals by aerobic granules (Figure 7.20).

7.6 ECONOMY

Most research about granular sludge has been limited to laboratory experiment: cultivation, formation mechanism, and characteristics. Little literature exists containing full costs and pilot-plant-scale

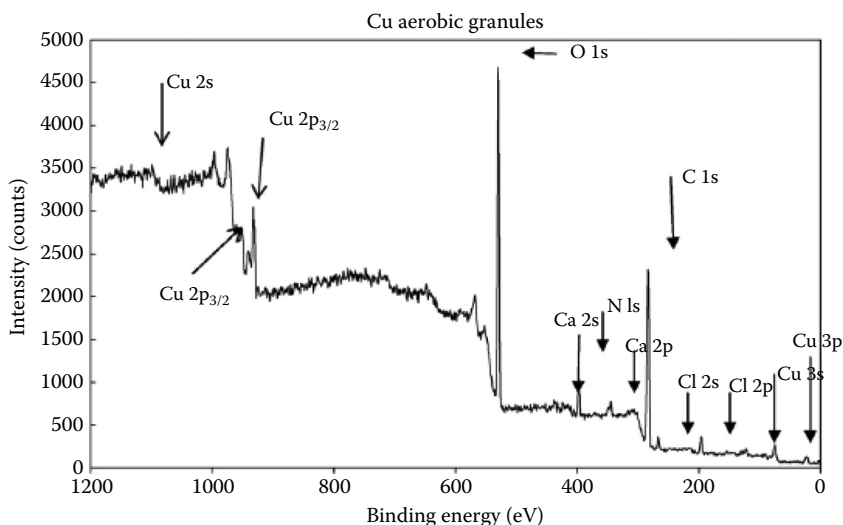


FIGURE 7.18 XPS survey scanning spectrum of Cu^{2+} -contaminated aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purifi. Technol.*, 58, 400–411, 2008.)

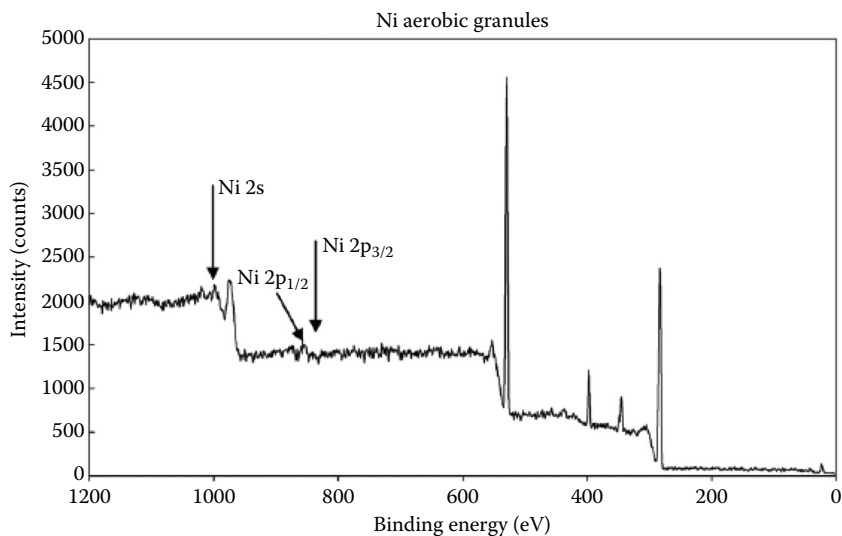


FIGURE 7.19 XPS survey scanning spectrum of Ni^{2+} -contaminated aerobic granules. (Adapted from Xu, H. and Liu, Y., *Sep. Purif. Technol.*, 58, 400–411, 2008.)

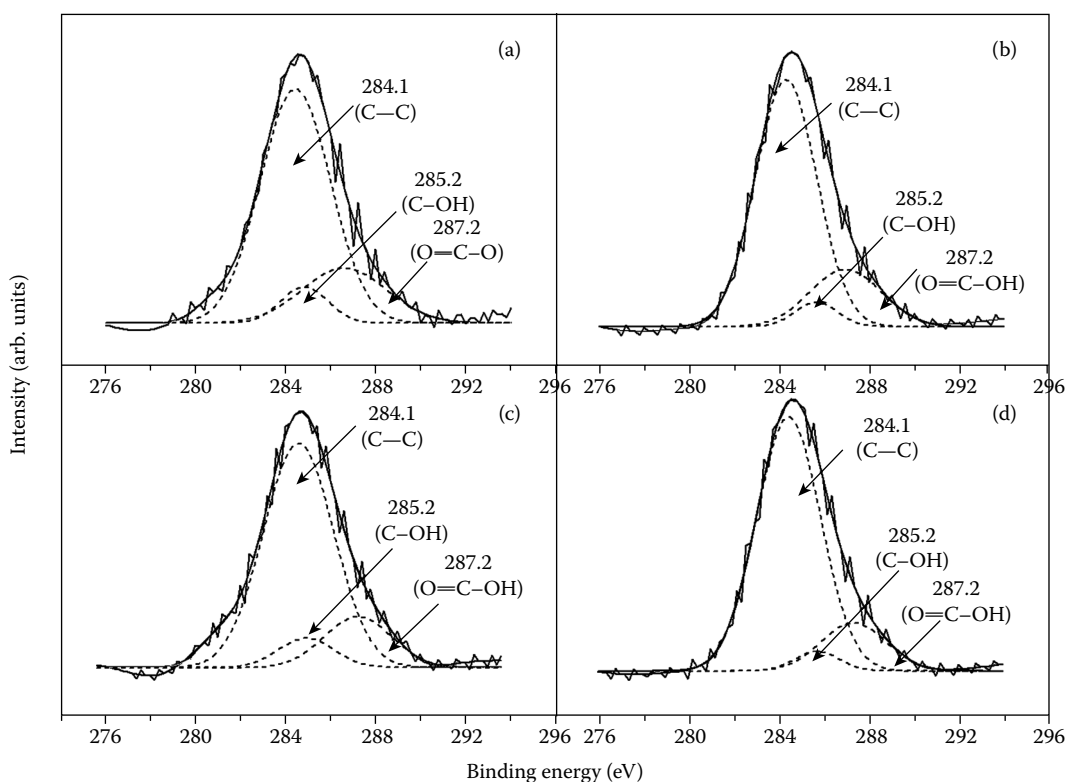


FIGURE 7.20 XPS spectra of aerobic granular sludge: (a) fresh, (b) Co(II)-loaded, (c) Zn(II)-loaded, and (d) Co(II)/Zn(II)-loaded granules. (Adapted from Sun, X.F. et al., *J. Colloid Interface Sci.*, 324, 1–8, 2008.)

successful application. Studies on metal biosorption were evaluations of adsorption capacity and mechanism, and cost evaluation remains to be explored.

For metals uptake, the advantages of granular sludge are high microbial density and excellent settling ability, so are the adsorption capacity and easy postseparation. In the pilot-scale granular sludge treatment system, adsorbents can be harvested as excess sludge, which is treated as waste. Thus, the cost of granular sludge is lower than those of chemically synthesized adsorbents or biosorbents developed from an expensive culture medium. Considering local availability, processing required, and treatment conditions, different biosorbents are difficult to compare. Therefore, much work is needed to demonstrate application costs at the industrial scale. A first step would be the design and operation of a continuous or column test. Potential problems are whether additional solid–liquid separation is needed to satisfy effluent quality.

7.7 COMMENTS ON FUTURE DIRECTIONS

7.7.1 MECHANISM RESEARCH

1. The mechanisms involved in biosorption or metal–microbe interactions should be further studied with great efforts by utilizing various techniques and their combinations [32]. Important influencing factors, such as pH and selectivity of co-ions for biosorption systems, have not been fully understood.
2. Mathematical models of equilibrium and kinetics, in particular mechanical models such as the surface complexation models, to simulate the multimetal ion or co-ion biosorption system, are important aspects of future biosorption studies [3] and should be developed.
3. Development of dynamic models to simulate the biosorption process and offer useful information for its application should receive more attention [51].
4. Molecular biotechnology, a powerful tool to elucidate the mechanism at the molecular level, should be considered more closely in the future to construct an engineered organism with higher sorption capacity and specificity for target metal ions.

7.7.2 APPLICATION OF BIOSORPTION TECHNOLOGY

Despite the failure in an attempt to commercialize biosorption in wastewater treatment, it is necessary to continue to explore the various aspects relevant to the application.

1. The physico-chemical conditions, for example, pH and multi-ionic composition, should be chosen to simulate the real wastewater on the basis of thermodynamics and reaction kinetics studies.
2. Optimization of the parameters of biosorption process, including reuse and recycling by studying diffusion resistance and fluid dynamics on a sorption column or chemical engineering reactors, such as a fluidized bed reactor.
3. Immobilization of biomaterials is another key aspect for the purpose of biosorption application. It is important for decreasing the cost of immobilization and consequently distribution, regeneration, and reuse of biosorbents [51]. Although the continuous process of immobilized cells has been realized at the laboratory scale, there is still a long way to go for biosorption commercialization. Selection of good and cheap support materials for biomaterial immobilization, improvement of reuse methods, and enhancement of the properties of immobilized biosorbents such as pore ratio, mechanical intensity, and chemical stability are also important factors for application of the full-scale biosorption process.

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8 Arsenic Pollution: Occurrence, Distribution, and Technologies

Huijuan Liu, Ruiping Liu, Jiuwei Qu, and Gaosheng Zhang

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8.1 ARSENIC CHEMISTRY AND ARSENIC POLLUTION SOURCES

8.1.1 ARSENIC CHEMISTRY

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters, and organisms [1]. It is classified as a nonmetal or a metalloid, but it is a gray-like metal material usually present in the environment in hexagonal crystalline form [2]. Arsenic is usually combined with other elements such as oxygen, chlorine, or sulfur. Arsenic generally includes organic arsenic and inorganic arsenic.

In the natural circulation of arsenic, organic arsenic, for example, monomethylarsonate (MMA) and dimethylarsinate (DMA), mainly results from the arsenic methylation effects of different organisms such as bacteria, fungi, and mammals [3], mostly in surface waters [1]. In the past several decades, the worldwide use of As-contained pesticides and herbicides has resulted in the increase of organic arsenic in environments. Organic arsenic is generally less harmful than the inorganic form.

Comparatively, the environmental behaviors, distribution, and treatment technologies of organic arsenic have resulted in fewer studies than those of inorganic arsenic. This may be ascribed to the lower prevalence of organic arsenic pollution in water, and to its lower toxicity effects, when compared with inorganic arsenic species. Interestingly, the methylation of inorganic arsenic is demonstrated to reduce the toxicity, which is contrary to mercury (Hg).

Soluble, inorganic arsenic exists in either one of two valence states, oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)], depending on local oxidation–reduction conditions [4]. Arsenic trioxide, As_2O_3 , is also an important species of inorganic arsenic, and has a long history of use in Chinese and Western medicine for the treatment of diseases such as acute promyelocytic leukemia, ascribed to its being active against malignancies and showing some activity in patients with accelerated phase chronic myelogenous leukemia and multiple myeloma [5]. Nevertheless, this chapter mainly focuses on As(III) and As(V), owing to their dominant presence in water environments and their contributive effects to worldwide arsenicism.

Arsenite exists in four different species such as H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-} ; similarly, arsenate exists as H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . Redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (pH less than about 6.9), whereas at higher pH, HAsO_4^{2-} becomes dominant. However, H_3AsO_4 and AsO_4^{3-} may be present under extremely acidic and alkaline conditions, respectively. Under reducing conditions at pH less than about 9.2, the uncharged arsenite species H_3AsO_3 will predominate [6,7]. The dissociation and species transformation of these species as a function of pH have been reported earlier [4].

As(III) mainly exists under anoxic conditions in underground water and sediment, and As(V) is often found in aerobic surface waters. In a typical water body however, the simultaneous presence of As(III) and As(V) is often observed.

The existing forms of arsenic may also be classified as soluble arsenic and particulate arsenic, depending on its adsorption onto colloids or not. Particulate arsenic may generally be removed through filtration units such as media filtration and membrane filtration. This kind of arsenic species classification is of importance in practice, because most technologies are devoted to the transformation of soluble arsenic to particulate arsenic, which will be discussed in detail later.

8.1.2 SOURCES OF ARSENIC POLLUTION

Anthropogenic activities and natural geochemical processes are the two main sources contributing to arsenic pollution in the water environment.

As for anthropogenic contribution, the most important point-pollution source is the discharge of wastewater and waste foils from industries such as mining and smelting. Additionally, the use of arsenical pesticides, herbicides, and crop desiccants and the use of arsenic as an additive to livestock feed, particularly for poultry [1], contribute to nonpoint arsenic pollution all over the world.

In natural geochemical cycles, aqueous arsenic mainly comes from As-containing minerals, rocks, sediments, and soils through processes such as weathering, desorption [8], and reductive dissolution [9,10]. The occurrence of aqueous arsenic concentration increase is often observed to be with the changes in pH, oxidation–reduction conditions, and the reduction in the surface areas of oxide minerals or in binding strength between arsenic and mineral surfaces. Atmospheric precipitation also contributes to arsenic pollution, especially in surface waters; however, there is still a lack of sufficient data to quantitatively evaluate its impact on drinking water sources [1].

Arsenic occurs as a major constituent in more than 200 minerals, including elemental As, arsenides, sulfides, oxides, arsenates, and arsenites [1]. The most abundant As ore mineral is arsenopyrite, FeAsS , which is mainly formed under high-temperature conditions in the Earth's crust, but is also reported in sediments and orpiment by the microbial precipitation effect [11,12].

Arsenic concentrations in rocks, sediments, and soils generally vary from several mg/kg to several decade mg/kg, and the high arsenic concentrations in sediments are usually positively correlated with the more pyrite or Fe oxides present. Datta and Subramanian [13] found concentrations averaging 2.0 mg/kg (range 1.2–2.6 mg/kg) in sediments from the River Ganges, 2.8 mg/kg (range 1.4–5.9 mg/kg) in sediments from the Brahmaputra River, and 3.5 mg/kg (range 1.3–5.6 mg/kg) in sediments from the Meghna River [13]. However, in contaminated sediments and soils (e.g., tailing piles and tailing-contaminated soils), arsenic concentrations as high as several decade thousands mg/kg are reported [14,15].

In unpolluted areas, concentrations of As in the atmosphere are usually as low as 10^{-5} – 10^{-3} mg/m³, but increase to 0.003–0.18 mg/m³ in urban areas and to higher than 1 mg/m³ close to industrial plants [16]. It is estimated that anthropogenic sources of atmospheric arsenic (around 18,800 tons per year), mainly from industrial processes (e.g., smelting) and fossil fuel combustion, amounted to around 70% of the global atmospheric As flux [17]. Although the health effect of atmospheric As on drinking-water sources has not been suitably evaluated, it has been demonstrated to be a major health threat to residents in parts of Guizhou Province, China, who consume foods that are dried over domestic coal fires and directly inhale domestic coal-fire smoke [18].

8.2 OCCURRENCE AND DISTRIBUTION OF UNDERGROUND ARSENIC PROBLEMS

8.2.1 OVERVIEW OF WORLDWIDE ARSENIC POLLUTION

Quite a few countries (e.g., Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Vietnam, Nepal, Myanmar, Cambodia, and the United States) have large aquifers that have been identified to suffer from arsenic occurrence at concentrations above 0.05 mg/L [1]. Arsenic associated with geothermal waters has also been reported in several areas, including hot springs from parts of Argentina, Japan, New Zealand, Chile, Kamchatka, Iceland, France, Dominica, and the United States [1]. Most of the groundwater is contaminated with arsenic at levels from 100 to over 2000 $\mu\text{g/L}$. Typical As concentrations in different kinds of natural waters have been well determined previously [1]. Generally, arsenic levels in seas and estuaries are low with average concentrations of several ppb. In underground water, the arsenic concentration is dependent on local geochemical conditions, varying from <0.5 ppb to as high as 5000 ppb. Anthropogenic activities, such as mining, oil extraction, and arsenical herbicide production, significantly increase arsenic levels in related water bodies such as underground water, geothermal water, sediment porewater, and brine [1].

It is noteworthy that the occurrence of arsenic is the result of complicated geochemical and hydro-geological processes. The presence of arsenic in different As-rich aquifers is ascribed to different geochemical effects. Smedley and Kinniburgh [1] systematically classified the As-rich aquifers in the world into reducing environments, arid oxidizing environments, mixed oxidizing and reducing environments, and sulfide mineralization and mining-related arsenic problems [1].

8.2.2 ARSENIC POLLUTION IN BANGLADESH

The groundwater As contamination problem in Bangladesh is the worst in the world. Bangladesh extends between longitudes 88°01' and 92°40' east and latitudes 20°25' and 26°38' north. In Bangladesh, arsenopyrite has been identified as the prime source of As pollution [19].

The British Geological Survey (BGS) [20] reported that the groundwater As problem in Bangladesh is the unfortunate combined effect of three factors: source of As (As is present in aquifer sediments), mobilization (As is released from the sediments to groundwater), and transport (As is flushed in the natural groundwater circulation) [20]. There are two prevailing hypotheses to describe the mobilization of As into the groundwater in Bangladesh: (1) pyrite oxidation, and (2) oxyhydroxide reduction [21–23]. The distribution of As in the groundwater of Bangladesh has been generalized in Ref. [24]. Of the 36 districts that have sufficient data on the arsenic levels in groundwater from the shallow aquifer (less than 150 m deep), 14 indicate that more than 50% of their ground water exceeds the Bangladesh standard of 0.05 mg/L for arsenic.

Arsenic in Bangladesh underground water mainly exists as the following four species: H_2AsO_3^- , H_2AsO_4^- , methyl arsenic acid $[\text{CH}_3\text{AsO}(\text{OH})_2]$, and dimethyl arsenic acid $[(\text{CH}_3)_2\text{As}(\text{OH})]$ [21]. BGS [20] has analyzed the 2022 samples collected in deepened shallow tube wells. It is indicated that 51% of the samples are above 0.010 mg/L [the World Health Organization (WHO) Guideline Value], 35% are above 0.050 mg/L [the Bangladesh Drinking Water Standard], 25% are above 0.10 mg/L, 8.4% are above 0.30 mg/L, and 0.1% are above 1.0 mg/L, and the maximum As concentration found in this survey is as high as 1.67 mg/L [20]. The typical ranges of arsenic concentrations in underground water and tube well water, and the analytical report of 41 districts of Bangladesh where As found in groundwater was >0.05 mg/L have been reported in [20,25].

There are also many investigations on arsenic contamination in surface waters [20,25] and soils [26] and on arsenic content in food, forage plants, plant tissues, and plants grown in contaminated sites or irrigated by arsenic-polluted water [27].

8.3 ARSENIC TOXICOLOGY AND ARSENIC-RELATED DISEASES

8.3.1 ARSENIC TOXICOLOGY

Arsenic has a long and nefarious history; its very name has become synonymous with poison. In the fifteenth and sixteenth centuries, the Italian family of Borgias used arsenic as their favorite poison for political assassinations. Some have even suggested that Napoleon was poisoned by arsenic-tainted wine served to him while in exile.

Arsenic interferes with a number of essential physiological activities, including the actions of enzymes, essential cations, and transcriptional events in cells [28], and damages the nerves, stomach, intestines, and skin. The toxicology of arsenic is generally classified into acute and chronic toxicity. The high levels of inorganic arsenic (greater than 60 ppm) in food or water can be fatal. The main early manifestation of acute arsenic poisoning includes burning and dryness of the mouth and throat, dysphasia, colicky abdominal pain, projectile vomiting, profuse diarrhea, and hematuria. Muscular cramps, facial edema, cardiac abnormalities, and shock can develop rapidly as a result of dehydration [29]. Long-term exposure to arsenic via drinking water results in chronic health risks, including cancer of the skin, kidney, lung, and bladder, as well as other diseases of the skin, the neurological system, and the cardiovascular system [30]. Chronic arsenic toxicity due to drinking arsenic-contaminated water has been one of the worst environmental health hazards affecting eight districts of West Bengal since the early 1980s [31].

Generally, there are four recognized stages of arsenicosis (or chronic arsenic poisoning) as follows [32–34]:

Preclinical: The patient shows no symptoms, but arsenic can be detected in urine or body tissue samples.

Clinical: Various effects can be seen on the skin at this stage. Darkening of the skin (melanosis) is the most common symptom, often observed on the palms. Dark spots on the chest, back, limbs, or gums have also been reported. Edema (swelling of hands and feet) is often seen. A more serious symptom is keratosis, or hardening of skin into nodules, often on palms and soles. The WHO estimates that this stage requires 5–10 years of exposure to arsenic.

Complications: Clinical symptoms become more pronounced and internal organs are affected. Enlargement of the liver, kidneys, and spleen have been reported. Some research indicates that conjunctivitis (pinkeye), bronchitis, and diabetes may be linked to arsenic exposure at this stage.

Malignancy: Tumors or cancers (carcinoma) affect the skin or other organs. The affected person may develop gangrene or skin, lung, or bladder cancer.

Arsenicosis is greatly associated with the arsenic concentrations in drinking water. Exposure to high levels of arsenic in drinking water leads to excess cancer risk (e.g., skin and lung). However, exposure to lower levels ($<100\text{--}200\text{ }\mu\text{g/L}$) does not significantly increase the risks of arsenic-related cancers. Recently, more and more studies are focusing on the effects of long-term exposure to low levels of arsenic [35,36].

Long-term exposure to arsenic would lead to a build-up of arsenic in ectodermic tissues (e.g., hair and nails) and an increase of arsenic concentration in the urine of a patient. Generally, the higher arsenic content in these tissues is positively related to the higher arsenic concentrations and the longer exposure to arsenic-polluted water, as reported previously by Eisler [37].

8.3.2 DISTRIBUTION OF ARSENIC-RELATED DISEASES IN THE WORLD

The first chronic endemic arsenism via drinking water in the world was found in Taiwan in 1968, and the largest population influenced by arsenic in drinking water was in Bangladesh. It has been estimated that globally, tens of millions of people are at risk due to exposure to excessive levels of arsenic. To date, exposure to high concentrations of arsenic via drinking water is reported to be associated with chronic symptoms such as skin lesions [38,39], peripheral vascular disease [40], hypertension [41], blackfoot disease [39,42], and a high risk of cancers [39,43].

West Bengal and India have long been known to suffer from the problem of arsenic-contaminated groundwater, which is claimed to be the largest calamity in the world [34]. Only in the Bengal Basin, more than 40 million people drink water containing excessive As. After the independence of Bangladesh, the government endeavored to provide safe drinking water to the people (by installing tube wells that extract water from subsurface alluvial aquifers) in order to reduce the risks of water-borne diseases. Unfortunately, another serious problem of arsenicosis, which is induced by arsenic-contaminated groundwater, affected this poor, agricultural country.

It was reported that about 25 million people in Bangladesh are at risk of As poisoning and 3695 (20.6%) out of 17,896 people examined suffer from arsenicosis [1,25,31]. Chowdhury et al. [25] reported that 22 out of 64 districts in Bangladesh had arsenicosis patients and 21 districts had people with arsenical skin manifestations [25]. They surveyed only 98 villages in these districts and found As patients in 95 villages. From these 95 villages, they surveyed at random 6973 people, and 2309 people (33.1%) were found with arsenical skin lesions [25].

Additionally, a survey from the School of Environmental Studies and Dhaka Community Hospital source said that 47 districts are contaminated with As, which represents a total of 241 villages where As patients are suspected, thousands are currently As patients, and a total of 40 deaths are due to As-related diseases. According to some estimates, arsenic in drinking water will cause 200,000–270,000 deaths from cancer in Bangladesh alone [34,44].

In the mainland of China, the first chronic endemic arsenism via drinking water was found in Xinjiang Autonomy Region in 1983. Up to 2004, chronic endemic arsenism via drinking water was found in Taiwan, Xingjiang, Inner Mongolia, Shanxi, Ningxia, Jilin, Qinghai, Anhui province and certain suburbs of Beijing, and involved eight provinces, including 40 counties and 1047 villages, with a 2,343,238 population exposed to high-arsenic water [45].

As for the distribution of high-arsenic areas and exposed at-risk populations in China, the Inner Mongolia, Shanxi, Xingjiang, and Jilin regions have the highest populations exposed to high-arsenic water, which accounts for about 50% of the total As-exposed population in China. The highest arsenic concentration that has been detected is 1.86 mg/L in Inner Mongolia and 0.783 mg/L in Shanxi. According to the latest survey [46], the average prevalence of arsenism patients is 9.65%,

which includes 0.57% serious patients, 1.47% medium patients, 5.74% mild patients, and 1.86% suspected patients. Skin cancer cases due to arsenic exposure have also been reported [46].

It has been reported that people of different ages are susceptible to arsenism if they are exposed to high-arsenic drinking water, and the prevalence of arsenism increases with increasing age and extended years of residence. The youngest patient that has been reported is only 3 years old [45].

Taiwan district has also been facing serious underground arsenic pollution. On the basis of the large-scale arsenicosis cases who were exposed to high levels of arsenic concentration in well water (higher than 1000 $\mu\text{g/L}$), the United States Environmental Protection Agency (U.S. EPA) assessed the risks of skin cancer [47,48] and bladder and lung cancer [49–51] due to the arsenic in drinking water [52].

8.3.3 DRINKING WATER STANDARD ON ARSENIC

The WHO first revised the guideline for arsenic from 0.05 to 0.01 mg/L in 1993 [53]. Then, Germany lowered its permissible limit of arsenic to 0.01 mg/L in 1996, and the Australian drinking water limit was also lowered from 0.05 to 0.007 mg/L [34]. The current standard in France, Vietnam, and Mexico is 0.05 mg/L for arsenic in drinking water [34]. In the European Union, the arsenic standard level is now set to 0.01 mg/L [34]. The U.S. EPA has also implemented the reduction of permissible values of arsenic in drinking water from 0.05 to 0.01 mg/L in 2002 [4]. In China, the newly issued drinking water standard decreased the permissible arsenic level to 0.01 mg/L in 2006 [54]. The stricter standard requires more feasible technologies in engineering for arsenic pollution control.

8.4 TECHNOLOGIES FOR ARSENIC REMOVAL

Arsenic pollution, arsenic-related diseases, and the strict standard have generated numerous studies on the technologies and processes for arsenic removal. Generally, the removal of arsenic from water mainly includes (1) transformation of arsenic from aqueous to particulate arsenic through adsorption, precipitation/coprecipitation, coagulation, biological process, and so on, and then removal of particulate arsenic by the liquid–solid separation units (e.g., sedimentation, media filtration, and membrane filtration); (2) removal of arsenic species by the exchange of surface active sites on ion exchange resin; and (3) removal of arsenic by physical pressure-driven processes (i.e., membrane filtration).

On the other hand, As(III), which is commonly present in underground water, is neutral under natural pH conditions and is difficult to remove by adsorption, precipitation/coprecipitation, and ion exchange. The oxidation of As(III) to negatively charged As(V) is important for facilitating As(III) removal, and is usually used in engineering.

In the following subsections, the different techniques, that is, coagulation/filtration, lime softening (LS), adsorption, ion exchange, membrane, and biological treatment, for arsenic removal are discussed. Generally, each technique shows its advantages and disadvantages in practice, which should be carefully evaluated before choosing a process in engineering.

8.4.1 OXIDATION

Frankly, oxidation can only transform As(III) to As(V) rather than remove arsenic from aqueous phase, and oxidation should be coupled with a removal process such as coagulation, adsorption, or ion exchange. Nevertheless, oxidation is of critical importance for the achievement of optimal performance of arsenic removal for the processes noted above [4].

The conversion of As(III) to As(V) is often accomplished by providing an oxidizing agent (e.g., chlorine, permanganate, ozone, and hydrogen peroxide) at the head of any proposed arsenic removal process. However, other kinds of oxidants in solid phase, such as Filox-R™, manganese ore, freshly

formed manganese dioxide, and ferric and manganese binary oxide (FMBO), could also contribute to As(III) oxidation, through the effects of interfacial oxidation and/or catalytic oxidation. When these solid-phase oxidants are used, As(III) oxidation and arsenic adsorption often occur simultaneously and contribute to arsenic removal.

Most of the oxidants that are commonly employed in drinking water treatment, that is, chlorine, permanganate, and ozone, are highly effective for this purpose. However, chlorine dioxide and monochloramine are not so effective in oxidizing As(III) [4]. Ultraviolet (UV) radiation alone is also ineffective for As(III) oxidation, but UV oxidation of As(III) may be catalyzed by the presence of sulfite, ferric iron, or citrate. Other kinds of oxidants, such as ferrate, hydrogen peroxide, and potassium peroxydisulfate peroxides, can also preferably oxidize As(III), but will not be discussed in this chapter due to the difficulty in using them in engineering.

8.4.1.1 Chlorine

Chlorine is a very effective oxidant and can steadily oxidize As(III) to As(V) in less than 1 min. It can be easily used in gas phase and in large-scale water treatment plants; however, in rural areas liquid sodium hypochlorite is preferred because of its safety during operation. The stoichiometric oxidant demand is 0.95 mg of chlorine (as Cl_2) per mg of arsenite. The ability of chlorine to oxidize arsenite to arsenate is found to be relatively independent of pH in the range 6.3–8.3 [4]. Dissolved ferrous ion (Fe^{2+}), manganese ion (Mn^{2+}), and organic matter show no significant side effects on the oxidation rate of As(III). However, a higher dosage of chlorine is required for the removal of both Fe^{2+} and Mn^{2+} in practice. Chlorine may also act as a secondary oxidant while being added at the head, and can facilitate the regeneration and polishing of media surfaces in media filtration units. Chlorine dosage should be carefully calculated to obtain As(III) oxidation, reductive species oxidation, chlorine consumption in treatment units, disinfection purpose, and residual chlorine demand.

There is an important issue that should be evaluated before using chlorine in the formation of disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetate acids (HAAs). It is a less serious problem than that in surface water, due to the lower DBP precursor concentration in underground water. Other issues associated with chlorine are sensitivity of the treatment process to chlorine and operator safety, because it is corrosive.

8.4.1.2 Permanganate

As a powerful oxidizing agent, permanganate is first used for the oxidation of Fe^{2+} and Mn^{2+} and the removal of iron and manganese in underground water. It is also used in surface water treatment for taste and odor control, DBP formation control, coagulation and/or filtration aiding, and so on. In the treatment of urgent source water pollutants that require oxidation, permanganate is also used in some cases due to its being easy to dose as compared with other oxidants. Similarly, permanganate can oxidize arsenite to arsenate effectively and rapidly. Freshly prepared manganese dioxide (δMnO_2), which is formed after permanganate reduction, could also oxidize As(III) [55,56], and would be discussed later. Subsequent removal of δMnO_2 is required when permanganate is used. Permanganate is effective in refreshing the arsenic removal activity of a filter through the *in situ* coating of δMnO_2 on filter media, but will inevitably decrease the running period at cost. Permanganate oxidation produces hardly any DBP and is valuable for a drinking water source whose DBP precursor concentration is high. However, the disinfection potential should be evaluated, and secondary disinfectant is required under this condition. Permanganate is widely available and is relatively stable with a long shelf life. Consequently, it is easy to transport to and conserve in rural villages.

The use of permanganate has several disadvantages. First, it is difficult to handle. It is very corrosive and stains almost everything purple. The second drawback is the formation of δMnO_2 , removal of which requires a solid–liquid separation such as filtration. Additionally, the dosage of permanganate should be carefully controlled to avoid the pink color in the effluent. It is thought to be an expensive oxidant in some countries, although in China it is not.

8.4.1.3 Ozone

Ozone is the most powerful and rapid-acting oxidizer produced. It is created by exposing oxygen to high energy such as an electric discharge field or to UV light. The only byproduct from oxidation with ozone is oxygen, which is dissolved in aqueous systems. The stoichiometric oxidant demand is 0.64 mg of ozone per mg of As(III), and As(III) oxidation may be easily finished within 1 min at this dosage. In the pH range from 6.3 to 8.3, the ability of ozone to convert As(III) to As(V) is relatively independent of pH [4]. Ozone shows promising capabilities of inactivating most microorganisms, but the residual disinfectant concentration is not satisfactorily assured, especially in urban cities. However, in villages where the distribution system is small scale, secondary ozone might be feasible, although evaluation of this is necessary.

In Europe, and increasingly in the United States, ozone is more and more widely used as an oxidant and disinfectant in large-scale drinking water treatment plants. However, in rural areas of developing and underdeveloped countries, the use of ozone is inhibited by its high cost. That ozone must be produced on site is another disadvantageous factor for its application in rural areas for As(III) oxidation. Additionally, the UV and the ozone formed by the exposure of oxygen to UV may be used as primary and secondary oxidants in small systems for arsenic removal, owing to its possibility of being installed as an instrument in engineering.

8.4.1.4 Oxidants in Solid Phase

Manganese oxides are interesting metal oxides that exhibit oxidative, adsorptive, and catalytic activities. Commercial Filox-R™, an MnO₂-based medium, is a kind of solid-phase oxidant and has been used in engineering for the oxidation of Fe²⁺, Mn²⁺, sulfite, As(III), and so on [4]. Precisely, Filox-R™ is a catalyst rather than an oxidant because the oxidation of As(III) to As(V) is accomplished by the oxygen in water, which is facilitated by the catalysis effect of Filox-R™. Consequently, the stoichiometric oxidant demand in the Filox-R™ oxidation process is dependent on the reactions between oxygen and reductive species such as As(III) and Fe²⁺. The conversion rate of As(III) by Filox-R™ increases with lower pH conditions, higher dissolved oxygen (DO) concentrations, and elevated empty bed contact time (EBCT) values [4].

There are other kinds of manganese oxides, that is, synthetic MnO₂, freshly prepared δMnO₂, and δMnO₂-coated quartz (which may be produced in the processes of removing Mn(II) and Fe(II) [55–57]), that are valuable for As(III) oxidation. In comparison with Filox-R™, these manganese oxides could convert As(III) through heterogeneous oxidation effects, and the capabilities of adsorbing arsenic are satisfactory [55–57]. However, the Mn²⁺ that results from reductive dissolution reactions and its concentrations should be well evaluated to meet the guidelines of drinking water standards.

8.4.2 COAGULATION/FLOCCULATION FOLLOWED BY FILTRATION

8.4.2.1 Coagulation/Flocculation

Coagulation using metal salts with subsequent filtration is the most commonly used treatment method for arsenic removal, especially in large-scale water treatment plants, and is considered as one of the best available technologies (BATs) by the U.S. EPA for arsenic removal [4].

Coagulation is the process of destabilizing the surface charges of colloidal and suspended matter to allow for the agglomeration of particles. This process results in the formation of large, dense floc, which is amenable to removal by clarification and/or filtration. Coagulation is typically described as a process consisting of three steps: coagulant formation, particle destabilization, and interparticle collisions. The first two steps, coagulant formation and particle destabilization, occur during rapid mixing, and the third step occurs during flocculation. Comparatively, coagulation is the destabilization of colloids by neutralizing the forces that keep them apart, and flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into large

agglomerates or clumps. In this chapter, the authors would like to express “coagulation” in brief. Similarly to oxidation, coagulation processes could not remove arsenic from solution, but transform aqueous arsenic to particulate arsenic, which should be removed by subsequent sedimentation and/or filtration processes.

During coagulation, arsenic is transformed to particulate arsenic through three main mechanisms: precipitation, coprecipitation, and adsorption. Precipitation refers to the formation of insoluble compounds of $\text{Fe}(\text{AsO}_4)$ or $\text{Al}(\text{AsO}_4)$. Coprecipitation is defined as the incorporation of soluble arsenic species into a growing hydroxide phase via inclusion, occlusion, or adsorption. And adsorption refers to the electrostatic interaction and/or formation of surface complexes between soluble arsenic and the solid oxyhydroxide surface sites. All the three mechanisms can independently contribute to contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role, whereas coprecipitation and adsorption are both active in arsenic removal. Several factors affect the coagulation process, including coagulant dosage, pH, turbidity, natural organic matter (NOM), anions and cations in solution, zeta potential, and temperature. Additionally, the addition of permanganate is beneficial to arsenic removal by ferric precipitation, mainly through the effect of oxidizing As(III) to As(V) rather than the adsorption capability of *in situ* formed δMnO_2 (Figure 8.1) [58].

Arsenic removal with metal salts has been used since at least 1934 [59]. The most widely used coagulants for arsenic removal are aluminum salts such as aluminum sulfate, and ferric salts such as ferric chloride or ferric sulfate, which hydrolyze to form aluminum and iron hydroxide particulates, respectively. Ferrous sulfate has also been used, but is less effective [60,61]. Generally, iron-based coagulants, including ferric sulfate and ferric chloride, are more effective in removing As(V) than their aluminum-based counterparts. For example, Gullede and O'Connor [62] spiked water with As(V) and tested 10–50 mg/L alum and ferric sulfate at pH 5–8 in a bench-scale study. The ferric sulfate achieved higher removal than the alum (88.6–99.0% versus 18.5–93.6%). This is because iron hydroxides have higher affinity toward As(V) species and are more stable than aluminum hydroxides in the pH range 5.5–8.5 [62]. A fraction of the aluminum remains as a soluble complex, which is incapable of adsorbing As(V) and can pass through the filtration stage. The optimal pH ranges for coagulation with ferric and aluminum salts are 5–8 and 5–7, respectively. At pH values above 7, the removal efficiency of aluminum-based coagulants decreases significantly [62].

Excellent arsenic removal is possible with either ferric or aluminum coagulants, with laboratories reporting over 99% removal under optimal conditions, and residual arsenic concentrations of

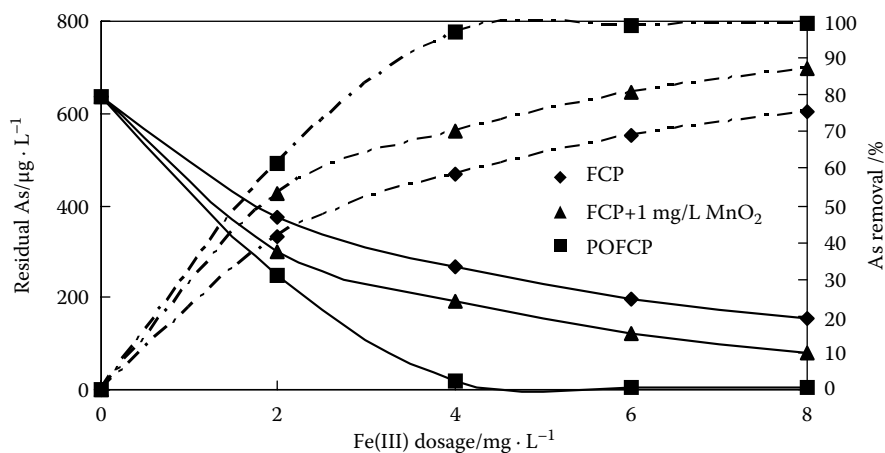


FIGURE 8.1 Comparison of As removal between permanganate-facilitated ferric coprecipitation (POFCP) and combined effects of FCP and $\text{MnO}_2(\text{s})$ adsorption. (Adapted from Liu, R.P. et al., *Environ. Sci.* (in Chinese), 26(1), 72–75, 2005.)

less than 1 $\mu\text{g/L}$ [63]. Numerous bench- and pilot-scale studies and some short-term full-scale evaluations have been performed to evaluate arsenic removal using conventional coagulation/filtration. Full-scale plants typically reported a somewhat lower efficiency, from 50% to over 90% removal. Scott et al. [64] found that arsenic removal was 81–96% using 3–10 mg/L of ferric chloride in a full-scale conventional treatment plant [64].

The presence of coexistent ions and their effects on arsenic removal by coagulation with iron-based coagulants have also been investigated. It has been reported that chloride, sulfate, carbonate, and nitrate show little adverse effect on arsenic removal [65]; however, silicate and phosphate significantly reduce arsenic removal.

The effects of silicate on arsenic removal with ferric hydroxide precipitation at different silicate concentrations are strongly pH dependent, as indicated in Figure 8.2 [66]. The presence of 1.4 mg/L silicate as Si decreased arsenic removal from 99.3% to 62.8% at pH 9.2 and from 98.5% to 67.4% at pH 7.4. Silicate showed a lower extent of inhibiting arsenic removal at lower pH levels of 6.6, which correspondingly decreased arsenic removal from 92.5% to 84.7%. Davis et al. [67] also reported that the higher pH level was normally related to silicate's higher degree of inhibiting arsenic removal with preformed ferric hydroxide precipitates [67].

The negative effect of silicate on arsenic removal by ferric chloride precipitation may be ascribed to (1) the decreased ζ potential of ferric precipitates and the increased repulsive forces between arsenic and ferric precipitates due to the presence of silicate (Figure 8.3), (2) the inhibited precipitation, aggregation, and flocculation of ferric hydroxides (Figure 8.4), and (3) the increased filterable iron concentration and subsequent decreased content of precipitates for arsenic adsorption (Figure 8.5) [25].

To investigate the dominant mechanism involved in silicate hindering arsenic removal, the ratio of residual arsenic to iron ($R_{\text{As/Fe}}$) was compared for filtrates passing through the different membrane filters: 0.45 μm microfiltrating membrane (0.45MFM), 0.20 μm microfiltrating membrane (0.20MFM), and 60 kDa pore size ultrafiltration membranes (60KDUFM). Although the concentrations of arsenic and iron decreased steadily after sequential filtering with 0.45MFM, 0.20MFM, and 60KDUFM, the $R_{\text{As/Fe}}$ values increased from 4.43 to 40.51 mg/mg (Figure 8.6), indicating the existence of high levels of aqueous ionic soluble arsenic in the filtrate. Consequently, the effects of silicate increasing repulsive charges and decreasing surface sites available for arsenic, rather than

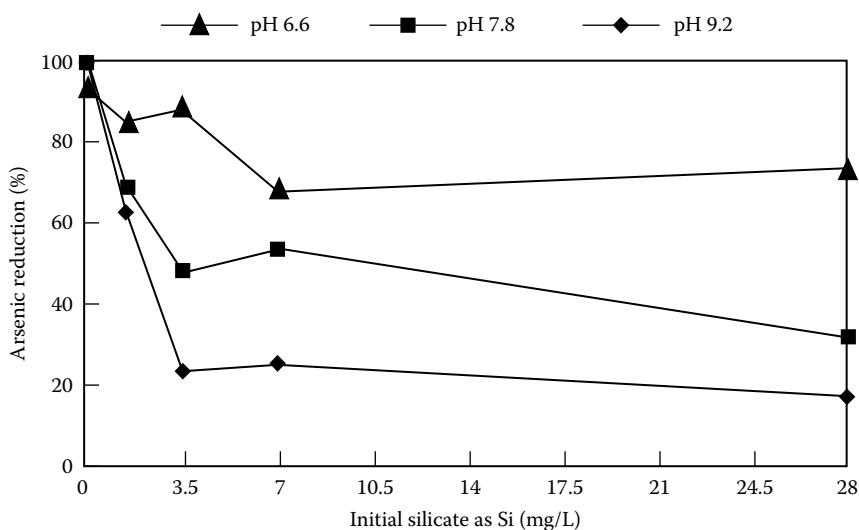


FIGURE 8.2 Effects of silicate on arsenic coprecipitation with ferric hydroxide at different pH levels. (Adapted from Liu, R.P. et al., *Environ. Eng. Sci.*, 24(5), 707–715, 2007.)

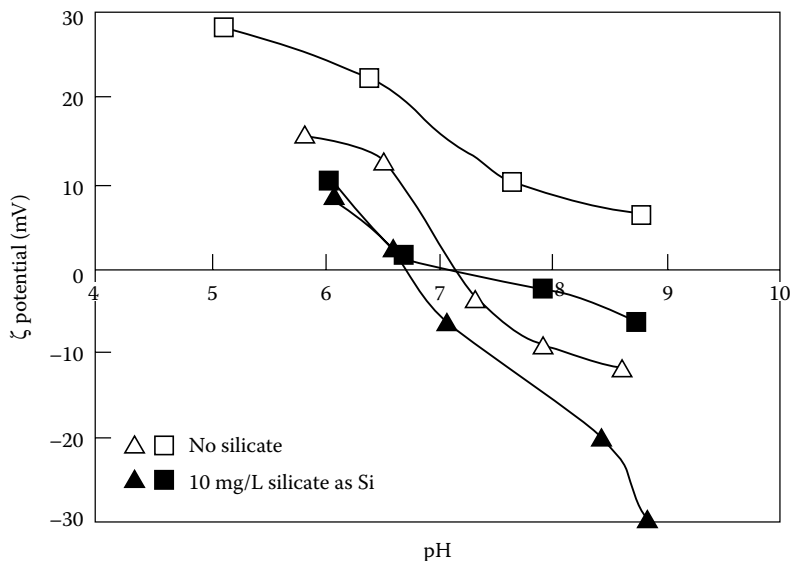


FIGURE 8.3 Effects of silicate on ζ potential of ferric hydroxide in the absence and presence of 40 mg/L Ca^{2+} . (Adapted from Liu R.P. et al., *Environ. Eng. Sci.*, 24(5), 707–715, 2007.)

facilitating the formation of tiny ferric colloids with adsorbed arsenic, are more pronounced in silicate hindering arsenic removal [25].

Fortunately, the widely presented calcium ion (Ca^{2+}) reduces the adverse effects of silicate, and facilitates arsenic removal to a certain extent [65,68,69] and Ca^{2+} favoring ferric aggregation are more significant than Ca^{2+} improving arsenic removal, in comparing with the increased ζ potential of ferric (hydro)oxides due to the presence of Ca^{2+} [69].

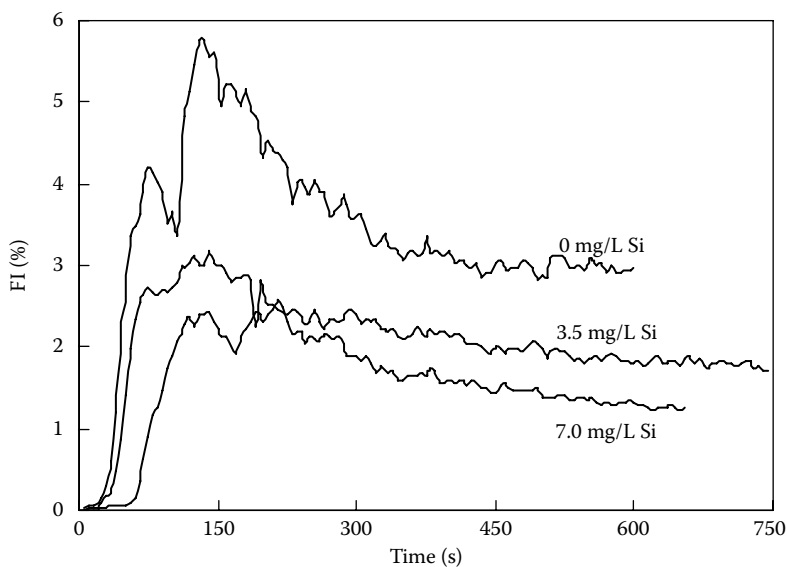


FIGURE 8.4 Effects of silicate on the dynamic on-line flocculating index (FI) value of ferric hydroxide precipitates. (Adapted from Liu, R.P. et al., *Environ. Eng. Sci.*, 24(5), 707–715, 2007.)

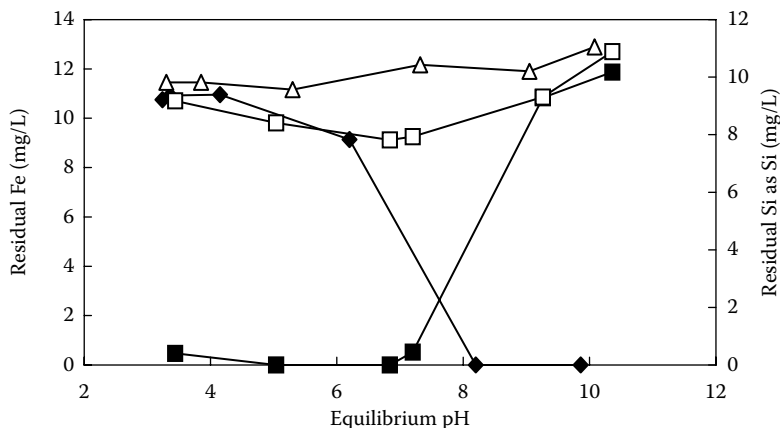


FIGURE 8.5 Residual silicate and filtered iron concentration variation at different pH levels. (Adapted from Liu, R.P. et al., *Environ. Eng. Sci.*, 24(5), 707–715, 2007.)

8.4.2.2 Filtration

Filtration units aim to remove particulate arsenic, destabilized colloids, flocs, and so on. The process of filtration involves the flow of water through a fixed bed of granular media, which is called media filtration, or forcedly through a semipermeable membrane by a pressure differential at low speed, which is called membrane filtration. Units of sedimentation or clarification are required when turbidity in the source water is higher than 10 NTU; most underground water fortunately would not exceed this value.

As for the design and optimization of a filter for arsenic removal, the parameters of media materials, namely, grain size and size distribution, filtration velocity, and filter depth, should be well evaluated. The common materials are sand, anthracite coal, garnet, and ilmenite. If direct filtration or contact filtration is employed, relatively low velocity is preferred except that the floc is satisfactorily formed before filtration.

Membrane filtration includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (R/O). Generally, NF and RO remove components through chemical diffusion.

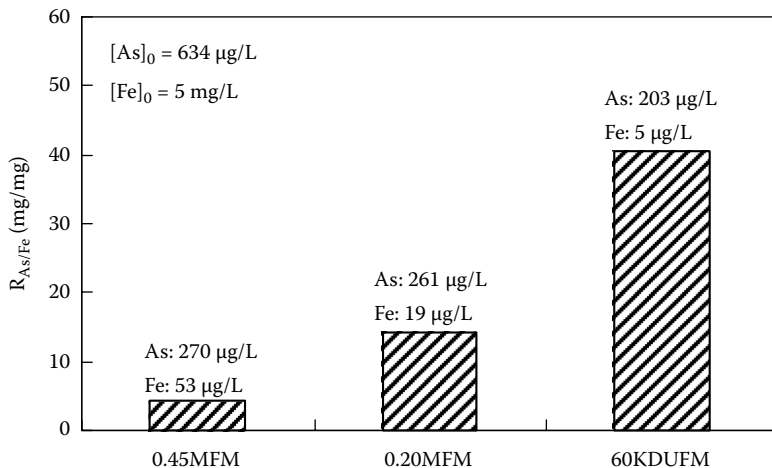


FIGURE 8.6 Ratio of residual arsenic to iron ($R_{As/Fe}$) in filtrate after sequential filtering through 0.45MFM, 0.20MFM, and 60KDUFM. (Adapted from Liu, R.P. et al., *Environ. Eng. Sci.*, 24(5), 707–715, 2007.)

UF and MF remove components through physical sieving. MF and UF show little potential of removing aqueous arsenic, but could promisingly remove particulate arsenic species. Consequently, MF and UF may be chosen as the membrane type following coagulation, which are more cost-effective than NF and R/O.

As for the coagulation/MF process, the actual efficiency of arsenic removal is highly dependent on the quality of the raw water. pH adjustment might be required prior to coagulation. The dosing of polyelectrolytes as coagulant aids may lead to enhanced permeate fluxes of MF; however, the polyelectrolyte has no effect on residual arsenic concentration [57].

Conclusively, coagulation followed by filtration can effectively remove many suspended and dissolved constituents from water besides arsenic, notably iron, manganese, phosphate, and fluoride. Great reductions are also possible in turbidity, odor, and color. Therefore, coagulation/filtration to remove arsenic will improve other water quality parameters, which is valuable in engineering.

8.4.3 ADSORPTION

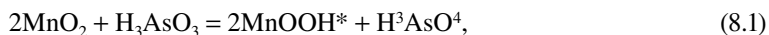
Adsorption is one of the most widely used technologies in the treatment of both drinking water and waste water. Numerous adsorbents, such as active carbon, metal oxides, mineral oxides, hydrotalcites, agriculture products, industrial wastes, bioadsorbents, and polymer resins, have been proposed for the removal of different pollutants, including arsenic [70]. The surface modification of adsorbents, that is, active carbon, gravel sand, and zeolite, is also an important strategy for the design and application of adsorbents. There are also some commercial adsorbents available for arsenic removal, such as Kanchan™ Arsenic Filter, ArsenX^{np}, and Electromedia® IX [70].

Most adsorbents mainly focus on the removal of arsenic from aqueous phase, and cannot contribute to the conversion of As(III) to more easily adsorbed As(V). The addition of oxidants is usually inevitable for the achievement of high arsenic removing potential [4]; however, this unfortunately increases the operational complexity of the treatment system and is disadvantageous for its application in rural areas. This chapter introduces two adsorbents that readily oxidize and adsorb arsenic.

8.4.3.1 Manganese Oxides

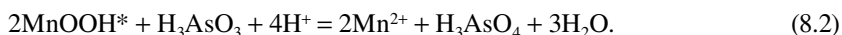
Manganese oxides, which mainly include synthetic MnO₂, natural manganese oxide minerals, and biogenic manganese oxide, have been widely used as adsorbent, solid oxidant, and catalyst, due to their important environmental interfacial characteristics.

The mechanism involved in the heterogeneous oxidation of As(III) by birnessite has been well investigated. Nesbitt et al. [71] demonstrated by x-ray photoelectron spectroscopy (XPS) that the oxidation of As(III) by the synthetic 7°A birnessite surface proceeded by a two-step pathway, involving the reduction of Mn(IV) to Mn(III) [71]:



where MnOOH* is an Mn(III) intermediate reaction product.

This reaction is followed by the reaction of As(III) with MnOOH* [71]:



An additional reaction could include the adsorption of As(V) by the MnO₂ surface:



where Mn-OH represents a reactive hydroxyl group on the MnO₂ surface and (MnO)₂AsOOH represents the As(V) surface complex.

Manning et al. [56] investigated arsenic removal using synthetic birnessite (MnO_2), indicating that As(III) is oxidized by MnO_2 followed by the adsorption of the As(V) reaction product onto the MnO_2 solid phase [56]. The most likely As(V)– MnO_2 complex is a bidentate binuclear corner-sharing (bridged) complex occurring at MnO_2 crystallite edges and interlayer domains. The As(V)–Mn interatomic distance determined by Extended x-ray Absorption Fine Structure analysis was 3.22 Å for both As(III)- and As(V)-treated MnO_2 [56]. Interestingly, the reductive dissolution of MnO_2 by As(III) causes a surface alteration and promotes more active sites for As(V), which is demonstrated to be beneficial to As(V) adsorption [56].

In the As(III)– δMnO_2 system, the addition of permanganate slightly increases arsenic removal and shows a much less positive effect on As(III) removal by ferric hydroxide precipitation [55]. NOM decreases and Ca^{2+} increases arsenic removal by δMnO_2 . The mechanisms of Ca^{2+} favoring arsenic removal include the increased ζ potential and the facilitated destabilization of freshly prepared δMnO_2 due to the presence of Ca^{2+} [55].

Column experiments were conducted to evaluate the As removal potential for a natural manganese oxide using different particle sizes and flow rates [72]. Generally, total adsorption capacity varies with flow rate and particle size, which were interpreted using the effective diffusivity of arsenate in the grain as a single adjustable parameter by a transport model including Langmuir adsorption and mass transfer. Transport was influenced by nonlinear adsorption and intraparticle diffusion, and diffusivities between 0.6 and $7.0 \times 10^{-11} \text{ m}^2/\text{s}$ that included intraparticle diffusion were calculated [72].

8.4.3.2 FMBO

As noted above, traditional adsorbents are generally effective for As(V) removal, but fail in the case of As(III). To remove As(III) effectively, a novel FMBO material, which combines the oxidation property of manganese dioxide and the high adsorption features of iron oxides to As(V), was developed by our group [73,74]. The FMBO adsorbent was prepared from low-cost materials, such as potassium permanganate (KMnO_4) and iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), using a simultaneous oxidation and coprecipitation method [74]. The prepared FMBO with a high surface area ($265 \text{ m}^2/\text{g}$) was amorphous. The Fe/Mn molar ratio of this adsorbent was about 2.86 on the surface, a little lower than that of bulk, which was in the range of 2.93–3.02. Iron and manganese were evenly distributed on the surface and existed mainly in the oxidation states +III and +IV, respectively. The presence of abundant surface hydroxyl groups (Fe-OH) was determined [74].

The FMBO adsorbent was effective for both As(V) and As(III) removal, particularly As(III). The maximal adsorption capacities of As(V) and As(III) were 0.93 and 1.77 mmol/g, respectively [74]. Figure 8.7 shows the adsorption isotherms for As(III) and As(V) by Fe–Mn adsorbent. The adsorbent could effectively oxidize As(III) to As(V) within 16 h under tested conditions. The kinetics of arsenite removal and change in concentrations of arsenic species in the aqueous phase with time are demonstrated in Figure 8.8. No significant Mn release was observed during As(III) removal when the solution pH value was over 6.5. Arsenic removal was enhanced by the presence of metal cations (Mg^{2+} and Ca^{2+}), whereas it was inhibited by coexisting oxyanions such as CO_3^{2-} , SiO_3^{2-} , and PO_4^{3-} , especially at high concentrations. The presence of F^- , Cl^- , SO_4^{2-} , and humic acid did not significantly affect arsenic removal [74].

FMBO had much higher adsorption capacity toward As(III) than As(V). This was interesting because if only oxidation occurred as mentioned above, maximal adsorption capacities toward As(V) and As(III) oxidized and then adsorbed should be the same. The higher maximal As(III) adsorption capacity than that of As(V) indicated that something else must take place on removal of As(III). It was suggested that fresh adsorption sites for arsenic adsorption were created at the solid surface during As(III) oxidation, resulting in an increase of formed As(V) removal.

The removal of As(V) was achieved by forming an inner-sphere complex on the surface of the adsorbent. However, the removal mechanism of As(III) is distinct from that of As(V) and much more complicated since both oxidation and sorption reactions are involved. To understand the process of As(III) removal, a control experiment was conducted to investigate the effect of Na_2SO_3

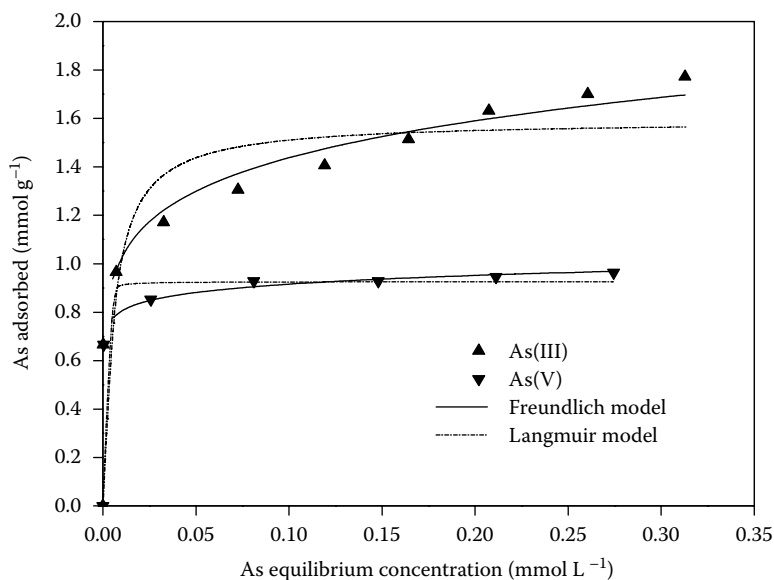


FIGURE 8.7 Adsorption isotherms for As(III) and As(V) by Fe-Mn adsorbent in a 200 mg/L suspension at pH 5.0 ± 0.1 at low equilibrium As solution concentrations. (Adapted from Zhang, G.S. et al., *Water Res.*, 41, 1921–1928, 2007.)

treatment on arsenic removal, which can provide useful information on the As(III) removal mechanism. The adsorbent was firstly treated with Na_2SO_3 , which can lower its oxidizing capacity by reductive dissolution of the Mn oxide, and then reacted with As(V) or As(III). From the experimental results along with FTIR and XPS analyses, an oxidation and sorption mechanism was established and the processes of As(III) removal could be depicted as follows [73].

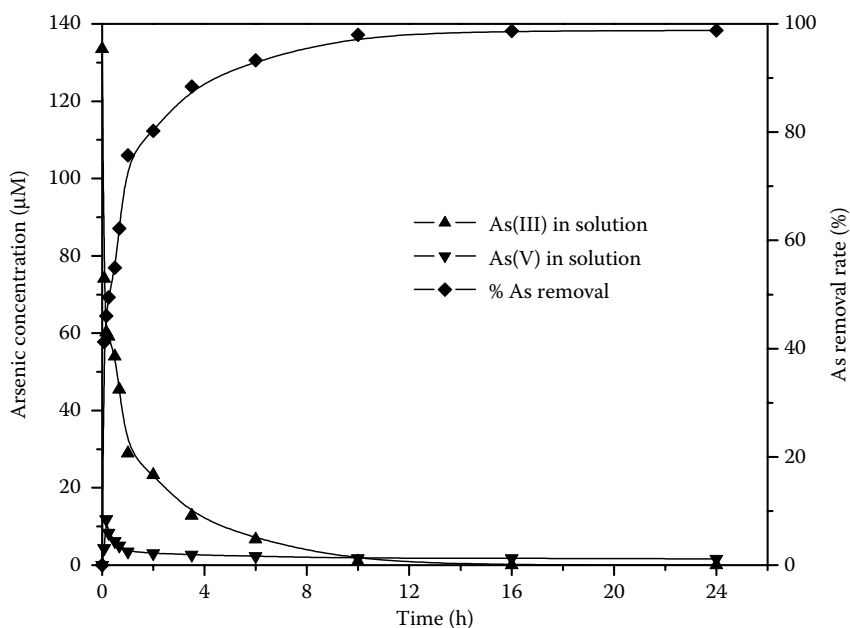
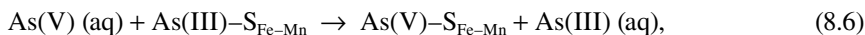
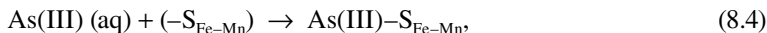


FIGURE 8.8 Kinetics of arsenite removal and change in concentration of arsenic species in aqueous phase with time. (Adapted from Zhang, G.S. et al., *Water Res.*, 41, 1921–1928, 2007.)

As(III) was firstly transported to the solid–water interface by convection or diffusion from bulk solution. Then, As(III) was adsorbed onto the surface by the formation of a surface complex. Adsorbed As(III) near the Mn atoms was oxidized to As(V) by MnO_2 and the formed As(V) was released into the solution with the reductive dissolution of MnO_2 . During this process, fresh active adsorption sites were formed at the solid surface. As(V) was then transported to the solid–water interface and adsorbed onto the surface of the Fe–Mn adsorbent, occupying empty adsorption sites or replacing sorptive As(III). The whole process can be briefly represented by reaction/reactions 8.4 through 8.6 [73]:



where $(-\text{S}_{\text{Fe-Mn}})$ represents an adsorption site on the Fe–Mn adsorbent surface, $\text{As(III)-S}_{\text{Fe-Mn}}$ represents the As(III) surface species, and $\text{As(V)-S}_{\text{Fe-Mn}}$ represents the As(V) surface species. This process proceeded until As(III) or the available MnO_2 was depleted.

During As(III) oxidation, fresh adsorption sites for arsenic adsorption were created at the solid surface, due to the reductive dissolution of manganese dioxide. This was responsible for the higher As(III) uptake.

FMBO can be easily loaded on the surface of porous granular materials such as diatomite, which allows it to be conveniently used in a packed column. In summary, the novel FMBO adsorbent is highly efficient, of low cost, and environmentally friendly and has high potential of being used in the removal of As(III) from water [73].

8.4.4 LIME SOFTENING

LS is a chemical–physical treatment process commonly used to remove calcium and magnesium cations from water. The addition of lime to water raises the pH, thereby causing a shift in the carbonate equilibrium and the formation of calcium carbonate and magnesium hydroxide precipitates. These formed precipitates can be amenable removed by the filtration process. The arsenic in raw water would not only adsorb onto the calcium and magnesium precipitates, but would also form weak complexes with Ca^{2+} and Mg^{2+} . Quantitatively, the interactions between arsenate and Ca^{2+} lead to the formation of calcium–arsenate complexes, and CaHAsO_4 , $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, and $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ are the dominant species whose water solubilities vary from 2.9×10^{-2} to 5.8×10^{-2} M [75]. As for the calcium–arsenite complexes, Qiu and Liu [76] reported that the water solubility of $\text{Ca(AsO}_2)_2$ was 3.5×10^{-3} M [76]. In drinking water treatment, arsenic levels are in the range of several decades ppb to several ppm. The formation of calcium–arsenic complexes and its contribution to arsenic removal is relatively minor. However, as in the case of industrial wastewater with high arsenic levels (several thousand ppm), lime precipitation may be an important strategy for arsenic removal.

To remove As(V) in underground water, lime is added to increase the solution pH above 10.5. In this range, magnesium hydroxide precipitates, and As(V) is removed by coprecipitation with it. As(V) removal by coprecipitation with calcium carbonate is poor (less than 10%) [4]. LS solely for arsenic removal is uneconomical and is generally considered cost-prohibitive. Only when LS is used to remove hardness from water, this process can be used to simultaneously remove arsenic. There are several drawbacks of LS methods. Firstly, it is difficult to reduce arsenic concentration in water to less than $10 \mu\text{g/L}$ by LS alone [4]. Sludge disposal is another problem in this treatment method [77], because the total volume of waste produced from LS is typically higher than that produced by coagulation/filtration and coprecipitative processes. Prior to disposal, this waste residual will require thickening and dewatering, most likely using mechanical devices [77].

8.4.5 ION EXCHANGE

Ion exchange is a physical–chemical process in which ions are exchanged between a solution phase and a solid phase. Synthetic ion exchange resins are widely used in water treatment to remove many undesirable ions from water. These resins are based on a three-dimensional cross-linked polymer skeleton, called the “matrix,” which is commonly composed of polystyrene and divinylbenzene. A large number of ionizable functional groups are attached to the matrix through covalent bonding. These groups are exchanged for ions of similar charge in solution that have a strong exchange affinity for the resins. Charged functional groups fall into four types, namely strongly acidic (e.g., sulfonate, $-\text{SO}_3^-$), weakly acidic (e.g., carboxylate, $-\text{COO}^-$), strongly basic [e.g., quaternary amine, $-\text{N}^+(\text{CH}_3)_3$], and weakly basic [e.g., tertiary amine, $-\text{N}(\text{CH}_3)_2$] [78].

Arsenic removal is accomplished by continuously passing water through one or more columns packed with exchange resins under pressure. In this process, arsenate anion species in the water were exchanged with the negatively charged groups of the resins and were immobilized on the solid phase. As(V) can be removed by using strong-base anion exchange resin in either chloride or hydroxide form. These resins are insensitive to pH in the range 6.5–9.0 [78]. Arsenate can be effectively removed from solution, producing effluent with less than 1 $\mu\text{g/L}$ arsenic by various strong-base anion exchange resins that are commercially available, whereas arsenite, being uncharged, cannot be removed in this way. Therefore, unless arsenic is present exclusively as arsenate species, an oxidation pretreatment step will be necessary for arsenic removal.

Different ions have different exchange affinities toward the same resin. For example, some common anions compete for sites on a strong-base anions resin according to the following selectivity sequence [4,78]:



Traditional sulfate-selective resins are suited for arsenate removal. Nitrate-selective resins can also remove arsenic, but are not as effective as sulfate-selective resins. Arsenate removal is relatively independent of solution pH and influent arsenic concentrations. However, competing anions, most notably sulfate and nitrate, have a strong effect. For low-sulfate waters, ion exchange resin can easily remove over 95% of arsenate, and treat over a thousand bed volumes before breakthrough. In addition, high levels of total dissolved solids (TDSs) may adversely influence the efficiency of arsenate removal. The ion exchange process is not an economical treatment technology if source water contains over 500 mg/L of TDSs or over 50 mg/L of sulfate [4,78].

In summary, the ion exchange technique is an effective and simple procedure for arsenic removal. But some problems should be considered. One is the phenomenon known as chromatographic peaking, which can cause the As(V) level in the treatment effluent to exceed that in the influent stream. Another problem is resin fouling. Resin fouling occurs when mica or mineral scale coats the resin or when ions bond the active sites and are not removable by standard regeneration methods. This may have a great influence on the resin’s capacity as the media becomes older.

8.4.6 MEMBRANE SEPARATION

Membrane separation processes are receiving much attention due to their provision of extremely low arsenic level in treated water without solid byproducts [79]. MF and UF alone could not effectively remove arsenic. Quite a few studies investigated the potential of NF membranes (aromatic polyamide and composite polyamide) and RO membranes (polyamide, cellulose acetate, polyether urea, and polyvinyl alcohol) for the removal of arsenic at different pH and arsenic levels from 10 to 600 ppb [80–82]. NF and RO were found to remove arsenate ions over 90% and 95%, respectively [81,82]. However, both use relatively dense membranes requiring high operating pressures (240 kPa [81] and 550–690 kPa [83] for NF membranes, and 750 kPa [82] and 138–1345 kPa [84] for RO membranes).

NF and RO produce very low fluxes (water recovery is 15% for NF and between 10% and 50% for RO). Furthermore, the removal efficiency of NF drops to 65% when water recovery is 65% and to 16% when water recovery is 90%. Additionally, the avoidance of membrane fouling risks often requires high-quality influent for NF and RO processes. Consequently, in engineering, NF and RO are not recommended for arsenic removal in rural villages in developing and underdeveloped countries.

There are some emerging studies on the pretreatment procedures prior to MF and UF (which transform aqueous arsenic to species that are unable to pass through MF or UF membranes) for arsenic removal by cost-effective and energy-saving techniques. Coagulation and adsorption are feasible for this strategy, which is discussed above. Recently, Gecol et al. [85] proposed the addition of surfactants (cetylpyridinium chloride, CPC) to the contaminated water stream to achieve high arsenic rejection by UF [regenerated cellulose (RC) and polyethersulfone (PES)] [85].

In detail, when ionic surfactant (e.g., cationic surfactant) is added to contaminated drinking water above its critical micelle concentration (CMC), it forms micelles (aggregates of 20–200 surfactant molecules) that can effectively bind oppositely charged anionic arsenic species. When a water stream containing these surfactant aggregates is passed through a suitable UF membrane, these surfactant aggregates with bound inorganic arsenic ions are physically too large to pass through membrane pores [85].

The addition of surfactant was observed to significantly increase arsenic removal, which was found to be between 90.9% and 100%. It is clearly indicated that the cationic surfactant micelles can effectively bind the oppositely charged As(V) anions, replacing the counterion Cl^- and forming $\text{CP}[\text{As}(\text{V})]$ micelles. The resultant $\text{CP}[\text{As}(\text{V})]$ micelles are physically too large to pass through the PES and RC membrane pores and are retained in the retentate side. The removal of arsenic is lower at decreased pH values, and this is attributed to the difference in arsenic dissociation under different pH conditions. The surface micelles in feed water reduce the permeate flux significantly since micelles, being larger than the pore size of the membranes, accumulate on the membrane surface. Comparatively, at pH 5.5, the clean water permeate fluxes of 10 kDa PES, 10 kDa RC, and 5 kDa PES decrease by 77.8%, 24.5%, and 37.1%, respectively. At pH 8, the clean water permeate fluxes of 10 kDa PES, 10 kDa RC, and 5 kDa PES decrease by 75.1%, 21.7%, and 32.7%, respectively. This indicates that the molecular interaction between surfactant and PES membrane is more pronounced than the RC membrane [85].

However, surfactant concentrations in the permeates are high under different experimental conditions, which should be well controlled before the application of these technologies in engineering.

8.4.7 TECHNOLOGIES SELECTION STRATEGY

The advantages and disadvantages of different technologies have been compared and discussed above. It is inferred that there is no single technique that could resolve all the arsenic-related problems in practice, and each technique has its advantages and disadvantages, as concluded earlier [70].

On the contrary, these technologies should be well compared and evaluated before choosing a process for a specified engineering. Generally, the following factors should be carefully considered while selecting a technique in engineering: arsenic concentration in polluted water, coexistent ions and their effect on arsenic removal, the local standard for arsenic in drinking water, treatment capacity of the system, gross investment, acceptable operating fees, educational background of the operator of the system, available field areas, existence of distribution systems or not, requirements of auto-control systems, and the population that is being served.

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9 Treatment of Metal-Bearing Effluents: Removal and Recovery

Ghinwa M. Naja and Bohumil Volesky

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9.1 PHYSICO-CHEMICAL TREATMENT

9.1.1 CHEMICAL PRECIPITATION

The most common method for heavy metal removal from wastewater is chemical precipitation. As shown in [Figure 9.1](#), the basic treatment process for precipitating heavy metals includes pretreatment, pH adjustment, flocculation/clarification, sludge thickening, sludge dewatering, and effluent polishing [1].

The general principle of heavy metal removal by chemical precipitation is based on the low solubility of heavy metal hydroxides. The treatment reduces the heavy metal content of the water dramatically, thus the residual concentrations of heavy metals in the overflow from the settling tank are usually below the environmental limits. Furthermore, the process can handle relatively high flow rates of wastewater containing high concentrations of heavy metals, and so it is suitable for the treatment of many industrial and mining effluents. However, the efficiency of the treatment hinges on the rates of formation and of settling of the solid metal hydroxides. The fact that these rates are usually low in water with low metal content leads to an increase in the consumption of lime and/or caustic soda in the process, and to the design of large mixing and settling tanks. Furthermore, the treatment generates toxic sludge that has to be dewatered, stabilized, and disposed of.

Three theories have been put forward to explain the effects and efficiency of chemical precipitation. The first theory uses the fact that heavy metal salts when treated with alkaline substances,

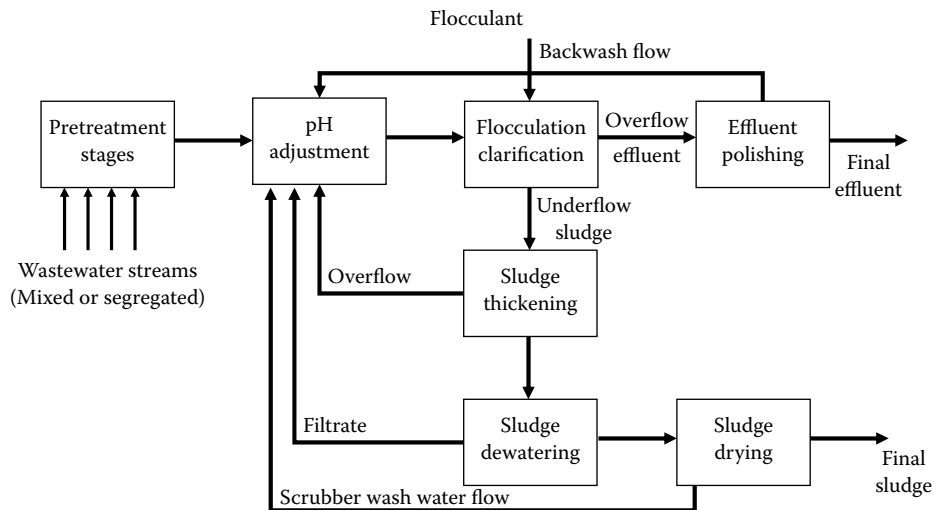


FIGURE 9.1 Basic waste treatment process for heavy metals.

form heavy voluminous precipitates that carry down colloidal suspensions by means of mechanical entrapment. Salts of iron, aluminum, and zinc fall into this category. The second theory is based on electronic principles. It has been demonstrated that colloidal particles possess an electric charge. Since these charges are alike, the particles repel each other and thus tend to remain in suspension. If a colloidal particle with an opposite charge is added, the charges neutralize and settling of the particles is affected. This explains the efficiency of the multivalent ions and why ferric salt is more efficient than ferrous salts. Clay suspensions are also claimed to exert a charge-neutralizing effect. The third theory pertains to a physical behavior. Insoluble substances that have a large particle surface area can effectively sorb colloids. They can also act as nuclei for the initiation of precipitation. Activated charcoal is a material with this type of action. Of the three theories mentioned above, the second one is generally predominantly accepted.

9.1.1.1 Pretreatment

Prior to precipitation, the wastewater will be subjected to a pretreatment stage. Pretreatment is used to remove materials such as grease and scum before sedimentation to improve process feasibility. Common pretreatment stages include oil removal and chromate reduction [Cr(VI) to Cr(III)].

If significant levels of oil are present in metal-bearing wastewater streams, the oil must be removed before clarification to prevent interference with the settling of the precipitated solids. The oil is usually removed by skimming, and emulsified oil can be removed by ultrafiltration. Chromium will only precipitate in the trivalent form and thus it must be reduced from its hexavalent form prior to precipitation. Hexavalent chromium reduction is achieved at low pH levels (~2–3) with a reducing agent—usually sodium metabisulfite. Owing to the low pH level involved, chromium-bearing wastewater is usually segregated for pretreatment before being mixed with other metal-bearing wastewater streams [2].

9.1.1.2 pH Adjustment

The precipitation of metals occurs at various pH levels depending on a number of factors. For wastewater streams that contain various heavy metals, the pH level for precipitation must be carefully chosen so that all of the metals have an acceptable level of insolubility. If this is not possible, the stream will have to be segregated to treat the particular component metal at an appropriate pH level [3]. Typical minimum pH values for precipitation are given in [Table 9.1](#), depending on the solubility

TABLE 9.1
Minimum pH Values for Complete Precipitation of Metal Ions as Hydroxide

Metal	Sn ²⁺	Fe ³⁺	Al ³⁺	Pb ²⁺	Cu ²⁺	Zn ²⁺	Ni ²⁺	Fe ²⁺	Co ²⁺	Mn ²⁺
pH	4.2	4.3	5.2	6.3	7.2	8.4	9.3	9.5	9.7	10.6

Source: U.S. Environmental Protection Agency (U.S. EPA). Processes, procedures and methods to control pollution from mining Activities. U.S. EPA # 430/9-73-011, 1973.

product K_{sp} of the metal hydroxide [4]. To precipitate metals in the hydroxide form, caustic soda and lime are frequently used for pH adjustment. In large wastewater treatment systems, lime is preferred due to its lower cost, whereas in small wastewater treatment systems, caustic soda is used due to ease of handling. In the case where fluoride or phosphate removal from the wastewater is required, lime is used for pH adjustment since it will generally cause precipitation of the fluorides and the phosphates. Precipitate particle size (and filterability) appears to be greater when lime is used. The use of lime or caustic soda seems to have no great effect on the rate of sedimentation, but the volume of sludge will be twice as great when using lime as when using caustic [5].

9.1.1.3 Coagulation/Flocculation/Clarification

As the metal hydroxides come out of solution due to pH adjustment, chemicals are often added to promote coagulation and flocculation. The inorganic coagulants are often trivalent cations to neutralize the negative charge of the colloids. The higher the valency, the more effective the coagulating action will be (Schultz–Hardy theory: a trivalent ion is ten times more effective than a divalent ion). When choosing a coagulant, its harmlessness and its cost must be taken into account. Thus, trivalent iron or aluminum salts have been and continue to be widely used in all water coagulation treatments. Organic coagulants may also be used. These are cationic polyelectrolytes that directly neutralize the negative colloids. Inorganic polymers (activated silica) and natural polymers (starches, alginate) were the first to be used as common flocculants. The appearance of the widely varying synthetic polymers has changed flocculation results considerably. Of chief importance is the timing of the introduction of the coagulant and that of the flocculant. In fact, a flocculant usually does not take effect until the coagulation stage is over. The use of synthetic flocculants often results in a minimum amount of sludge. Combined with modern separation techniques, this can lead to the production of very dense sludge that can be directly treated in a dewatering unit.

High-molecular-weight polymers are fed to the neutralized waste as it enters the clarifier at a dosage of 10–100 ppm [5]. Exact flocculant dosage is usually determined by individual bench tests. Prior to the clarification stage, flash mixing and flocculating chambers allow the flocculant to be well mixed into the wastewater and provide gentle particle contact to aid the formation of larger, heavier particles, which will settle well in the clarification stage.

The clarification stage involves the removal of the solids (the flocs) from the wastewater stream. This is typically a gravity settling process that occurs in a sedimentation tank or in an inclined plate clarifier, also called a Lamella clarifier. Under proper conditions, precipitated solids can be concentrated about 10:1 in a clarifier. Clarifier performance is largely a function of the settling surface that increases by utilization of the Lamella clarifier. In summary, a clarifier has to usually perform three different functions in order to do its task well [1]. The settling tank thus must

- Provide for effective removal of suspended solids from the effluent
- Have an adequate sludge removal capacity
- Thicken the sludge satisfactorily.

Any failure in one of these functions will impair the performance of the settler and, if serious, destroys the effectiveness of the process almost completely. A poor design results in the propagation of the problem to successive units within the plant, and inevitably in a decrease in the overall performance of the treatment.

9.1.1.4 Solid–Liquid Separation

If further reduction in the level of suspended solids is required, the effluent can be polished. Filtration using backwash sand in-depth filters is the most popular method for suspended solids removal in the polishing stage. The overflow from the settler/clarifier enters the filtration process. After passing downward through the granular medium, it can be discharged. During backwashing, wash water passing upward through the filter (fluidizing the sand filter medium) carries out the impurities that accumulated in the filter bed. A continuous backwash sand filter can provide continuous streams of polished effluent and reject flow so that the filter never needs to be shut down for backwashing. The reject flow would be returned to the front end of the treatment system for further processing. The effluent from this type of sand filter is usually quite clear, containing only 3–5 ppm of total suspended solids [6].

Apart from gravity settling, membrane filtration processes offers another approach to concentrating the solids from the wastewater stream and producing clear effluent. Ultrafiltration could be quoted as an example. It is a physical membrane separation process whereby the membrane acts as a barrier to precipitate particles, and prevent their passage into the discharge stream. No flocculants are needed and the total suspended solids in the effluent are essentially zero. Thus tighter effluent limits are met and even high flow rates can nowadays be handled [7]. Ultrafiltration systems are based on the cross-flow membrane technology. A bundle of parallel hollow fiber membranes is sealed into a shell to form a cartridge. Each cartridge has a process inlet, outlet, and a pair of permeate outlets. Inside each fiber, waste is separated at the membrane surface. Cleaned effluent passes through the membrane, whereas contaminants are rejected and exit at the opposite end. Turbulent flow across the membrane surface reduces waste build-up and minimizes cleaning.

9.1.1.5 Sludge Thickening

The flocculation/clarification stage is usually followed by the sludge-thickening stage. A sludge thickener is typically a conical bottom tank that receives the underflow from the clarifier and provides storage where further gravity settling of solids can take place. The sludge concentrated at the bottom of the tank contains about 4–6% solids [5]. The advantage of operating with a high solids content sludge is that it generally improves the operation and performance of the dewatering equipment.

9.1.1.6 Sludge Dewatering

Dewatering of the concentrated sludge can be accomplished using a wide variety of equipments such as centrifuges, rotary vacuum filters, belt presses, and filter presses [8]. Rotary vacuum filters produce a relatively dry cake (20–25% solids) and can operate continuously so that they are suitable for applications involving large volumes of sludge. For most industrial applications, filter presses (plate and frame pressure filters) are the most economical method of producing a dry cake (20–30% solids). Filter presses have wide applicability and are probably the most common type of dewatering equipment in use [5]; however, they do not operate on a continuous-flow basis. A filter press consists of a series of plates lined with polypropylene filter cloths. The plates form chambers into which the sludge is pumped. The solids are retained by the filter media, whereas the filtrate flows through the porous filter cloths. The filtrate flow is discharged from the press to the front end of the treatment process (prior to the clarification stage). As the filter cycle progresses, the chambers become completely full of solids and at this point, no more sludge can be pumped into the press. The press must then be opened and the dry cakes are discharged. Therefore, the term “press” is a misnomer because no mechanical squeeze is involved. It should be noted that only the thickening of neutralized metal hydrates by means of a clarifier and subsequent dewatering of sludge has been discussed to this

point. The neutralized waste can also be pressure filtered directly, depending on its concentration (about 300–500 ppm of suspended solids).

9.1.1.7 Sludge Disposal

With increased production of industrial wastes, sludge management is becoming increasingly important [9]. There exist various methods of disposing sludge (landfill 25%, ocean dumping 10%, incineration 40%, and land application 25%). Metal-bearing sludges are difficult to handle and, due to their toxicity, their final disposal is often troublesome and expensive. If incorrectly disposed of, these sludges could be a potential source of pollution of surface and ground waters. There appears to be little problem concerning the incineration of waste sludges with respect to heavy metals, but this depends on where and how the pollutant is released. Ocean dumping is being less used compared to land applications and sludge landfilling. In determining the sludge disposal site, many factors need to be considered, such as type of soils, ground water table, hydrology, composition, and pH of the sludge. With a sludge pH of less than 6.5, the potential for release of cadmium, chromium, lead, mercury, and selenium increases. Suitable disposal sites are areas where natural (clay, rock) or artificial means (plastic liner) can prevent excessive amounts of leachate from getting into the ground water. Where these conditions do not exist, it may be necessary to install a collection system at the bottom of the pond so that leachate can be collected and piped to a treatment system for removal of soluble metals salts. The U.S. EPA has suggested limiting sludge land application as a function of specific metal content and soil cation exchange capacity [10]. Chemical treatments have been developed to reduce the leaching possibilities of metal-bearing sludges and may be used in conjunction with a land fill program to further minimize potential leachate contamination. One other solution could be to remove metals from these sludges (Section 9.1.4).

9.1.2 TREATMENT METHODS

Chemical precipitation of metal may be accomplished in either batch (Figure 9.2) or continuous treatment systems (Figure 9.3). Batch treatment is usually preferred when the volumes to be treated are small, or where the waste may be variable from day to day and require modification of the treatment as characteristics change [1].

9.1.2.1 Batch Treatment

Batch treatment systems can be economically designed for flows as high as 50,000 gpd. A batch system is usually designed with two tanks, each one of sufficient volume to handle the waste generated in a specific time. When one tank is full, a mixer is used to provide a homogeneous mixture,

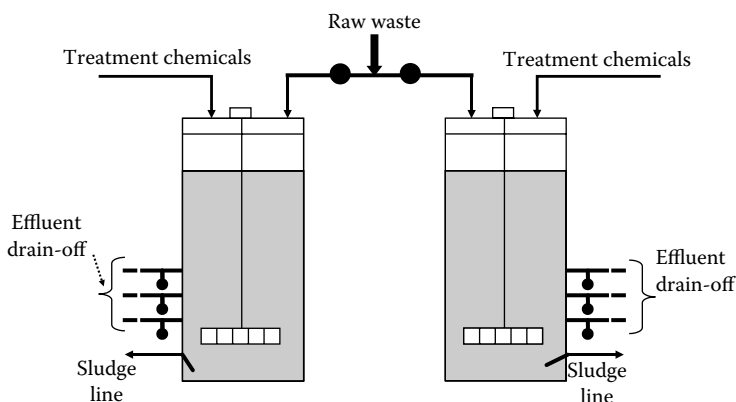


FIGURE 9.2 Typical batch treatment system.

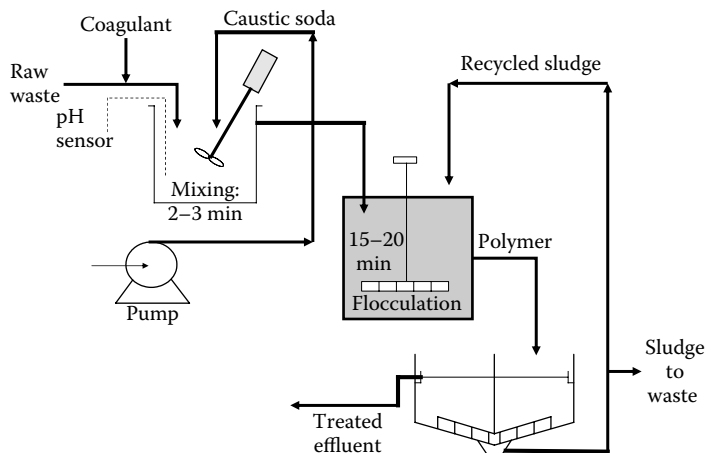


FIGURE 9.3 Typical continuous-treatment system for heavy metals.

and a sample is taken and analyzed to determine the amount of metal contaminants present. Chemical addition, based on the metal contaminants present and pH of the waste, is then calculated and the required amount of chemicals added. The tank contents are then mixed, using pH for controlling purposes and for metal removal, and allowed to settle for 2–4 h.

When treatment is complete, a second sample can be taken and analyzed to ensure that all contaminants have been removed. If, for any reason, contaminants are still present, treatment can be repeated or alternative treatment applied. When the operator is satisfied, that the treated waste is suitable for discharge, the clear liquor is decanted. The settled sludge is drawn off periodically for disposal. The advantages of a batch treatment system are that nothing is discharged from the plant until the operator is satisfied that it meets effluent requirements. The system is also simple in its design and is easy to operate (Figure 9.2).

9.1.2.2 Continuous Treatment

When wastewater characteristics are uniform or when volumes are large, a continuous treatment system is applicable. A usual continuous-flow treatment system has an equalization tank of several hours to a day of detention time to even out any fluctuations in the wastewater characteristics and provide a uniform feed to the treatment system.

The first process step is the adjustment of the pH by addition of acid or alkali to the proper level of optimum precipitation. This chemical addition is controlled by a pH probe in the reaction tank, which activates the speed control of the chemicals feed pump. A polymer is usually added to aid coagulation. Reaction times are in the range of 15–60 min.

The waste stream then flows to a sedimentation basin where the metal precipitate settles out of solution, leaving a clear treated overflow for discharge to the receiving water body (Figure 9.3).

9.1.2.3 Sludge Recirculation

Recirculation of precipitated sludge to be mixed with the raw waste at the time of chemical addition can have beneficial effects. The presence of precipitated particles provides a seed for the newly formed precipitate to agglomerate. In a batch treatment, the settled sludge is collected at the bottom of the tank. When a new batch is put in the tank, the mixer is turned on to resuspend the sludge and mix it with the tank contents.

In continuous treatment systems, the sludge can be recycled either externally to the clarifier or internally within the clarifier. With external recirculation, the sludge is pumped out of the sludge hopper in the clarifier and introduced to the raw feed in the chemical mixing tanks. With internal

recirculation, the clarifier is designed with an internal mixer and baffles that provide recirculation within the clarifier.

9.1.3 APPLICATIONS

9.1.3.1 Zinc

The precipitation process most frequently involves adjustment of pH with either lime or caustic to achieve alkaline conditions, and precipitation of zinc hydroxide. Lime addition has been the widely accepted method for pH adjustment, despite the concurrent precipitation of calcium sulfate at elevated sulfate concentrations in some waters. The precipitation of calcium sulfate along with zinc hydroxide increases the total amount of sludge to be disposed of. Table 9.2 summarizes some results of zinc precipitation to its hydroxide. These values reflect a wide range of industrial systems; the treatment is usually not just for zinc removal alone. In cases where cyanide or chromate is also present in the waste, as frequently occurs in zinc and brass plating, cyanide removal and chromate reduction must precede metal hydroxide precipitation. Settling efficiency affects effluent concentration, as it can be seen in Table 9.2 by improvements in effluent zinc levels resulting from filtration of settled effluent. Incomplete cyanide treatment will increase effluent zinc levels, due to complexation, as will improper control of the treatment process pH.

9.1.3.2 Lead

In the precipitation process, lead is normally precipitated in the form of carbonate (PbCO_3) or hydroxide Pb(OH)_2 . The lead form precipitated depends on the amount of carbonate in or added to the wastewater, and the treatment pH. Initial acidic wastes are typically low in carbonate, and precipitation treatment of these waters would normally yield lead hydroxide unless supplemental carbonate was added. Lead carbonate precipitate is more crystalline than lead hydroxide, resulting in desirable settling and sludge dewatering characteristics. A large excess of carbonate, or treatment above pH 9.0, may yield less effective precipitation, however. Optimum pH range for lead carbonate precipitation is between 7.5 and 9.0.

In forming insoluble lead hydroxide, lime is the treatment chemical of choice, although caustic has also been used. The results with caustic or lime treatment are equivalent but there is an interference with lead hydroxide precipitation as calcium ion concentration increases.

TABLE 9.2
Summary of Hydroxide Precipitation Treatment Results for Zinc in Wastewaters

Industrial Source	Zinc Concentration (mg L^{-1})		Comments
	Initial	Final	
Zinc plating	—	0.2–0.5	pH 8.7–9.3
General plating	4.1–120	0.39–2.9	pH 7.5–10.5
Vulcanized fiber	100–300	1.0	pH 8.5–9.5
Brass wire mill	36–374	0.08–1.60	Integrated treatment for copper recovery
Tableware plant	16.1	0.02–0.23	Sand filtration
Viscose rayon	20–120	0.88–5	pH 5
Metal fabrication	—	0.5–1.2	Sedimentation
	—	0.1–0.5	Sand filtration
Blast furnace gas scrubber water	50	0.2	pH 8.8
Zinc smelter	744–1500	26–50	
Ferroalloy wastes	3–89	0.29–7.9	

9.1.4 METAL RECOVERY FROM SLUDGES

The settled sludge from a clarification basin is frequently in the range of 1–2% solids. Hydroxide precipitation of the metals produces sludge that is usually gelatinous in character, thereby increasing the difficulty of dewatering. Lime will produce considerably greater quantity of sludge than caustic, but that kind of sludge is easier to dewater. Similar to the case with wastewater sludges, the composition of these water treatment sludges varies from plant to plant, necessitating individual attention [9]. Some sludge compositions for North American plants are available in Table 9.3.

Metal recovery from sludges has been studied [11]. Digesting the sludge in an acid medium, neutralization, and electrolytic recovery have been investigated [12,13]. The cost estimate for recovery of copper, nickel, and chromium in a small plant was \$13.25 kg⁻¹, which was quite high compared to the current market prices. However, since these metal values are steadily increasing, one approach is to stockpile these metal-bearing sludges, either separately or in a regional disposal site, so that they are available for economical metal recovery in the future.

Nevertheless, digestion of the sludge can be done biologically. The further paragraphs will compare acid and microbial leaching for metal removal from municipal sludge.

A number of chemical methods for toxic metal solubilization from sludges have been studied [14,15]: ion exchange [16,17], utilization of chelating agents (EDTA and similar) [18–20], aerobic digestion coupled with or without hydrochloric acid [21–23], or oxidative acid hydrolysis [24]. The relatively high operating costs and sometimes insufficient yield of metal solubilization are obstacles in their practical applicability. The acid leaching (H₂SO₄, HCl, HNO₃, CH₃COOH) with or without heating are the processes that have been given more attention. The requirement of large amounts of acid to adjust pH and large amounts of alkali for residual sludge neutralization after the leaching

TABLE 9.3
Metal Composition in the Sludges and Their Recommended Levels

	Composition (mg kg ⁻¹ of Dry Sludge)							
	Al	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Plant #1 ^a	27,640	5.0	87	215	933	28	110	419
Plant #1 ^b	26,320	2.6	66	200	1053	42	234	392
Plant #2 ^a	43,630	9.2	401	1070	445	141	278	413
Plant #2 ^b	22,120	10.0	1719	1827	395	177	336	596
Plant #3 ^a	74,097	1.4	50	178	323	17	23	359
Plant #3 ^b	77,734	0.7	26	147	365	13	15	285
Plant #4 ^a	30,907	4.5	124	737	4613	30	177	379
Plant #4 ^b	18,589	4.0	87	625	5696	26	129	343
Plant #5 ^a	32,484	2.3	99	1211	2914	142	266	181
Plant #5 ^b	18,039	1.9	97	1282	2450	151	225	151
Plant #6 ^a	28,786	0.8	349	1017	1458	50	43	1430
Plant #6 ^b	27,430	7.7	321	603	1519	45	118	1205
Plant #7 ^c	21,705	11.2	116	3689	166	23	447	1024
Plant #8 ^c	19,340	7.9	98	2279	444	13	646	646
Plant #9 ^a	13,520	2.0	155	391	418	222	106	1456
Plant #6 ^c	27,009	3.7	288	462	1013	274	155	1926
Recommended levels	—	15	1,000	1000	1500	180	500	2500

^a Secondary activated sludge.

^b Aerobically digested sludge.

^c Anaerobically digested sludge.

makes these processes unattractive from a practical standpoint. Consequently, interests have also focused on developing new microbiological methods. Two microbial leaching processes have been studied to remove toxic metals from sewage sludge. The bioleaching process with iron-oxidizing bacteria requires a lowering of the initial sludge pH to 4.0 and the addition of ferrous sulfate as a substrate, whereas the microbial leaching process with elemental sulfur as a substrate does not require an initial addition of acid. The principal advantage of the microbiological processes is a considerable reduction in the usage of significant quantities of acid to solubilize metals.

When comparing the microbial processes with acid leaching treatment [11,12,25], some conclusions could be drawn:

- The indigenous adapted sulfur- or iron-oxidizing bacteria can be utilized for toxic metal removal from sludges.
- The use of a microbial leaching process with elemental sulfur and ferrous sulfate as substrates permits to considerably reduce the quantity of acid required for metal extraction with a reduction of 100% and 83%, respectively.
- Bioleaching process with sulfur as a substrate for sulfur-oxidizing bacteria was revealed to be better than the acid treatment process and microbial leaching with ferrous sulfate and iron-oxidizing bacteria for solubilization of all metals examined.
- Microbial leaching process with ferrous sulfate as a substrate permits a better solubilization of cadmium, copper, manganese, and zinc than the acid treatment with sulfuric acid. However, the solubilization of aluminum, chromium, nickel, and lead was less than that for acid leaching.

9.1.4.1 Alum Sludges

These sludges are usually fairly high in moisture content—98% or more. The biochemical oxygen demand (BOD) is low, about 50 mg L^{-1} , but the chemical oxygen demand (COD) is fairly high, from 500 to 1500 mg L^{-1} . The pH of waste alum sludge is about 6, and ~40% of the solids are volatile. The major impact of these waste alum discharges is the formation of mudbanks along the stream.

One of the main problems of waste alum sludge is its very high moisture content. Thickeners have been used in some places to reduce this and make the sludge more efficient to handle. Tube settlers have been introduced for waste alum sludge and appear to be quite effective in increasing the solids concentration.

Dewatering waste alum sludge is difficult. The specific resistance of alum sludges is about $10\text{--}40 \times 10^{12} \text{ m kg}^{-1}$, which is approximately the same as activated sludge. Interestingly, the specific resistance of alum sludge decreases with increasing solids concentration. Alum sludges at even high solids concentrations behave as a liquid, with Newtonian flow characteristics. Centrifugal dewatering is possible with high polymer dosages. It has been found that a 2 lb polymer/ton of solids had almost no effect on solids recovery, but the addition of 1 lb polymer/ton more polymer resulted in a jump to better than 90% solids recovery. In other words, the recovery–polymer dose curves were very steep. Cake solids of about 15% were obtained, which was considered acceptable since a drying system followed centrifugation. Pressure filters are used to dewater alum sludges in a number of cities, with lime conditioning to aid the dewatering.

9.1.4.2 Lime Sludges

Lime CaO can be used for removing many of the impurities in wastewater. By adding sufficient quantities of lime, the pH can be raised to about 11.5 and calcium carbonate, metal hydroxides, and phosphates are precipitated. The phosphorus present is precipitated mostly as calcium hydroxyapatite $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. The small quantities of aluminum, magnesium, and manganese oxides aid in the removal of silt and other impurities.

It is possible to recover lime from the sludge produced in lime precipitation. One method is to centrifuge the slurry at low solids recoveries so as to remove only the heavy CaCO_3 . The magnesium

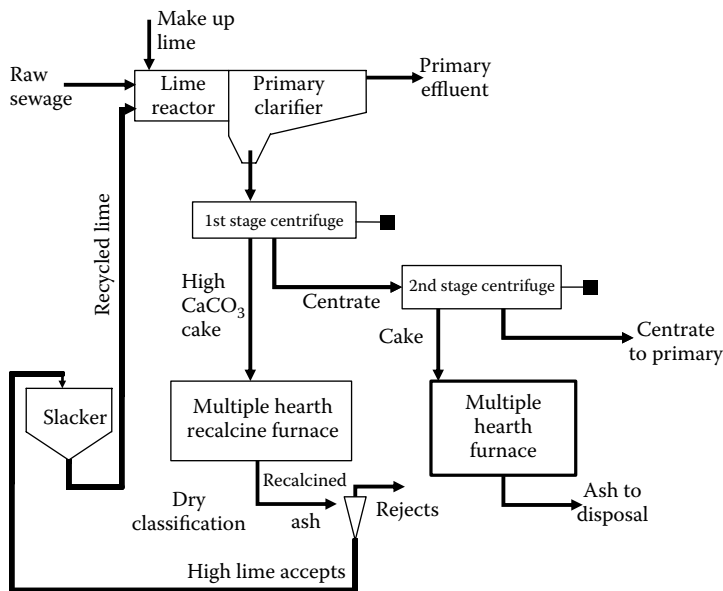
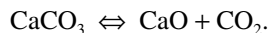
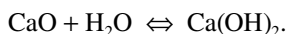


FIGURE 9.4 Sludge treatment by centrifugation.

hydroxide and other light solids are then dewatered in a second centrifuge (Figure 9.4). The CaCO_3 cake is then recalcined with the addition of heat according to the following reaction:



The recalcination process is fairly simple because the cakes produced in centrifuges and vacuum filters are quite dry, with solids ranging from 40% to 50%. Lime sludges with a high pH, however, have proved difficult to dewater. The recalcination process can be conducted in a rotary kiln or in a fluidized bed furnace. In both cases, the CO_2 produced can be used to dissolve some of the hydroxides or for recarbonizing the finished water to bring the pH down. A recently completed study showed that the addition of lime to the primary clarifier produced a thick sludge that centrifuges and could easily process. Approximately 60% of the calcium carbonate fed to the first centrifuge was recovered in the cake, whereas 50–75% of the other solids were rejected as the centrate. The calcium carbonate slurry was subsequently dewatered to 50% solids and incinerated. The lime produced in recalcining is CaO or quicklime, a dangerous compound. It is often slaked by adding water following the reaction below and the resulting hydrated product Ca(OH)_2 is much safer to handle:



Quicklime can also be used in the dewatering or drying of biological sludge by mixing the lime and sludge in a common concrete mixer. The above reaction is exothermic, and thus sludge is dried and disinfected as a result of the high temperatures produced. This process, used in some European treatment plants, yields a product that is marketable as a soil conditioner, especially where the soil is acidic; however, it lacks permeability and has poor water-holding capacity.

9.1.4.3 Iron Sludges

The sludges formed by both ferric and ferrous compounds are surprisingly soft and fluffy and difficult to dewater to more than 10% or 12% solids. Such sludges still behave as liquids. The recovery of iron from such operations is theoretically possible but not economically feasible.

9.2 ION EXCHANGE MATERIALS

Ion exchangers are insoluble granular substances that have in their molecular structure acidic or basic radicals that can exchange, without any apparent modification in their physical appearance and without deterioration or solubilization, the positive or negative ions fixed on these radicals for ions of the same sign in solution in the liquid upon contact with them [26]. This process, known as ion exchange, enables the ionic composition of the liquid being treated to be modified without changing the total number of ions in the liquid before the exchange.

For each reaction involving two ions A and B, the equilibrium between the respective concentrations A and B in the liquid and in the ion exchange substance can be shown graphically (Figure 9.5).

Under conditions of equilibrium, and for a concentration B of X% in the solution, the exchange material becomes saturated up to a concentration of Y%. When the two ions A and B have the same affinity for the exchange material, the equilibrium curve corresponds to the diagonal of the square. The more marked the exchange material's preference for ion B, the further the curve moves in the direction of the arrows. The form of the curve for a given system of two ions depends on a number of factors: nature and valence of the ions, concentration of ions in the liquid, and the type of exchange material. To achieve substantially complete exchange, it is necessary to create successive equilibrium stages by percolating the water through superimposed layers of exchange material (Figure 9.6).

If we take a layer of exchange material entirely in form A, and if a liquid containing ions B or B' (the exchange material has a much greater affinity for ion B' than for ion B) is passed through it, successive equilibrium points between (A and B) and (A and B') give different series of concentration curves. The possible breakthrough or exhaustion curves (Figure 9.7) depend not only on the static equilibrium curve mentioned above, but also on the exchange kinetics between the liquid and the exchange material: this type of kinetics involves the penetration of solutes into the exchanger, and are governed by laws known as the "Donnan equilibrium laws."

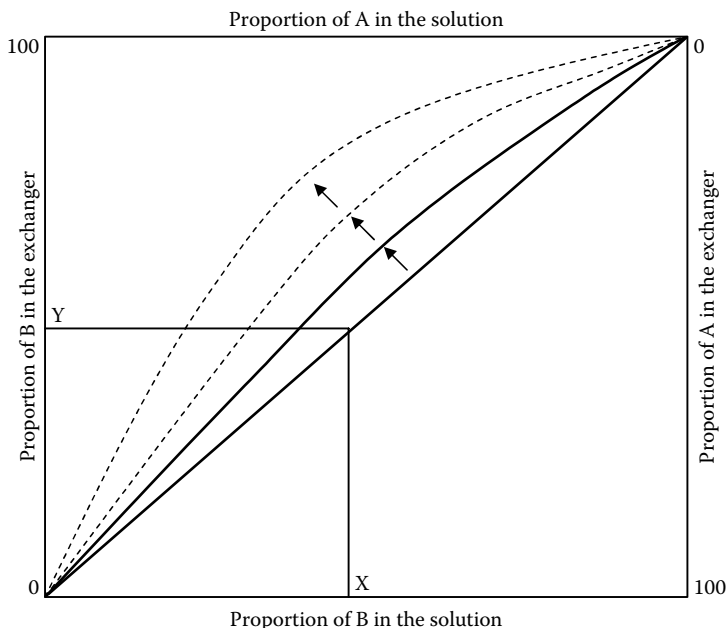


FIGURE 9.5 Ion exchange equilibrium curves.

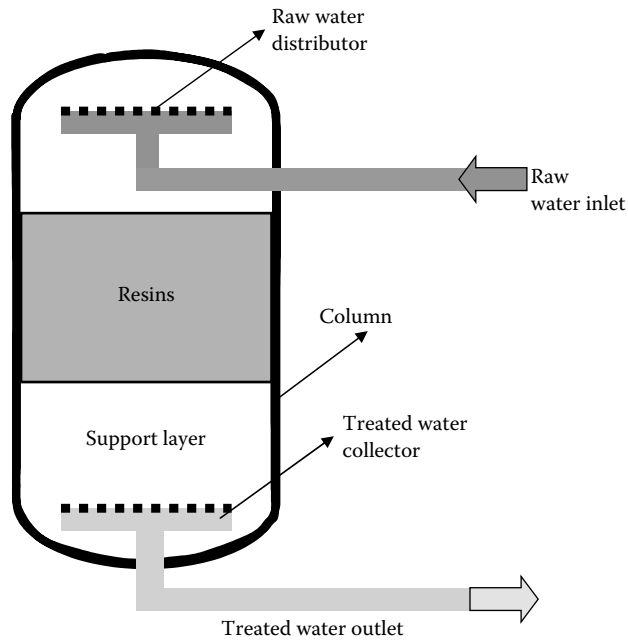


FIGURE 9.6 Common column filled with ion exchange material to treat raw polluted water.

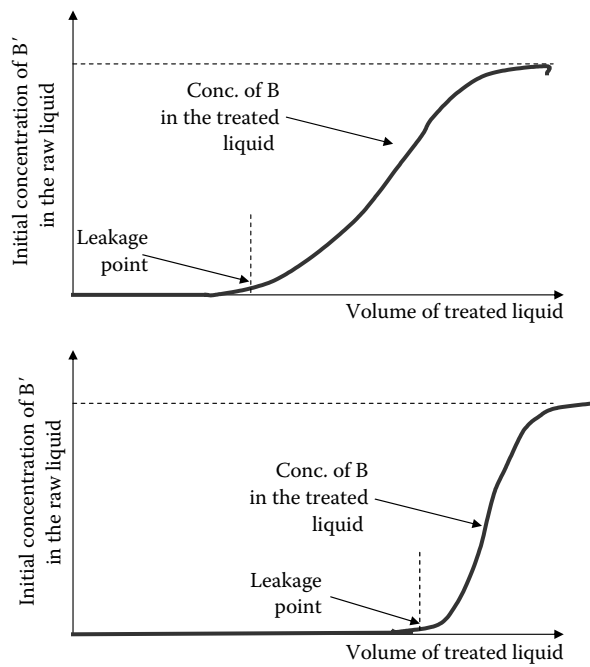


FIGURE 9.7 Exhaustion curves for an ion exchange material entirely in form A. The exchange material has a much greater affinity for ion B' than for ion B.

The first ion exchange substances were natural earths (zeolites); they were followed by synthetic inorganic compounds (aluminosilicates) and organic compounds; the latter materials are used today almost exclusively and, derived from hydrocarbon feedstocks, they are called resins. This term has been often wrongly extended to cover just about any kind of ion exchanger.

Ion exchange resins have proven to be an efficient means of controlling the concentration of heavy metals in wastewaters. There is a noticeable and expanding activity in the application of ion exchange to the recovery and recycling of water and heavy metals from waste. There are various types of resins available for the removal of different metals from effluents. Each resin has certain advantages and limitations and a proper choice, depending on effluent composition, should be made for its application.

9.2.1 TYPES OF RESINS

Ion exchange resins are insoluble polymers with chemical active groups that, when ionized, bond with opposite-charged metal ions. Those resins capable of exchanging cations are called cation exchangers. Resins capable of exchanging anions are called anion exchangers. The ion exchange function of a resin is generally limited by pH levels, flow rate, turbidity, type of regenerant, and complexity of wastewater. Organic resins generally feature a complex matrix, a three-dimensional network of hydrocarbon chains [27]. According to the structure, there are two categories: the resins of the gel type and those of the macroporous or loosely cross-linked type. Their basic macromolecular structure is identical, obtained in both cases by copolymerization of, for example, styrene and divinylbenzene. The difference between them lies in their porosity. Their high cross-linking degree increases their mechanical strength to both physical (pressure—negative pressure) and chemical (change in the ionic saturation, or exhaustion state) stresses. Gel-type resins have a natural porosity that results from the polymerization process and is limited to intermolecular distances. It is a microporous-type structure. Macroporous-type resins have an additional artificial porosity that is obtained by adding a substance designed for this purpose. Thus, a network of large canals known as macropores is created in the matrix. These products have a better capacity for adsorption and desorption of organic substances.

The cation exchangers can be categorized into two groups: strong acid and weak acid. Anion exchangers can also be divided into strong base and weak base groups. Those resins that remove a specific metal ion are known as chelating exchangers. [Tables 9.4](#) and [9.5](#) summarize the physical and chemical characteristics of the macroporous- and gel-type resins as well as the main suppliers of these types of ion exchangers.

9.2.1.1 Strong Acid Cations

They are characterized by having HSO_3 sulfonic radicals and acidities close to that of sulfuric acid. In current use these are sulfonated polystyrenes obtained by

- Copolymerization of styrene and divinylbenzene in emulsion form to obtain perfect spheres on solidification
- Sulfonation of the beads thus obtained.

The products obtained by this process are virtually monofunctional. Their physical and chemical properties vary depending on the percentage of divinylbenzene to styrene which, in turn, determines the degree of cross-linking, generally varying from 6% to 16%.

The ion exchange process follows the general reaction of this type:



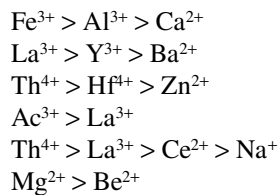
TABLE 9.4

Physical and Chemical Characteristics of Gel Resins (Strong Acid, Weak Acid, Strong Base, and Weak Base) as Well as the Main Suppliers of These Types of Ion Exchangers

Resins/Gel	Strong Acid	Weak Acid	Strong Base	Weak Base
Particle diameter (mm)	0.3–1.2	0.3–1.2	0.3–1.2	0.3–1.2
Moisture content (%)	45–48	46–53	45–48	46–53
pH range	0–14	1–14	0–14	1–14
<i>T</i> maximum (°C)	120	120	120	120
Turbidity tolerance (NTU)	5	5	5	5
Tolerance (g m ⁻³)	Chlorine 1.0	Iron 0.5	Chlorine 1.0	Iron 0.5
Total capacity (eq L ⁻¹)	1.4–2.2	3.5–4.2	1.2–1.4 (type I) 1.3–1.5 (type II)	1.4–2.0
Regeneration			NaOH 40–100	
	NaCl 80–300	110% of the	NH ₃ 30–60	
	H ₂ SO ₄ 80–250	capacity used	Na ₂ CO ₃ 60–130	—
	HCl 40–200		NaOH 40–200	
Supplier				
Bayer	Lewatit S100		Lewatit M 500 (I) 600 (II)	
Duolite	Duloite C20	Duloite C433	Duloite A101 (I) 102 (II)	
Dow Chemical	Dowex HCR-S	Dowex CCR-2	Dowex SBR (I) SAR (II)	Dowex WGR-2
Rohm&Haas	Amberlite IR120	Amberlite (IRC50, IRC84)	Amberlite IRA 400 (I) 410 (II)	Amberlite IRA68

Notes: The total exchange capacities of various categories of exchange materials are expressed in gram equivalents per liter of resin. The values of regeneration levels listed above are expressed in grams of pure product per liter of resin.

The selectivity of these resins is usually as follows:



9.2.1.2 Weak Acid Cations

These are polyacrylic resins characterized by the presence of HCO₂ carboxyl radicals that can be likened to organic acids such as formic or acetic acid. They differ from strong acid exchangers in two respects:

- They retain only the Ca, Mg, Na, and so on cations that are bound to bicarbonates, but they cannot exchange cations at equilibrium with strong anions (SO₄, Cl, and NO₃).
- They can be regenerated more easily and their regeneration rates are close to those of stoichiometric efficiency.

The ion exchange process follows the general reactions of this type:

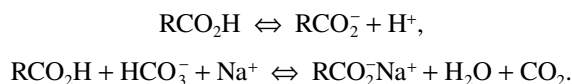


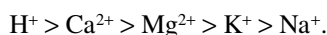
TABLE 9.5

Physical and Chemical Characteristics of Macrosporous Resins (Strong Acid, Weak Acid, Strong Base, and Weak Base) as Well as the Main Suppliers of These Types of Ion Exchangers

Resins/Macroporous	Strong Acid	Weak Acid	Strong Base	Weak Base
Particle diameter (mm)	0.3–1.2	0.3–1.2	0.3–1.2	0.3–1.2
Moisture content (%)	40–46	52–57	40–46	52–57
pH range	0–14	5–14	0–14	5–14
<i>T</i> maximum (°C)	150	150	150	150
Turbidity tolerance (g m ⁻³)	5	5	5	5
Tolerance (g m ⁻³)	Chlorine 1.0	Iron 0.5	Chlorine 1.0	Iron 0.5
Total capacity (eq L ⁻¹)	1.7–1.9	2.7–4.8	1.0–1.1 (type I) 1.1–1.2 (type II)	1.2–1.5
Regeneration	NaCl 80–300 H ₂ SO ₄ 80–250 HCl 40–200	110% of the capacity used	NaOH 40–100 NH ₃ 30–60 Na ₂ CO ₃ 60–130/ NaOH 40–200	—
Supplier				
Bayer	Lewatit SP112	Lewatit CNP80	Lewatit M 500 (I) MP 600 (II)	Lewatit MP64
Duolite	Duloite C26	Duloite C464	Duloite A 161 (I) 162 (II)	Duloite A378
Dow Chemical	Dowex MSC-1		Dowex MSA1 (I) MSA2 (II)	Dowex MWA-1
Rohm&Haas	Amberlite IR200		Amberlite IRA 900 (I) 910 (II)	Amberlite IRA93

Notes: The total exchange capacities of various categories of exchange materials are expressed in gram equivalents per liter of resin. The values of regeneration levels listed above are expressed in grams of pure product per liter of resin.

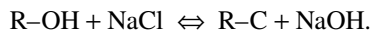
The selectivity of these resins is usually as follows:



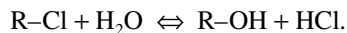
9.2.1.3 Strong and Weak Base Anions

Anion exchangers can be divided into weak or intermediate and strong base anion exchangers. These two types can be distinguished in practice as follows:

- The weak base types do not retain very weak acids such as carbonic acid or silica, but the strong base types retain them completely.
- The strong base types alone are able to release the bases from their salts following the typical reaction:



- The weak base types are more or less sensitive to hydrolysis, in the form of the displacement, by pure water, of the anions previously attached to the resin:



The strong base types are practically unaffected by this phenomenon.

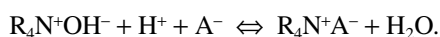
- The weak base types are regenerated more easily.

The existence of quaternary ammoniums in the molecule is typical of the strong base anion exchangers. All the strong base resins used for demineralization purposes belong to two main groups commonly known as type I and type II. The former consists of simple quaternary ammonium radicals, and the latter consists of quaternary ammonium radicals with alcohol function. Each type has its own field of application, depending on the nature of the water to be treated and the conditions applying to the regeneration cycle. The two types differ in the following respects:

- In type I, the basicity is strong and the capacity low; the regeneration efficiency is poor.
- In type II, the basicity is weaker and the capacity higher; the regeneration efficiency is also better.

The weak anion exchangers consist of a mixture of primary, secondary, tertiary, and sometimes quaternary, amines. The nucleus of the molecule is highly varied in nature and may be aliphatic, aromatic, or heterocyclic.

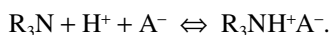
The exchange process of the strong base type follows the reaction:



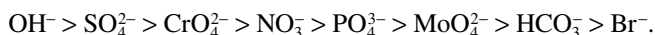
The selectivity is as follows:



The exchange process of the weak base type follows the reaction:



The selectivity is as follows:



9.2.1.4 Adsorbent Resins

These are products that are designed to retain nonionic compounds (basically organic molecules) in solution in polar and nonpolar solvents by means other than ion exchange and by a reversible technique. This process of adsorption on solids is very complex and involves various types of interaction between the adsorbent surface and the adsorbed molecules. For this reason, the adsorptive capacity of the resins depends on numerous factors such as the chemical composition of the skeleton (polystyrenic, polyacrylic, and formophenolic), the type of functional groups of polar adsorbents (secondary and tertiary amines, quaternary ammonium), the degree of polarity, the porosity (usually macroporous materials with pore sizes up to 130 nm), the specific surface area: up to 750 m² g⁻¹, the hydrophilic nature, and the shape of the grains.

Their possible uses include the following:

- Protection of the ion exchange system by retaining the pollutants present in feed water (humic acids, detergents, etc.)
- Decolorization of sugar syrups, glycerin, grape musts, whey, and so on
- Separation, purification, and concentration processes in the pharmaceutical industry and synthetic chemistry.

The regeneration method of adsorbent resins basically depends on the product adsorbed. The traditional eluants are acids, bases, sodium chloride, methanol, adapted organic solvents, and, in certain cases, pure water or steam.

The choice of the correct adsorbent presents some difficulty; it must be guided by the properties of each adsorbent and the products to be retained. Therefore, laboratory or pilot studies are indispensable in the majority of cases.

9.2.1.5 Special Resins

Polyfunctional resins: These are products that combine the properties of strong resins with those of weak resins. This is the case with anion resins that are able to remove all the anions including silica and CO_2 while ensuring a high exchange capacity and an excellent regeneration efficiency due to their weak-base function.

Chelate resins: These comprise special functional groups (aminophosphoric, aminodiacetic, aminodioxime, mercaptan) that permit the selective retention of heavy metals from various effluents (zinc, lead, mercury, etc.), gas chromatographic separations of metals, and also the final softening of brine from the electrolysis process.

Resins for nuclear use: These involve products with a higher degree of purity than that of resins used in common operations. Among these are strong acid cation resins in H^+ form that are regenerated to 99%, and strong base anion resins in OH^- form with less than 0.1% of Cl^- .

Catalyzing resins: These conventional resins are used in a basic or acidic catalyst process (e.g., the inversion of glucose in the manufacture of liquid sugar). They could also be used with a metallic catalyst (e.g., a palladium resin for deoxygenation of demineralized water or sea water).

9.2.2 SPECIFIC APPLICATIONS

It is important to emphasize that the techniques related to ion exchange processes should not be used unless the raw water has been subjected to a form of preliminary treatment suited to its type, which must include the removal of suspended solids, organic matter, residual chlorine, chloramines, and so on. The continuous removal of heavy metals by ion exchange takes place in fixed-bed columns that are packed with cationic and/or anionic resins. The metals sorb onto the resins in exchange of hydroxide anions, protons, and/or light metal cations that are released into the solution. An ion exchange system can perform both heavy metal removal and neutralization of acidic water. Furthermore, ion exchange systems open the possibility of recovering heavy metals in the form of liquid concentrates. These concentrates can be either returned to the manufacturing process, or they can be

- Efficiently precipitated yielding small volumes of sludges for disposal or metal recovery
- Further processed directly to recover the metal(s) in solid and resaleable (reusable) form.

The higher the selectivity of a resin, the more strongly the metals are bound to it, and the more difficult it usually is to desorb them. This increases the consumption of a regenerant and hence the operating cost. Moreover, the resins are prone to fouling (poisoning) by organic substances [28]. Finally, as ion exchange resins are hydrocarbon based, their price is coupled with the price of crude oil and they are thus relatively expensive, with the price per kilogram ranging from USD10 to USD50 (prior to the year 2004). Therefore, in order to keep the operating cost sufficiently low, the ion exchange processes are usually applied only to effluents containing medium or low levels of heavy metals.

9.2.2.1 Nickel

The most commonly applied process for removal of nickel from wastewater is in the use of a strong acid cation resin. Unfortunately, this type of resin can only be applied if nickel is the only polyvalent metal ion in the wastewater. Consider a wastewater composed of nickel in the presence of ammonium molybdate. The nickel is most effectively recovered by the use of an aminophosphoric acid resin. The Russian-made chelating resin ANKF-80 used on a wastewater at pH 2 is approximately 19 times more effective than a conventional resin. Also available, but not as effective, is the Amberlite

XE-318, having an ion capacity of 34 g L^{-1} of resin. Another type of resin effective in nickel removal is a weak acid resin. This type of resin shows high selectivity for nickel ions even in wastewater polluted with organic carbon. A Wofatit CA-20 resin is the most effective weak acid resin manufactured and available. Another weak acid resin available is the Zerolit 236 possessing an ion capacity of 108 g L^{-1} of resin. The regenerant used for these resins is ammonium carbonate.

Strong acid resins such as Zerolit 525, Amberlite IR-20, and Amberlite 200 have ion capacities of 48, 31, and 30 g L^{-1} of resin, respectively. The regenerant used is again ammonium carbonate.

9.2.2.2 Copper

In the industrial production of copper, large amounts of acidic wastewaters are produced. There are mainly two specific types of resins applied for copper recovery. One resin is Dowex XFS-4195. This *N*-(hydroxyalkyl) picolyamines-based resin can be applied for very acidic wastewaters. Another resin, having the same base, is Dowex XFS-4196, which performs well for wastewaters of higher pH. The regenerant used in both cases is sulfuric acid.

Unfortunately, not all wastewaters can be purified of copper with ordinary ion exchangers. Wastewaters that contain organic ligand, for example, cannot be treated in this way because they form a coordination complex. Complex compounds having carboxylic acid groups such as tartaric, citric, and lactic acids will interfere with the efficiency of a standard ion exchanger. In these cases the stability for the copper complexes are lower. The chelating resin will successfully remove copper ions from such wastewaters.

9.2.2.3 Zinc

Zinc can be extracted from wastewaters as a Zn^{2+} cation or ZnCl_4^- anion. The zinc cation may be sorbed by a cation exchanger or a chelating resin and the anion by an anion exchanger. Zinc salts are present in wastewaters from, for example, the kaolin industry and the blowdown of cooling towers. For the kaolin industry, a strong acid resin may be employed for the removal of the Zn^{2+} cation, using sodium chloride as a regenerant. In the case of the cooling tower blowdown water, phosphoric acid resins such as Duolite ES-63 or Duolite TSAP-40 are commonly employed.

9.2.2.4 Mercury

As a metal, mercury is probably one of the worst water pollutants. The source of most mercury pollution is the wastewater produced from chlorine and alkali manufactures. Resins containing the thio group possess high affinity for mercury ions. The Imac-TMR resin is an example. Their operational capacity depends on the concentration of mercury present in the wastewater (see Table 9.6).

Other types of molecules that exhibit high affinity for mercury ions contain the $\text{R-S-C(NH)}-\text{NH}_2$ (isothiuronium) group, an example of which could be resin Srafion-NMRR. Another highly active chemical group is R-NH-C(S)-SH , the dithiocarbonate group, which is found in the resin Nisso-ALM-125. Regeneration using sulfuric acid is applied to recover mercury from the resin.

TABLE 9.6
Operational Capacity of a Resin to Uptake Mercury

Hg Concentration (mg L^{-1})	Capacity for Hg (g L^{-1} of Resin)
0.6	48
0.8	57
1.0	66
4.0	80
6.0	88
8.0	95
10.0	100

Another resin available is the Nisso-ALM-126 whose capacity can be increased by heating the resin to a maximum of 50°C. Regeneration is not feasible in this case. However, the mercury can be removed from the resin by roasting it. Strong base resins can also be applied for the removal of mercury from wastewaters. For acidic wastewaters within a pH range of 2.5–3.5, Wofatit SDW or Varion AD resins can be used. They possess the ability to remove up to 85% of the mercury. The use of a strong acid resin such as the Amberlite IR-120 could produce an effluent containing levels of 0.05 mg L⁻¹ of Hg²⁺ from the initial solution containing 10 mg of Hg²⁺ per liter of wastewater.

9.2.2.5 A Case Study

A typical and ubiquitous industrial operation known to have a metal-pollution problem is metal plating. The amount of electroplating process effluent encountered in an average size operation generally varies between 25,000 US gal day⁻¹ and 100,000 US gal day⁻¹. For the case design calculations, the wastewater flow of 48,000 US gal day⁻¹ (182.4 m³ day⁻¹) has been chosen. It is assumed to contain 20 mg Zn²⁺ L⁻¹, 30 mg Ni²⁺ L⁻¹, 40 mg CuSO₄ L⁻¹, and 130 mg CrO₃ L⁻¹. The latter chromium content eventually complicates the treatment system considerably as will be demonstrated in the design of the treatment facility. Removal of the basic metals from the given solution is considered as a major objective. Chromium is a valuable element and its recovery would be highly desirable. However, since it cannot be retained in its chromate form on the same cationic ion exchanger as all the other metals, a special sequence of additional two ion exchange operations would have to be added to the basic cationic one. A typical treatment system is outlined in Figure 9.8. The pH of the solution to be treated has a crucial effect on the uptake of metals from acidic solutions. The resin IRC-718 selected for the treatment process is more selective for metal ions and calcium interference is minimized at the optimum operation pH 4. Requirement for this pH level dictates the necessity of a pH adjustment in a tank that has to be placed prior to the sorption contact stage. Following the pH adjustment, the wastewater solution should be filtered to remove precipitates, particulate matter, and insoluble salts from the solution. The filtration step decreases the possibility of resin fouling.

The solution to be treated is pumped into two columns operating in a sequence. The whole arrangement could operate for five days until saturation of the bed. For practical reasons, it may be more convenient to regenerate the first column approximately half-way through this period, whereas the second one becomes first in their sequence. The newly regenerated column would be always

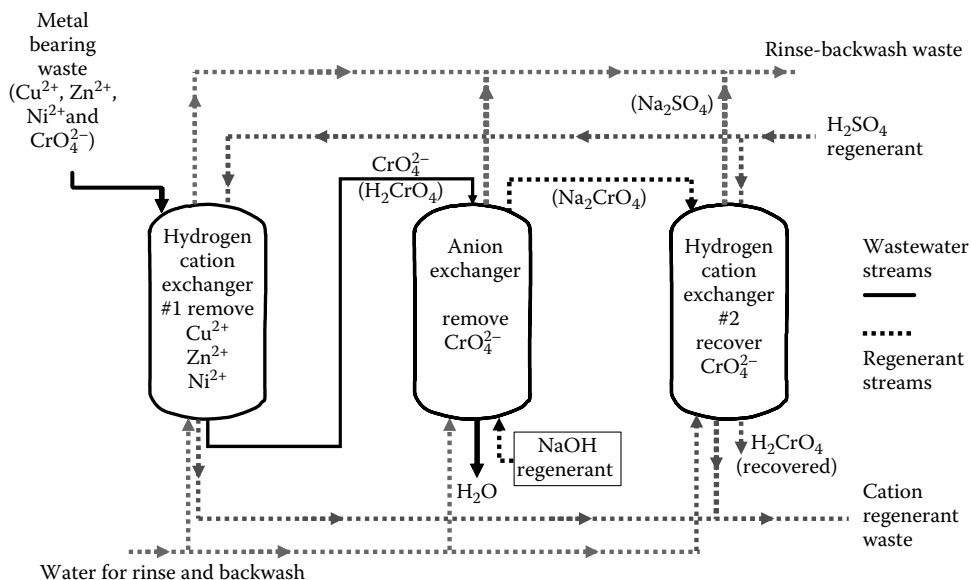


FIGURE 9.8 Ion exchange process: Schematic diagram of a case study.

phased in as a polishing second one in that sequence. This arrangement would require three columns, two operating whereas the third one would be on the regeneration cycle. The columns are designed to be backwashed to move any entrained solids under up-flow conditions. The partly fluidized bed expansion of 50% has been estimated for this operation. Regeneration is done with 5% of sulfuric acid. The operations of backwashing, regeneration, and rinsing are done *in situ*, in the same columns. The spent regenerant and rinse water from this first cationic exchange contain metal sulfates, $M_2(SO_4)_n$, and some sulfuric acid. They must therefore be neutralized in a separate operation and the metals precipitated prior to discharge to any receiving body.

9.3 REVERSE OSMOSIS

Reverse osmosis is based on the separation of the solvent from the influent waste stream by a pressure in excess of the osmotic pressure of the solution. The wastewater flows under high pressure through an inner tube made of a semipermeable membrane material. The purified solvent is removed from the outer tube, which is at atmospheric pressure (Figure 9.9) [29].

The disadvantages associated with reverse osmosis involve the sensitivity of the membrane. Organics as well as other impurities precipitate, which leads to membrane fouling. It is therefore necessary to have a consistent composition of the influent waste stream. Apart from the membrane sensitivity, the process also requires elevated pressures that drive up the operating costs of pumping.

9.3.1 PRINCIPLE OF REVERSE OSMOSIS

Reverse osmosis makes use of the properties of semipermeable membranes that allow water to pass through while solutes are retained except for certain organic molecules very similar to water (with a low molecular weight and strong polarity). If a concentrated saline solution is separated from a more dilute solution by such a membrane, the difference in chemical potential tends to promote the passage of water from a compartment with a low potential to that with a higher potential in order to dilute it (natural osmosis). To stop this diffusion, a pressure must be exerted on the “filtered” fluid. At equilibrium, the pressure difference established in this way is known as the osmotic pressure of the system (Figure 9.10).

A simple equation (9.1) relates osmotic pressure to concentration:

$$\Pi = \Delta C * R * T, \quad (9.1)$$

where Π is the osmotic pressure (Pa), ΔC is the difference in concentration in mol m^{-3} , R is the constant of an ideal gas = $8.314 \text{ (J mol}^{-1} \text{ K}^{-1})$, and T is the temperature in degrees kelvin.

Clearly, the smaller the molecule (i.e., the lower the molecular weight), the greater the osmotic pressure set up by the same difference in concentration. This explains why ultrafiltration leads to an osmotic backpressure that is much lower than that experienced with reverse osmosis.

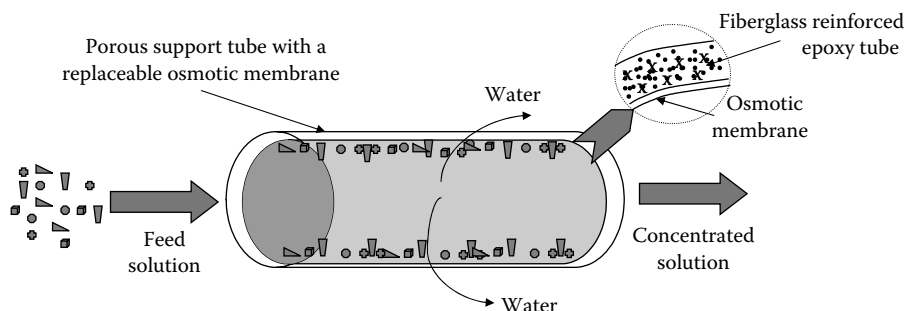


FIGURE 9.9 Tubular module section of a reverse osmosis operation.

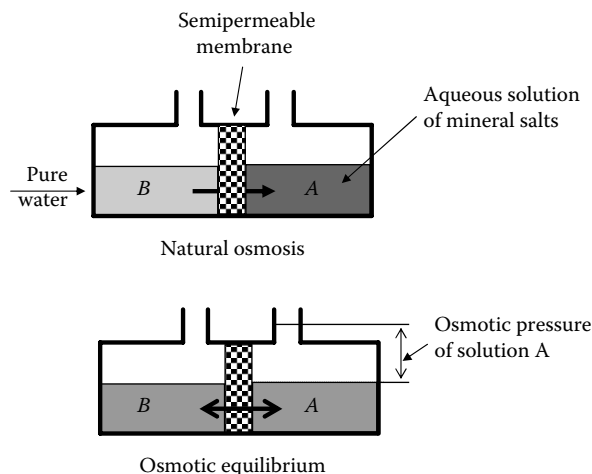


FIGURE 9.10 Osmosis phenomenon.

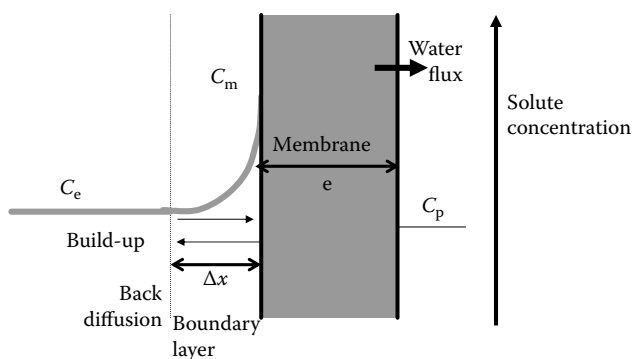


FIGURE 9.11 Concentration polarization during a reverse osmosis process.

In fact, to produce “pure” water from a saline solution, the osmotic pressure of the solution must be exceeded. In the same way, in order to obtain economically viable flows, at least twice the osmotic pressure must be exerted. For instance, for a brine containing several grams of salt per liter, pressures of 5–30 bar would be needed, and for sea water, pressures of 50–80 bar would be needed. A second phenomenon can amplify this effect.

As Figure 9.11 illustrates, when water is transferred, the molecules and ions retained by the membrane tend to accumulate along its entire surface, thereby increasing both the salinity actually “treated” by the membrane and the osmotic pressure that must be “overcome” in order to desalinate the solution. This results in higher energy costs, as well as in the risk of causing precipitation if the solubility product of one of the cation–anion couples is exceeded in the boundary layer all along the membrane.

This phenomenon is known as concentration polarization of the membrane and it is defined by the coefficient Ψ (Equation 9.2):

$$\Psi = \frac{C_m}{C_e}, \quad (9.2)$$

where C_m is the concentration of the liquid in contact with the membrane and C_e is the concentration of the liquid to be treated.

The concentration polarization phenomenon can be reduced to a minimum by maintaining a circulation flow across the upstream surface of the membrane. That limits the thickness of the boundary layer and facilitates the reverse diffusion of the rejected solutes; however, this also limits the fraction of desalinated water. This technique is used in industrial systems to maintain the coefficient Ψ between 1 and 1.4.

To describe the phenomena observed, best models call upon the laws of diffusion, water being considered dissolved by the polymer making up the membrane (water used for swelling the polymer); this water moves under the effect of the pressure gradient, whereas the salts move under the effect of their concentration gradient alone.

For a saline solution, the water and salt flux rates may be obtained by Fick's and Henry's laws for water (Equation 9.3) and for salts (Equation 9.4):

$$Q_p = K_p \frac{S}{e} (\Delta P - \Delta p) K_t, \quad (9.3)$$

where Q_p is the flow of water through the membranes, K_p is the membrane permeability coefficient for water, S is the membrane surface area, e is the thickness of the membrane, ΔP is the hydraulic pressure differential across the membrane, Δp is the osmotic pressure differential across the membrane, and K_t is the temperature coefficient.

Thus, the flow of water through the membrane is directly proportional to the effective pressure gradient, represented by the difference between the hydraulic and the osmotic pressure.

The coefficient K_t takes the viscosity of water into account. The latter decreases when the temperature rises. Therefore, the flow is greater when the temperature rises (2.5–3% difference per degree at about 15°C).

$$Q_s = K_s \frac{S}{e} (\Delta C) K_t, \quad (9.4)$$

where Q_s is the flow of salt through the membrane, K_s is the membrane permeability coefficient for solutes, S is the membrane surface area, e is the thickness of the membrane, ΔC is the ion concentration differential across the membrane ($C_m - C_p$ or $C_e * \Psi - C_p$), and K_t is the temperature coefficient.

The flow of salt is directly proportional to the gradient of concentration through the membrane; for a given membrane and a given solution, its value is independent of the applied pressure.

In practice, Table 9.7 summarizes the general tendencies in all reverse osmosis systems.

9.4 ELECTROCHEMICAL PROCESSES, ELECTROWINNING

Public concern over water contamination and the steep rise in heavy metal prices triggered both governmental and industrial activity in the removal and recuperation of heavy metals from domestic and particularly from industrial wastewater. As the world consumption of resources increases,

TABLE 9.7
General Tendencies in Reverse Osmosis Systems

	Product Flow Q_p	Product Salinity C_p
Pressure $\uparrow$	$\uparrow$	$\downarrow$
Temperature $\uparrow$	$\uparrow$	=
Salinity $\uparrow$	$\downarrow$	$\uparrow$
$\Psi \uparrow$	$\downarrow$	$\uparrow$

reserves will exhaust themselves even faster and the need for recycling is becoming more and more urgent. Traditionally, heavy metals are removed using precipitation (Section 9.1) or ion exchange methods (Section 9.2). Particularly, the most widely practiced precipitation, however, produces highly toxic sludge for which disposal is difficult and expensive. Electrolytic techniques can recuperate these metals from wastewater solutions either directly or when preconcentrated by ion exchange. Metals can then be profitably salvaged for resale and reuse. Six major electrochemical metal recovery methods will be discussed in detail: electrodialysis, forced flow, rotating cathode, mesh, packed bed, and fluidized bed recovery cells [25]. Generally, the capital costs for electrochemical processes range between two and three times the capital cost for a physico-chemical removal system. The operating costs are lower than physico-chemical systems due to the salvage value of the metal and the absence of chemical reagents [30,31].

9.4.1 BACKGROUND

In electrochemical processes, an electric potential is used to move charged ionic particles in solution from one medium to another [32] (Figure 9.12). For example, positively charged metal ions can be plated out on an electronegative cathode by applying a potential in an electrolyte solution. By varying the electric potential, metals can be plated out selectively. Problems in removing metals even in concentrations below 200 mg L^{-1} using electrolytic methods have been overcome, thus providing industries with the tools to reduce concentrations below government guidelines. The problems of dilute electroplating are due to the low mass transfer rate of migrating ions in solution. As Fick's law states, the mass transfer rate decreases with decreasing concentration gradient, resulting in lower rate at which metal plates on the cathode. As the plating-out rate decreases, so does the efficiency of the process. Furthermore, creation of hydrogen gas at the cathode surface due to the redox reaction creates an additional barrier for metal ions to plate on the cathode. These two problems can be solved by either having very large cathode surfaces (flow-through processes) or by increasing turbulence in the solution (flow-by processes). Mesh, packed bed, and fluidized bed cathodes are examples of flow-through cathodes, whereas forced flow and rotating cathodes are examples of flow-by processes [31,33]. Figure 9.13 represents a general metal (nickel) recovery treatment using an electrochemical cell process in conjunction with cation- and metal-selective exchangers.

9.4.2 FORCED FLOW CELL (FLOW-BY CATHODE)

A forced flow cell is characterized by a mechanical or physical agitation of the contaminated solution around the cathode. The agitation can be created either by intensive solution circulation by

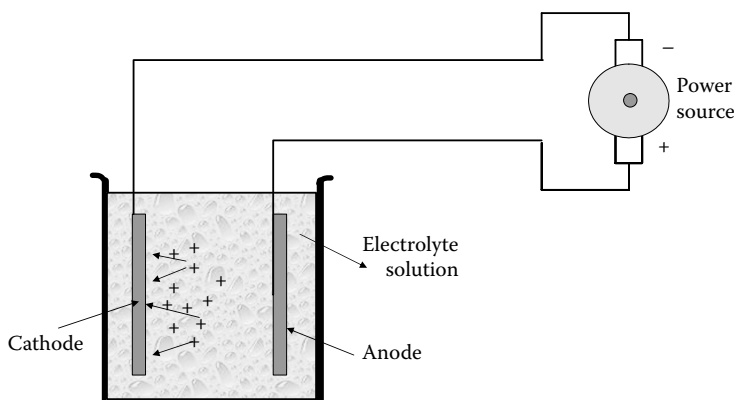


FIGURE 9.12 Electrochemical cell. Direction of travel of cations in an electrolyte solution applying a potential.

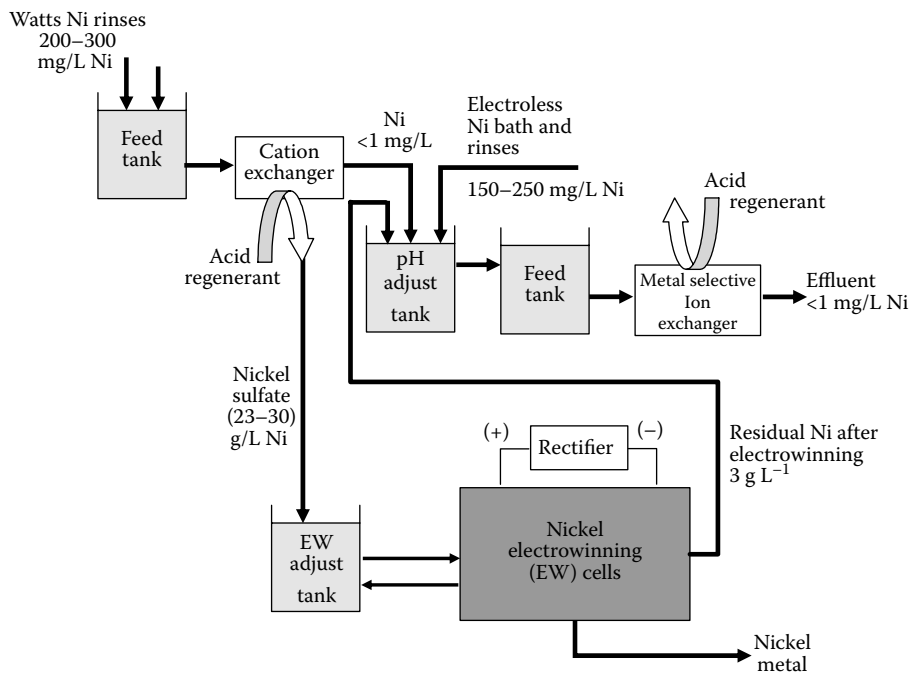


FIGURE 9.13 Nickel recovery treatment using an electrochemical cell process in conjunction with cation- and metal-selective exchangers.

using pumps or by venturies that introduce air bubbles at the bottom of the cell or by using static mixers. Since the process mechanism is simple, operating and capital costs are low. The metal is also easily recoverable since it plates out directly on flat immobile cathodes. However, the process suffers from low efficiencies when heavy metal concentrations are below 50 mg L^{-1} and cannot be made continuous due to the periodic removal of the cathodes for stripping. Owing to its low operating cost and good efficiencies above 50 mg L^{-1} , forced flow cells are often used in conjunction with preconcentration ion exchange or physico-chemical processes that are inexpensive and very efficient at concentrations below 50 mg L^{-1} . Figure 9.14 represents a general process scheme combining electrochemical, physico-chemical, and ion exchange treatments.

9.4.3 ROTATING CATHODES (FLOW-BY CATHODE)

As in forced-flow cells, the solution is agitated in order to increase the efficiency of the process. The difference resides in the fact that the agitation of the solution is accomplished by the brisk movement of the cathode. The most common arrangement is the rotation and impaction of cylindrical cathodes. Due to the process simplicity, the operating and capital costs are low. Furthermore, the process can be made continuous by impacting the rods together or by scraping the rods while in movement, and by collecting the metals as powder at the bottom of the cell. The process, however, still suffers from low efficiencies when concentration decreases below 50 mg L^{-1} and from possible breakdown problems due to the many moving parts. Figure 9.15 represents an electrowinning system using a rotating electrode to improve metal yields and allow economic metal recovery from solutions with lower metal concentrations.

9.4.4 MESH CATHODE (FLOW-THROUGH CATHODE)

Although flow-by cathodes are essentially two-dimensional cathodes, since their thickness is irrelevant, mesh cathodes and other flow-through cathodes are three dimensional due to the particulate

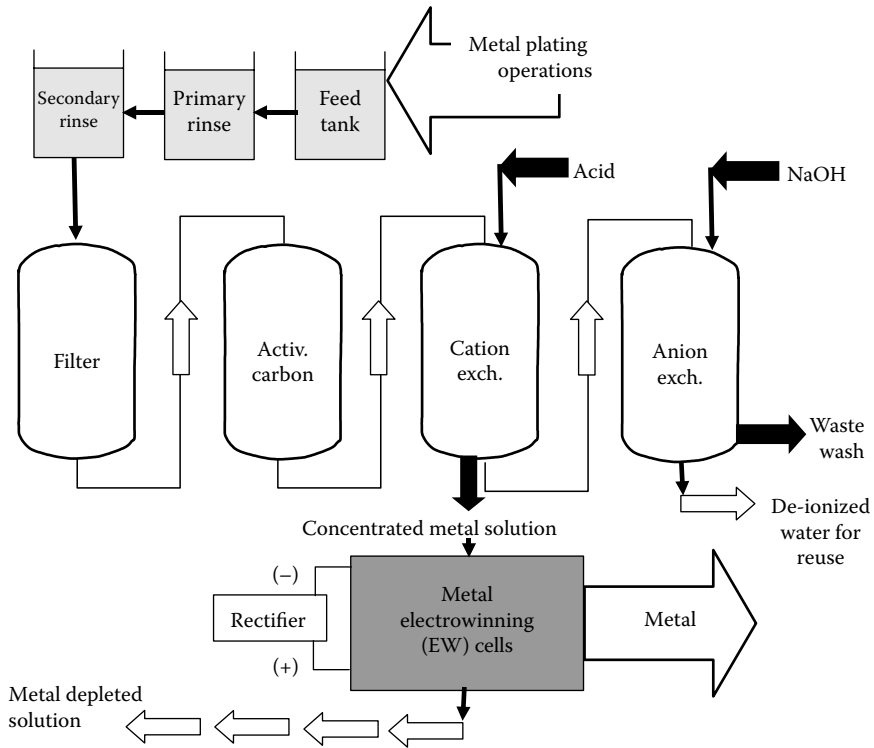


FIGURE 9.14 Ion exchange/physico-chemical/electrochemical combination.



FIGURE 9.15 An electrowinning system using a rotating electrode to improve metal yields and allow economic metals recovery from solutions with lower metals concentrations.

or fibrous nature of the cathode. Flow-through cathodes can also be distinguished by their very high real-to-apparent surface area ratio that can reach 10,000. The mesh cathode consists of an intertwining matrix of conducting fibers through which the contaminated solution flows and on which the metal deposits. The heavy metal can be recovered by using the mesh cathode as the anode in

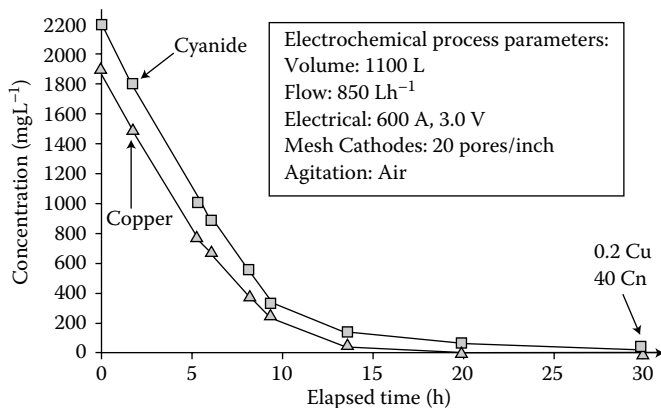


FIGURE 9.16 Kinetics of copper and cyanide electrochemical removal using a mesh electrode. The process parameters are indicated as a legend.

a conventional plating cell and by stripping the metal from the flat cathode. Mesh cathode cells have low removal limits (0.5 mg L^{-1}) and low capital costs due to the simplicity of the plating mechanism. As an example, Figure 9.16 represents the kinetics of copper and cyanide electrochemical removal (using a mesh electrode) from a heavy-metal-laden wastewater. It appears that after 30 h, the removal of 98% and 99% could be reached for cyanide and copper, respectively. However, some problems do exist in the operation of mesh cathodes: blockage in the mesh due to large particles being caught in the matrix or by unequal depositing of metals in the mesh, batch processing of the solution, and high operating costs due to the complicated process of recovering the heavy metals.

9.4.5 PACKED BED CELLS (FLOW-THROUGH CATHODE)

As in mesh cathodes, packed bed cells excel due to the high surface area of the cathode [34]. However, packed bed cathodes are made of packed metallic particles and not fibers such as in mesh electrodes. The particles are made of the same metal as the one being recuperated. The heavy metals plate out on the particle surface and are recuperated by either scraping off the metal from their surface or by melting them. Packed bed cells have the advantages in giving low residual metal concentrations (0.1 mg L^{-1}) and in the easy recuperation of heavy metals from the cathode. However, some inherent problems have made this process inaccessible to large industrial applications: high capital and operating costs due to the complicated mechanism, channeling in the bed, difficulties in scaling up of the process, high power consumption, and the batch processing of the solution.

9.4.6 FLUIDIZED BED CELLS (FLOW-THROUGH CATHODE)

Fluidized bed cells are being examined very closely due to their low removal limit (0.1 mg L^{-1}) [35]. Furthermore, some problems associated with packed bed cells are eliminated in fluidized flow. Fluidized bed cells differ from packed bed cells due to the circulating motion given to the particles by fluidizing the particle bed with the contaminated solution. Apart from low metal removal limits, fluidized bed cells also take advantage of easy metal recovery from the particulate cathode and, unlike packed bed cells, the possibility of making the process continuous by bleeding the particles in a recycle stream. Once again, the complexity of the process makes fluidized bed cells rather expensive. Problems with channeling and scale up and the high power consumption have also left the process at the experimental stage.

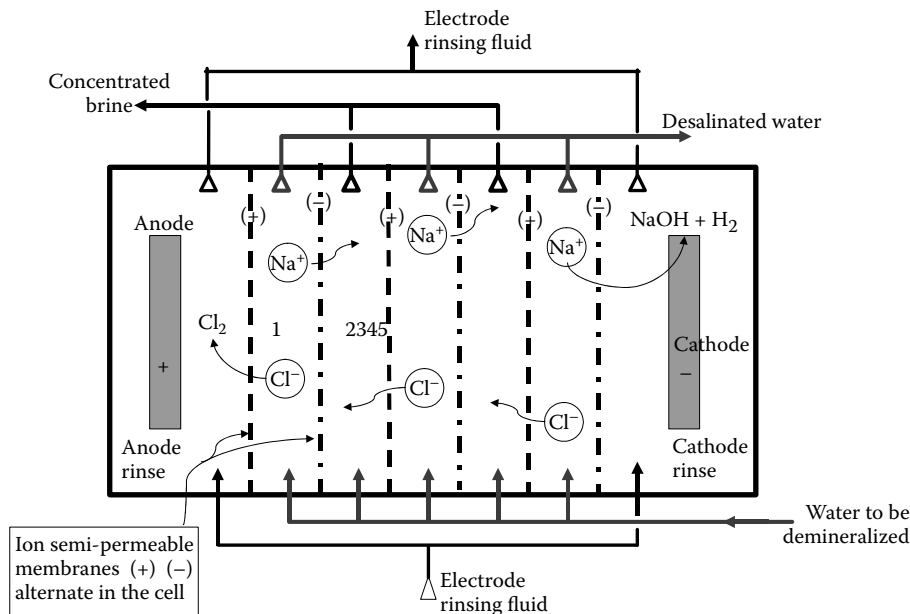


FIGURE 9.17 The principle of electrodialysis.

9.4.7 ELECTRODIALYSIS

Although electrodialysis does not remove heavy metals from solution, this process has proved very effective in concentrating heavy metals in the “brine” solution while simultaneously purifying the contaminated stream [36]. This is accomplished by separating a contaminated solution with an ion selective membrane and by applying an electrical potential across the system. As the potential is applied, cations (e.g., heavy metals in solution) migrate through semipermeable membranes toward the cathode, thus becoming concentrated in one solution compartment while the in-flow solution becomes purified. The concentrated solution can then be returned to an electroplating cell. Figure 9.17 represents the principle of the electrodialysis process. In the past, electrodialysis was limited by the strength, high cost, and efficiency of the cation selective membrane. However, continued improvements in membrane properties have resulted in day-to-day improvements of the electrodialysis process. The most attractive aspect of the process is the selective extraction performance of the membrane. For the present, its high removal limits (30 mg L^{-1}) and its relatively high power consumption make its industrial applications still rare.

9.5 ADSORPTION

Adsorption refers to the ability of certain materials to retain molecules (gas, metallic ions, organic molecules, etc.) on their surface in a more or less reversible manner. There is a mass transfer of sorbate from the bulk of liquid or gas phase to the surface of the solid. The solid sorbent thus acquires superficial (hydrophobic or hydrophilic) properties liable to modify the state of equilibrium of the medium (diffusion, flocculation) [37].

The adsorptive capacity of the solid depends on [38]:

- The developed surface area or specific surface area of the material. Natural adsorbents (clays, silica, etc.) possess specific surface areas that vary with the physico-chemical state of

the liquid medium (pH value, nature of the bound cations, surface saturation by organic molecules, etc.). Thus, certain clays such as bentonites (montmorillonite for instance) have a surface area that is accessible to most molecules and ranges from 40 to 800 m² g⁻¹. Their adsorptive capacity is quite variable but constitutes the main parameter in the regulation of transfers and in the mobility of elements in the natural environment. Industrial adsorbents (mainly activated carbon) can feature extensive surface areas (roughly between 600 and 1200 m² g⁻¹) that are characteristic of a very strong microporosity. Other adsorbents such as metallic hydroxides that are formed in the course of the coagulation–flocculation process also develop very large surface areas whose expanse is closely dependent on the pH value.

- The nature of the adsorbate–adsorbent bond, in other words, on the free energy of interaction (G) between the adsorption sites and that part of the molecule which is in contact with the surface. This energy is directly measurable in the case of gas adsorption. However, in a liquid medium, the calorimetric methods only record the differential enthalpy of adsorption that corresponds to the difference between the adsorption energy of adsorbed molecules and the desorption energy of bound water at the interface.
- The contact time between the solid and the solutes. At equilibrium, there is a dynamic exchange between the molecules of the adsorbed phase and those that remain in solution. Many theories have attempted to model the relation that exists between the number of molecules adsorbed (g g⁻¹, g m⁻², etc.) and the number at equilibrium. One of the most commonly employed theories in the field of adsorption on activated carbon is reflected in the Freundlich equation [39] (Equation 9.5) depicted in Figure 9.18:

$$\frac{X}{m} = K C_{\text{eq}}^{1/n}, \quad (9.5)$$

where X/m is the weight of pollutant retained per unit weight of the adsorbent, and C_{eq} is the equilibrium concentration of pollutant molecules in the aqueous phase. K and n are energy constants depending on the adsorbate–adsorbent couple at a given temperature, which is kept constant during the operation (isotherm).

In fact, hardly any modeling, no matter how “complex,” can adequately reflect the structure of the isotherm, and a fortiori explain the mechanisms of adsorption. The basic reason for this is that any surface is heterogeneous both as regards physical aspects and energy.

It is mainly the van der Waals-type attraction and the Coulomb electrostatic-type attraction that provided the basis for adsorption that is ultimately based in thermodynamics and reflected in the resulting affinity between the sorbate moiety and the sorption active site. For instance, it can be seen

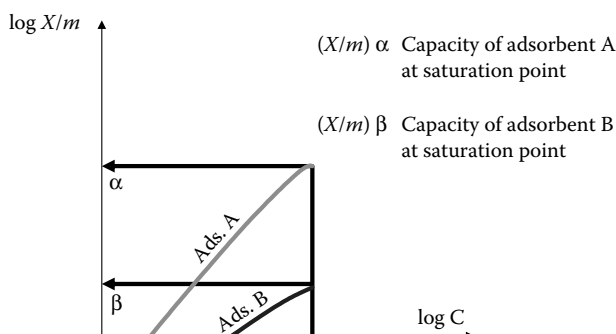


FIGURE 9.18 Freundlich isotherms.

that there is a strong affinity of aromatic molecules for the graphitic structure of carbon and a repulsion of the nonaromatic polar molecules.

9.5.1 MAIN ADSORBENTS

9.5.1.1 Activated Carbon

Experience shows that activated carbon has a broad spectrum of adsorptive activity, as most organic molecules are retained on its surface. The hardest to retain are the molecules that are the most polar and the linear ones with a very low molecular weight (simple alcohols, primary organic acids, etc.) [40]. Molecules that are slightly polar, generating taste and smell, and molecules with a relatively high molecular weight are for various reasons well adsorbed on carbon. It is interesting to note that, apart from these adsorbent properties, activated carbon can also provide a fine solid support for the growth of bacteria that are capable of breaking down a fraction of the adsorbed phase. In this combination, a part of the support is continuously being regenerated and capable of freeing sites, allowing new molecules to be retained. This combined action has successfully been used to enhance purification of certain types of wastewaters.

Activated carbon is available in two forms: powdered carbon and granular carbon. Powdered activated carbon (PAC) takes the form of grains between 10 and 50 μm and its use is generally combined with a clarification treatment. If it is added continuously to the water together with flocculating reagents, it enters the floc and is then extracted from the water with it. The PAC is about 2–3 times less expensive than granular activated carbon (GAC). The investment costs are low when the treatment involves only a flocculation/settling stage (an activated carbon feeder is all that is needed).

The physical characteristics of GAC vary considerably depending on the raw materials used to prepare the GAC (Table 9.8).

9.5.1.1.1 Main Applications

Activated carbon is used

- In the polishing treatment of drinking water or very pure industrial process water. In this case, the activated carbon will retain the dissolved organic compounds not broken down by natural biological means (self-purification of waterways): micropollutants and substances determining the taste and flavor of the water. The carbon will also adsorb traces of certain heavy metals.

TABLE 9.8
Physical Characteristics of GAC

Raw Material	Peat, Wood, Coconut, Anthracite, ...
Form	Crushed, extruded
Grain size ES (mm)	0.25–3
UC	1.4–2.2
Friability 750 strokes (%)	10–50
1500 strokes (%)	20–100
Bulk density (compacted)	0.25–0.55
Specific surface area (m^2g^{-1})	500–1300
Ash content (%)	4–12

Note: ES: effective size.

- In the treatment of industrial wastewater, when the effluent is not biodegradable or when it contains certain organic toxic elements [41,42] that rule out the use of biological techniques. In this case, the use of activated carbon often allows the selective retention of toxic elements and the resultant liquid can thus be degraded by normal biological means.
- In the “tertiary” treatment of municipal and industrial wastewater. The carbon retains dissolved organic compounds that have resisted upstream biological treatment, and thus removes a large part of the residual COD.

9.5.1.1.2 Adsorptive Capacity of Carbon

GAC is used as a filter bed through which the water to be treated passes, leaving behind its impurities that are thus extracted methodically: the water, as it progressively loses its pollutants, encounters zones of activated carbon that are less and less saturated and therefore more and more active. Whether treatment using activated carbon is economical or not largely depends on the adsorptive capacity of the carbon, expressed in grams of retained COD per kilogram (or volume) of activated carbon, which characterizes the “carbon requirements” for a given result [43]. For a given polluted water–carbon system, this capacity depends on the following [44,45]:

- *The depth of the bed:* The deeper the bed, the easier it deals with extended adsorptive fronts inside the bed without excessive breakthrough leakage—while still ensuring thorough saturation of the upper layers.
- *The exchange rate:* The experience shows that three volumes of water per volume of carbon per hour can seldom be exceeded when treating high levels of pollution. In the case of drinking water, in which the content of adsorbable products is very low, any decision as to the economic optimum has to take the high investment costs into account, with the result that higher bed volumes are used: 5–10 vol vol⁻¹ h⁻¹, with a smaller degree of carbon saturation.

The theory only gives an indication of the trend of the laws of adsorption. It still remains indispensable to call upon the experience of the expert and to carry out dynamic tests on columns of sufficient size so that results can be extrapolated.

A compact bed has three functions:

- *Filtration:* This must often be reduced to a minimum in order to avoid clogging of the bed which is unavoidable without efficient washing systems to break up the layers completely after each cycle. In addition, the carbon tends to extract adsorbable products from the floc with which it is in contact, causing premature saturation. That is why it is often advisable to use sand filtration as a preliminary clean-up step to remove suspended matter particles.
- *Medium for supporting microbial growth:* This phenomenon can contribute to the process of purification, but can also be very dangerous if not properly controlled (anaerobic fermentation gives off odors, clogging of the bed, etc.).
- *Adsorption:* This must remain the basic role of the carbon.

There are three possible arrangements:

- *Simple fixed beds:* This technique is widely used in drinking water treatment.
- *Fixed beds in series:* A series of several columns, which are regenerated by permutation, are used (Figure 9.19). Thus, a countercurrent extraction system is organized.
- *Moving beds:* These usually make use of the countercurrent principle (Figure 9.20). The base of the bed can even be fluidized.

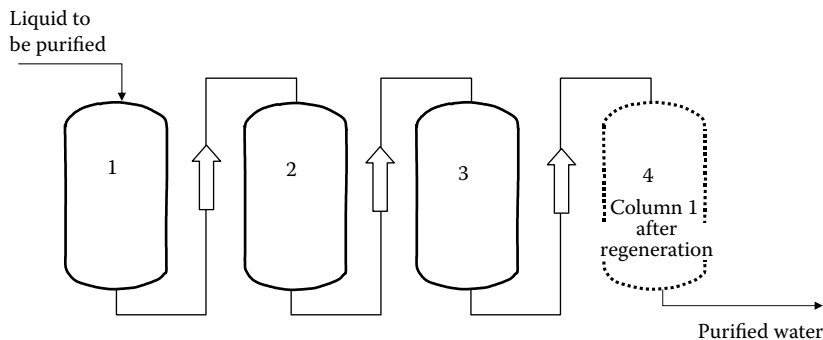


FIGURE 9.19 Diagram of fixed bed in series.

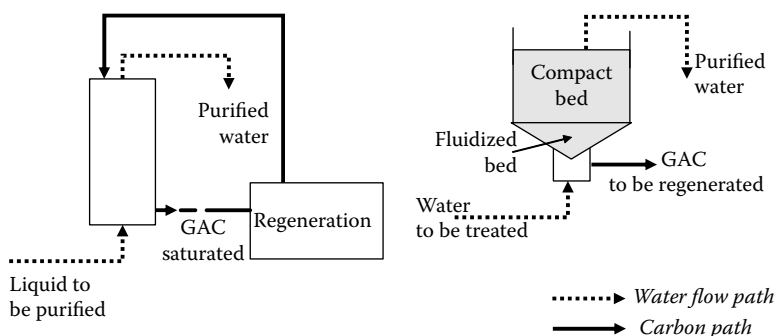


FIGURE 9.20 Diagrams of moving beds.

9.5.1.1.3 Regeneration of the Activated Carbon

Activated carbon (such as artificial adsorbents) is an expensive product. In most cases the cost of replacing the saturated carbon would be prohibitive [46]. It should therefore be regenerated, and three methods have been developed for this purpose:

- *Steam regeneration:* This method is restricted to regenerating carbon which has only retained a few very volatile products. However, steam treatment can be useful in unclogging the surface of the grains and disinfecting the carbon.
- *Thermal regeneration:* By pyrolysis and burning off of adsorbed organic substances. To avoid igniting the carbon, it is heated to about 800°C in a controlled anoxic atmosphere. This is the most widely used method and regenerates the carbon very well, but it has two disadvantages: (1) It requires considerable investment in a multiple-hearth furnace, a fluidized bed furnace, or a rotary kiln. The furnace must have monitoring devices for its gaseous atmosphere and temperature, a dewatering system at the inlet, and a carbon quenching system at the outlet. (2) It causes high carbon losses (7–10% per regeneration), so that after 10–14 regenerations, the GAC volume will, on average, have been entirely replaced. The use of electrical heating (infrared furnace, induction furnace) reduces these losses. However, these methods, which are expensive, are only used for the recovery of costly metals.
- *Chemical regeneration:* The advantage of this process is that for the same capital outlay, only minimum carbon loss occurs (about 1% of the quantity treated). However, the use of chemical reagents for regeneration (alkaline reagents, solvents) leads to the formation of eluates from which the solvent must be separated by distillation. The pollutants are then destroyed by incineration unless they can be recovered. The process is less widely used than thermal regeneration.

- *Biological regeneration*: This method of regeneration is somewhat complicated due to the necessity of controlling the microbial action and thus it is rarely applied on an industrial scale.

9.5.1.2 Other Adsorbents

Apart from the activated carbon, new adsorbents have been developed:

- *Inorganic adsorbents*: Alumina [47,48] and other metallic oxides [49]: they can have a very large specific surface area, but these solids adsorb more selectively than carbon. Their capacity depends very much on the pH value and their mesoporosity. Below the isoelectric point only negatively charged molecules are adsorbed on positively charge sites. In the current state of their development, these adsorbents are not competitive with activated carbon. However, some of these solids such as the alumina or the ferric oxyhydroxides have the advantage of removing arsenic, fluoride, phosphates, nitrates, and so on.
- *Organic adsorbents*: Macromolecular resins with specific surface areas of between 300 and 750 m²g⁻¹ [50,51]: their adsorptive capacity is generally lower when compared with that of activated carbon. However, these resins can have special adsorptive properties and are often easier to regenerate (low binding energy). Here the “scavengers” should also be mentioned, which are highly porous anionic resins. However, these resins have a smaller specific surface area and their action on polar substances (such as humic acids and anionic detergents) is partly due to their ionic charge, which distinguishes them from other adsorbents.

9.6 OXIDATION–REDUCTION

Some substances are found either in oxidized or in reduced form, and are converted from one to the other by gaining electrons (reduction) or by losing electrons (oxidation). A system comprising an acceptor and a donor of electrons is known as an “oxidation–reduction” system.

Oxidation–reduction reactions are used in the treatment of water for disinfection and to convert an element from its dissolved state to a state in which it may be precipitated (Fe, Mn, sulfur removal, etc.) [52].

The definition and monitoring of the pH value in a reaction is very important. Eh–pH diagrams exist in handbooks to represent the state of various forms of elements and their evolution depending on the pH and the redox potential, in order to

- Convert an element from its dissolved state to its gaseous state (e.g., denitrification)
- Break down a substance into several simpler substances, the presence of which is acceptable in water (e.g., phenols, etc.)
- Break down a nonbiodegradable substance into several simpler substances, which can be removed by bacterial assimilation during a later treatment phase (e.g., micropollutants).

Oxidation can take place by means of chemotrophic bacteria such as in the oxidation of iron and manganese, the oxidation of sulfur compounds, the oxidation–reduction of nitrogen compounds, and methane-forming reduction [53–56].

9.6.1 MAIN OXIDATION TECHNIQUES

This mainly concerns the following industrial waters and effluents:

Using oxidizing reagents:

- Cyanide-laden waters from electroplating or gas scrubbing
- Hydrazine-laden condensates: oxidation by H₂O₂ catalyzed on specific resins

- Nitrite baths from electroplating: oxidation by $\text{H}_2\text{O}_2 + \text{Cu}^{2+}$ (Fenton reagent), NaClO , or H_2SO_5
- Solutions of thiosulfates oxidizable from H_2O_2 .

Using air or oxygen [23,57]:

- Spent caustic soda, rich in S^{2-}
- Waters from pickling, loaded with Fe^{2+}
- Uranium leachates U^{4+} .

Most of these reactions present a high enough potential and rapid enough kinetics to permit regulation except in the case of thiosulfates. If other less dangerous reducing agents coexist, a posteriori monitoring to limit the over consumption of a costly oxidizing agent, as in the case of cyanide-laden effluents from gas scrubbing, is considered adequate. The use of air and oxygen in the equipment known as “oxidizers” requires high temperatures and pressures in order to achieve adequate kinetics and efficiency.

Ozone can also be used for oxidation reactions, especially for

- Effluents containing low CN or phenol concentrations
- Effluents from methionine units or those containing refractory compounds.

9.6.1.1 Application: Treatment of Cyanides

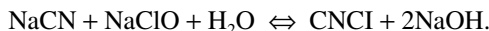
The oxidation of cyanides in an alkaline environment theoretically comprises two successive stages. The first one, in which there is practically no toxicity, is the cyanate state and then the nitrogen and bicarbonate state. Powerful oxidizing agents employed are sodium hypochlorite, chlorine, and permonosulfuric acid (Caro's acid). In practice, for economic reasons, only the first stage is employed.

First stage (cyanates):

The overall reactions that come into play are

- Using sodium hypochlorite: $\text{NaCN} + \text{NaClO} \rightleftharpoons \text{NaCNO} + \text{NaCl}$
- Using chlorine gas: $\text{NaCN} + \text{Cl}_2 + 2\text{NaOH} \rightleftharpoons \text{NaCNO} + 2\text{NaCl} + \text{H}_2\text{O}$
- Using Caro's acid: $\text{NaCN} + \text{H}_2\text{SO}_5 \rightleftharpoons \text{NaCNO} + \text{H}_2\text{SO}_4$.

The first two reactions occur almost instantaneously when the pH level is above 12, but the reaction speed drops rapidly if the pH level falls (critical threshold: pH 10.5). Whatever the pH level, an intermediate compound that is formed is cyanogen chloride CNCl , which is just as dangerous as hydrocyanic acid:



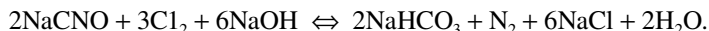
With a pH level starting at 10.5, however, cyanogen chloride is hydrolyzed the moment it is formed according to the reaction:



With Caro's acid, an adequate reaction speed is observed for pH level above 9.5.

Second stage (nitrogen):

The breakdown of cyanate into nitrogen occurs according to the reaction:



It also takes place at the pH level of 12, but requires three times the amount of reagent and a reaction time of about 1 h as it is impossible to regulate the potential.

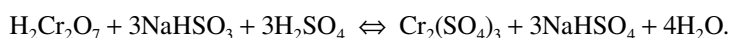
9.6.2 MAIN REDUCTION TECHNIQUES

The most common examples involve the reduction of oxygen, that of hexavalent chromium [58], as well as the destruction of residual oxidizing agents employed in disinfection. It is also necessary to mention the reduction of nitrites in the process of surface treatment (sulfamic acid or NaHSO_3).

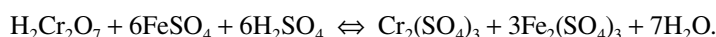
9.6.2.1 Application: Reduction of Hexavalent Chromium

The reduction of toxic hexavalent chromium into trivalent chromium which is less toxic and can be precipitated in the form of hydroxide occurs in an acid medium through the action of sodium bisulfate or ferrous sulfite.

Using sodium bisulfite:



Using ferrous sulfate:



The first of these reactions occurs almost instantaneously when the pH level is below 2.5, but the reaction speed falls rapidly when the pH level rises (the critical threshold is at pH 3.5).

The reduction of ferrous iron has fewer restrictions and may occur with a pH level below 6, with monitoring. It is less used because a significant amount of hydroxide sludge is produced during the final neutralization stage.

9.7 LIQUID–LIQUID EXTRACTION

The liquid–liquid extraction process is a basic operation that allows a component (solute) to be extracted from an inert liquid by another liquid known as a solvent [59]. The liquid phase 1 is a homogeneous mixture. The solvent must not be miscible with one of the two initial compounds. The inert compound and the solvent are usually not miscible. Liquid–liquid extraction is also governed by the laws of mass transfer and it is necessary to determine features that favour exchange, such as maximum interfacial area, wide concentration difference, and a notable transfer (or extraction) coefficient. There are two main types of industrial equipment employed in the liquid–liquid extraction process [60]:

- Contactors with several separate stages in series. At each stage, the functions of dispersion followed by separation of the two phases take place in two successive units: the mixing–settling tank and the hydrocyclone–settling tank.
- Differential contactors in which one phase is dispersed into the other on a countercurrent basis. Following this, the phases are separated in the two ends of a vertical column (Figure 9.21). The method of dispersion of the two phases may be by gravity, mechanical stirring, pulsation, etc. Spinning mechanical countercurrent contactors (Podbielniak) proved to be extremely efficient—for the price and elevated energy consumption.

Liquid–liquid extraction is used for phenol removal [61] from spent caustic soda from refineries using gas oil as a solvent. The efficiency of phenol removal reported was high (90–95%) when pulsed columns with perforated trays were used.

9.8 WETLAND METAL MINERALIZATION

A broadly accepted definition of a wetland is “an area that meets one or more of the following conditions: (1) areas supporting predominately hydrophytes, (2) areas with predominately undrained hydric soil producing anaerobic conditions, and (3) areas with a nonsoil substrate” [62]. Figure 9.22 pictures a constructed wetland (CW). Wetlands are also ephemeral in that they depend on

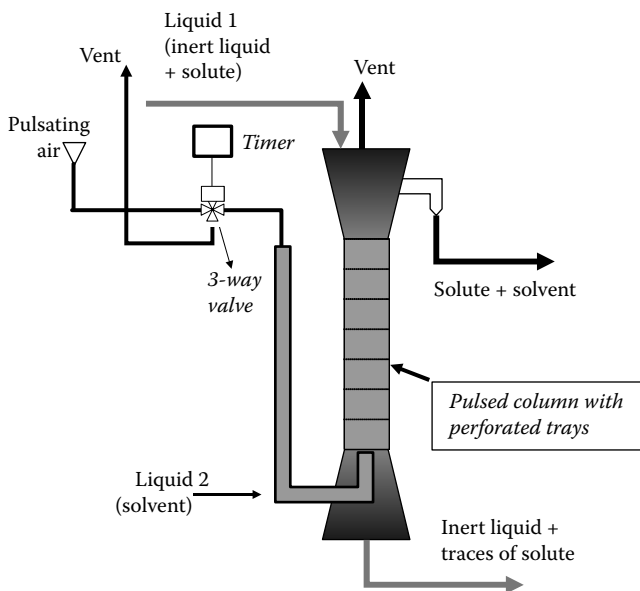


FIGURE 9.21 Diagram of a pulsed column liquid-liquid extraction.

perturbations to their environment in order to exist [63]. Without these disturbances, wetlands will eventually dry up and become stable soil substrate for other terrestrial ecosystems. It is this dynamic property of wetlands that makes them suitable for the treatment of polluted wastewaters because they have the capacity to absorb and smooth variations in hydrological input and reduce substantial concentrations of pollutants. Wetlands have also shown incredible tolerance to metals [64,65] and their ability to accumulate metals such as iron and manganese has been known for centuries. There are generally two types of CWs: (1) free water surface (FWS) and (2) subsurface flow (also referred



FIGURE 9.22 A constructed wetland.

to as vegetated submerged bed types, root zone method, microbial rock filters, and hydrobotanical systems). In engineering terms, both can be referred to as attached growth biological reactors. The FWS wetlands are constructed so that an exposed area of water will always exist, and also so that mixing will lead to oxygenation of the surface sediments. These wetlands have the disadvantage that they usually require some form of primary treatment to their influent waters [66]. The subsurface flow wetlands (SFWs) are the most common for treating metal-rich wastewaters. They are designed with an organic, porous medium and gradual slope so that no FWS exists, and so that the saturated conditions and organic matter decomposition lead to anoxic sediments. The lack of a FWS also has the advantage of avoiding odor and insect vector problems. If effluent acidity is a problem (as it always is in an acid amine drainage (AMD) and can sometimes be for industrial processes), then the SFW is very advantageous because it can be underlain with crushed limestone which, under the anoxic conditions, can slowly release alkalinity without becoming armored by metal precipitate coatings which would otherwise occur under oxic conditions [67]. Furthermore, SFWs are also advantageous compared with FWSs because they usually require less preliminary treatment [66].

9.8.1 ELEMENTS OF DESIGN

CWs are attempts at replicating and optimizing natural ecosystems. They are essentially systems that incorporate microbial, planktonic, invertebrate, soil, and hydrophytic components into a dynamic ecosystem [68,69]. For the purpose of CWs though, designers are usually only interested in three components: (1) vegetation; (2) microbes, algae, and microbially mediated processes; and (3) substrate conditions.

9.8.2 VEGETATION

Many plant species have been used in CWs. These include (most common to least) *Typha latifolia* (cattails), *Scirpus validus*, *Scirpus robustus* (bulrush), *Phragmites communis* (common reed), *Leersia oryzoides* (cutgrass), and *Lemna minor* (duckweed). Plants in CWs generally play two roles: (1) their roots provide increased surface area for the attachment of microbes and epiphytes, and (2) by their hydrophytic nature, wetland plants have the capability to transport oxygen down into their roots where some leakage occurs through radial oxygen loss, thus oxygenating the surrounding anoxic substrate. Although it may seem deceiving due to their dominant presence in wetlands, the plants themselves only account for at most ~1% of the total heavy metal removal via uptake [70]. Most of this removal occurs in the plant root tips, which is not advantageous if plant harvesting is a desired method for permanent metal removal, as roots remain in the substrate after harvesting. Another important function of emergent plants is that they accelerate the establishment of the necessary microbial population to less than a year, compared with almost two years without vegetation [71]. The most important role of emergent vegetation in the CW is their ability to transport oxygen into the anoxic sediment. This function is necessary to support aerobic microorganisms and remove dissolved metals through oxidization. Transport results from thermoosmosis of gases that requires a special plant morphological structure called aerenchyma, but does not actually require physiological activities. The oxygen-transporting capabilities of wetland plants vary among species. Studies have shown that *Typha* can transport the most with mixed assemblages following in the sequence [72]:

Typha latifolia > *Juncus effuses* > *Solanum americanum* > *Eleocharis quadrangulata*.

Not only do *Typha* exhibit the greatest capacity to transport oxygen, but they also concentrate most metals in their roots. Meiorin et al. [73] found *Typha* to accumulate 447–1220 mg kg⁻¹ dry weight of Mn in much larger concentrations than other species studied. Furthermore, the rhizospheres of *Typha* were found to be extremely conducive environments for aerobic heterotrophs such as *Thiobacillus* [74], which are essential for metal removal. Overall then, the literature indicates that *Typha* species might be the most appropriate wetland plants for heavy metal removal.

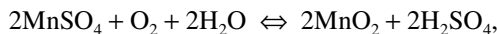
Some studies have also focused on the metal removal by *Sphagnum* species which, at times, can be substantial [65]. However, since the removal capacities of this plant are directly linked to its cation exchange capacity [75], which eventually becomes saturated [76], and *Sphagnum* species have a very low net productivity and so are dependent on outside sources for nutrients [75], their use in CWs does not promise sustainable heavy metal removal.

9.8.3 ALGAE, MICROBES, AND MICROBially MEDIATED PROCESSES

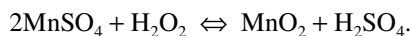
Algae and microbes are by far the most abundant living organisms in a wetland. The microbial population can sometimes reach 10^{10} mL^{-1} in organic sediments that are ubiquitous in wetland ecosystems [77]. The processes by which algae remove metals are bioaccumulation, biosorption, and either aerobic or anaerobic biologically mediated deposition by mineralization. The capacity of microbes and algae to sequester heavy metals or to cause their removal from solution is measured not only by the percent of metals retained, but also by the bioavailability of these metals in the marsh system after being removed from solution. Therefore, the ideal mechanism for heavy metal removal would be one where the removed metal could not re-enter the solution phase or the biota.

The metal accumulation capacity of certain algae is a remarkable phenomenon in nature. Their ability to sequester metals from solution was first noticed in the early 1970s when it was observed that lagoon effluents from lead/zinc mining and milling operations were causing dense mat-like growths of algae in receiving streams [78]. These algal growths were irregularly dense partly because the receiving waters were so polluted with heavy metals that the normal competitors of algae were practically eliminated.

The microbially mediated reactions can be broken down into those that occur in aerobic sediments and those that occur in anaerobic sediments. In aerobic regions, heterotrophic microbes such as *Arthrobacter*, *Pseudomonas*, and *Citrobacter* can mediate the following reaction [79]:

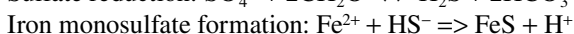
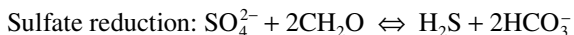


whereas *Metallogenium* mediates another reaction:



The overall effect is the precipitation of the insoluble Mn oxide into the sediments where it will hopefully remain. Another metal removal reaction results from the microbial decay of organic matter that promotes the formation of NH_3 and HCO_3^- , which increase the pH and cause hydroxide and Mn and Fe oxyhydroxide formation and consequent precipitation in aerobic zones [80]. These microbially mediated reactions are further enhanced by the fact that other dissolved metals adsorb onto the metal oxyhydroxides and are also precipitated from solution. In the latter adsorption reaction, Mn oxyhydroxides are more important than Fe oxyhydroxides [80] and there are many different bacteria that can oxidize Mn [77], making the removal of Mn by this process very important. Moreover, the formation of oxyhydroxides, especially those of Al [81], is not favored under acidic conditions, which also emphasizes the importance of the buffering limestone underlayer of SFWs to this oxidation reaction. Finally, Giblin et al. [82] found that Fe, Pb, and Mn were trapped in the sediments in a form that was unavailable for reuptake into the biota or resuspension back into solution, so these metals are, for the most part, permanently removed by the above processes.

In SFWs, the most important microbially mediated process to remove heavy metals is the anaerobic formation of H_2S . In anoxic regions, bacteria such as *Desulfovibrio* oxidize organic matter using sulfate as the electron acceptor and reducing it to H_2S . Some of the important chemical reactions include [69]:



Pyrite formation: $\text{FeS} + \text{S}^0 \Rightarrow \text{FeS}_2$

Pyrite formation: $\text{Fe}^{2+} + \text{H}_2\text{S} + \text{S}^0 \Rightarrow \text{FeS}_2 + 2\text{H}^+$

Pyrite formation: $\text{Fe}^{2+} + \text{HS}^- + \text{S}_x^{2-} \Rightarrow \text{FeS}_2 + \text{S}_x^{2-} + \text{H}^+$.

The formation of pyrite is better than Fe oxyhydroxides because pyrite accumulates within the organic substrates and is less likely to form surface deposits or be washed out during storm events [69]. Two of the biggest advantages of sulfate reduction are that it produces alkalinity and also that it is not constrained by accumulation limits or toxic effects. Pyrite is also negligibly soluble in acid or neutral water, so the formation of this mineral represents a long-term, sustainable mechanism for removing Fe from solution. However, the importance of sulfate reduction in heavy metal removal depends on the availability of sulfate in the influent waters and also on the type of metal sulfide complexes formed. The latter issue is unclear in the literature as Fe sulfides are the only complexes that have been extensively studied, whereas other metal complexes have been mentioned but their formation mechanisms were not included.

9.8.4 SUBSTRATE CONDITIONS

Many different substrates have been used in CWs. The overall goal of the substrate in an SFW is to provide nutrients and support for vegetation, while at the same time it must be porous so as not to inhibit lateral hydrological flow. The substrate can also have certain functions in metal removal because of its sorption properties. The best-known example of this is the use of *Sphagnum* as a substrate [65,75]. However, the performance of *Sphagnum* is limited because it does not have a very high nutrient status and because its sorption sites eventually become saturated. Another study, which investigated the sorption of Pb onto particles [83], reported that the amount of organic matter in the particles was the key factor limiting sorption. Therefore, it appears that the most appropriate substrate for metal removal in CWs requires a high percent of organic matter content. This is advantageous because wetlands themselves can contribute up to 67% of their annual net primary productivity to the sediments [70], replacing thus consumed sorption sites. The most frequently used substrate for treating AMD has been mushroom compost, which has a very high organic matter content (1–3%), combined with crushed limestone. Mushroom compost is a byproduct of the mushroom-growing industry and is formed by the anaerobic composting of a mixture of hay, manure, and agricultural wastes. Brodie et al. [71] evaluated the performance of several substrates but did not include mushroom compost. They found that there were no significant differences between the metal removal efficiencies of different substrates (soils included natural wetland, acid wetland, clay, mine spoil, and pea gravel). Except for the two natural wetland soils, none of the substrates investigated by Brodie et al. [71] could be used for long-term projects because of their low nutrient status. Furthermore, these results were difficult to interpret due to inconsistent experimental hydrologic flow rates. Therefore, further work regarding the effect of substrate type on metal removal should consider more commonly used substrates, especially mushroom compost.

9.8.5 METAL REMOVAL EFFICIENCIES

There are many publications that cite metal removal efficiencies of wetlands (Table 9.9). Unfortunately, these citations cannot contribute to further understanding of the complex process of heavy metal removal because very few concurrently give information on the respective wetland parameters. The removal efficiencies for the wetlands studied here range from 100% for Fe, Cu, or Pb to 0.6% for Cd.

The relevant literature [71,74,84,85] seems to agree that in terms of substrate and plant species selection, high organic matter is important in the substrate and that *Typha* species are associated with high metal removal rates. Furthermore, the metal removal efficiencies decrease with increasing

TABLE 9.9
Heavy Metal Removal Efficiencies of Various Wetlands and CWs from the Literature

References	Removal Efficiency (%)								
	Cd	Cr	Cu	Pb	Hg	Zn	Fe	Mn	Ni
[99]	50–90	50–90	50–90	80–95	50–90	50–90			
[82]	20–35	20–50	60–100	55–100		20–45	60–100	55–60	
[73]		40–53	5–32	30–83		6–51			12–32
[100]			99	94		98	86		
[80]			92						84
[80]	0.3		14			5.8	70	0.7	

Note: The removal efficiencies for each metal (calculation of removal efficiency assumed to be $(([\text{in}] - [\text{out}])/[\text{in}]) \times 100\%$).

flushing rate, wetland depth, and for some metals, with wetland area, experiment duration, and temperature. On the other hand, Mn removal increased with longer experiment durations. Some other wetland characteristics that are important to metal removal are length-to-width ratio, which increases with increasing Fe removal, and limestone, which also significantly improved Fe removal. The results also suggest that costs can be reduced by building shallower wetlands with natural substrate conditions (except for a little limestone). These financial implications might also enhance the capabilities of CWs as a low-tech alternative to heavy metal abatement of wastewaters.

9.9 BIOSORPTION

Metal accumulation has been demonstrated in a significant number of microorganisms (bacteria, algae, yeasts, and fungi) and this phenomenon is associated with a wide spectrum of microbial activities. Leaving aside the metabolically mediated metal sequestration by living microbial cells (*bioaccumulation*), which has been studied particularly from toxicological point of view, it has been observed that some microbial cells tend to bind metals even when they are dead and metabolically nonactive (Table 9.10). This type of metal uptake, termed *biosorption*, is usually rapid and sometimes very high, which makes it particularly interesting from the application point of view [86]. The metals may be bound in the biomass through a variety of mechanisms: adsorption, ion exchange, coordination, complexation, chelation, and microprecipitation seem to occur to a varying degree [87,30].

The metal-binding chemical groups of the biological materials include carboxylate, phosphate, hydroxyl, sulfhydryl, and amines, present in durable and decomposition-resistant cell walls [88,89].

TABLE 9.10
Metal-Binding Capacities of Selected Biomass

Biomass Species	Biosorbent Capacity (meq g ⁻¹)	References
<i>Sargassum natans</i>	2–2.3	[101]
<i>Ascophyllum nodosum</i>	2–2.5	[101]
<i>Rhizopus arrhizus</i>	1.1	[87]
<i>Eclonia radiata</i>	1.8–2.4	[102]
Peat moss	4.5–5	[103]
Commercial resins	0.35–5	[104]

The pH of the metal-bearing solution can play a critical role in influencing the metal-sequestering ability of the biomass materials [90–92].

Earlier patents awarded for the application of biomaterials in metal concentration indicate the technological potential of the biosorption phenomenon [93–95]. The packed-bed contacting column appears to be the most effective mode of bringing together the metal-bearing solution and biosorbent material [96]. Most often it is possible to wash the resulting metal-saturated biosorbent in the same column, releasing the deposited metal in a small volume of “desorption” solution which then contains the metal in high concentrations [30,97,98]. This makes the subsequent recovery of the metal possible by routine commercial methods (e.g., electrowinning). The regenerated biosorbent can be then used in many sequential metal sorption cycles. Multiple uptake desorption cycles further decrease already quite cost-effective potential of the biosorption process, making its applications economically very attractive. The recently published book on *Sorption and Biosorption* [30] summarizes the current knowledge in the field of biosorption.

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10 Management and Treatment of Acid Pickling Wastes Containing Heavy Metals

Lawrence K. Wang, Veysel Eroglu, and Ferruh Erturk

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10.1 INTRODUCTION

10.1.1 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 interfere with biological treatment processes in sewage treatment plants. In case the effluents are to be discharged directly to a water-course, treatment requirements will be more stringent and costly [1–9].

10.1.2 ACID PICKLING AND ACID CLEANING OF METAL SURFACES

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, in which acids or acid mixtures are used, is used to remove the oxide or scale of metals and corrosion products.

Acid cleaning is used to remove 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 [5]. 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 assure desired pickling rates [5].

Technically speaking, acid pickling is the treatment of metallic surfaces in order to remove impurities, stains, rust, or scale with a solution called pickle liquor, containing strong mineral acids, before subsequent processing (i.e., extrusion, rolling, painting, galvanizing, or plating) with tin or chromium. The two acids commonly used are hydrochloric acid and sulfuric acid.

10.1.3 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 less than 100 to –3000 L/ton, depending on whether once-through or recycle systems are used [1–2].

Carbon steel is usually pickled 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 over-pickling, and the total recovery of the pickling agent from the waste pickle liquor are desired [5,6].

The spent pickling liquor is called waste pickling liquor (WPL), which must be properly treated for disposal or reuse. Wastewaters from pickling include acidic rinsewaters, metallic salts, and waste acid. WPL is considered a hazardous waste by the U.S. Environmental Protection Agency (U.S. EPA).

10.1.4 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 process can be batch or continuous. In continuous strip pickling, more water is required for 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.

10.1.5 WPL TREATMENT AND RECYCLING

Lime or alkaline substances are used to neutralize the WPL. 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 become widely accepted [6]. The by-product of nitric acid pickling is marketable to a couple of secondary industries, including the fertilizer industry.

10.2 PICKLING PROCESS REACTIONS AND WPL CHARACTERISTICS

10.2.1 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.), scale (metallic oxides) is chemically removed from the metal surface. The process can be batch or continuous. In these processes, water is used in pickling and rinsing operations. In continuous pickling, wet fume scrubbing systems are also used. Effluent water from the pickling tanks, which is called 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 acid and dissolved iron per ton of steel pickled. WPL may also contain other metal ions, sulfates, chlorides, lubricants, and hydrocarbons. Rinsewater, 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, WPL, and rinsewater.

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.

10.2.2 SULFURIC ACID PICKLING REACTION

In sulfuric acid pickling, ferrous sulfate is formed from the reaction of iron oxides with sulfuric acid:



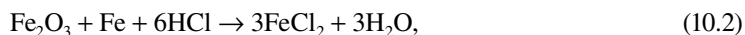
The ferrous sulfate that is formed in the above reaction is either monohydrate or heptahydrate ($FeSO_4 \cdot 7H_2O$).

10.2.3 HYDROCHLORIC ACID PICKLING REACTIONS

During the hot forming or heat treating of steel, oxygen from the air reacts with 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 [6].

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, the U.S. EPA recently surveyed the industry and produced a background information document containing detailed information on the various processes in the industry, pollution control devices, and emissions [6].

When iron oxides dissolve in hydrochloric acid, ferrous chloride is formed according to the following reactions:



Since Fe_3O_4 is $\text{Fe}_2\text{O}_3\text{FeO}$, 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:



An inhibitor is usually added to reduce the acid attack on the base metal while permitting its action on iron oxides. The rate of pickling increases with 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 [6].

10.3 TREATMENT OF WPLs AND CLEANING WASTES

10.3.1 TREATMENT, DISPOSAL, OR RECYCLE

Throughout the late 1980s, spent pickle liquor was traditionally land disposed by steel manufacturers after lime neutralization. The lime neutralization process raises the pH of 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 onsite by steel manufacturers [5,6].

Treated wastewater effluents, in general, can be discharged to either a watercourse or a public sewer system. In the former case, the treatment requirements will be more stringent.

The WPL, rinsewater discharges, and fume scrubber effluent can be combined in an equalization tank for subsequent treatment. Basically three methods are used to treat WPLs:

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.

10.3.2 NEUTRALIZATION AND CLARIFICATION (SEDIMENTATION OR DAF)

In old plants, neutralization and sedimentation are applied to the treatment of wastewaters in general, including WPLs. A typical treatment system for continuous pickling water is shown in [Figure 10.1](#) [1,3].

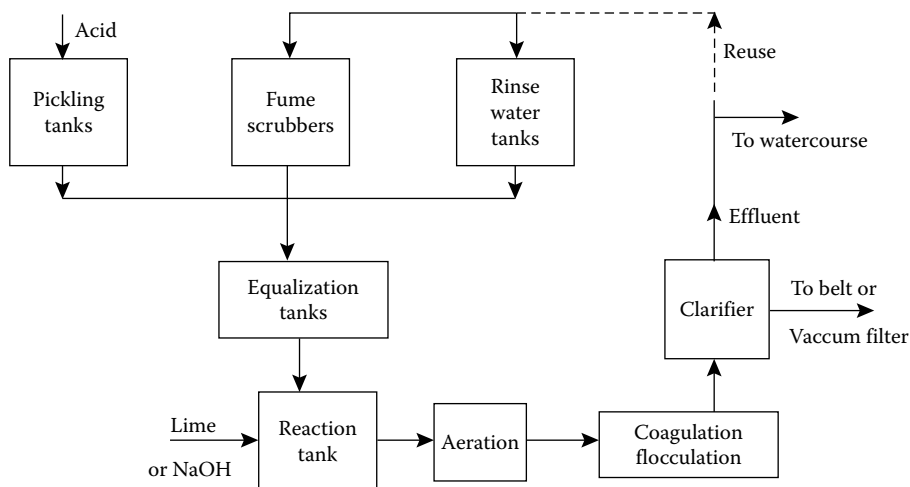


FIGURE 10.1 Typical treatment system for pickling. (Adapted from Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.)

In an integrated steel mill, a central wastewater treatment system is used to treat wastewater from pickling lines, cold rolling mills, and coating lines.

Pickling wastewater has a low pH and contains dissolved iron and other metals. The blowdown and dumps from 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 skimmed, and the water phase containing 200–300 mg/L of oils is treated together with wastewaters from pickling, cold rolling, and coating lines. The combined wastewater flows to a settling and skimming tank where solids and oil are removed. Effluent from the settling/skimmming 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 wastewater. 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 of and the water phase is returned to the clarifier effluent.

The clarifier shown in Figure 10.1 can be a sedimentation clarifier, a DAF clarifier, or a dissolved air flotation-filtration (DAFF) clarifier, depending on space availability, pretreatment requirements, effluent limitations, and costs [7–12]. Modern pickling plants use DAF or DAFF for more cost-effective clarification, or more efficient clarification respectively.

10.3.3 CRYSTALLIZATION AND REGENERATION

The use of lime or other alkaline substances to neutralize acid is quite costly, especially when large capacities are involved. There is also potential resale value in the acids and ferrous ions. Therefore, recovery of these substances will reduce the pollution load, their sale or reuse will represent a profit to the industry.

Crystallization is one of the treatment methods for sulfuric acid WPL. 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 the solubility of FeSO_4 . The solubility of ferrous sulfate as a function of temperature and sulfuric acid concentration is shown in Figure 10.2 [4]. In this figure, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is dominant in region A, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ in region B, and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in region C.

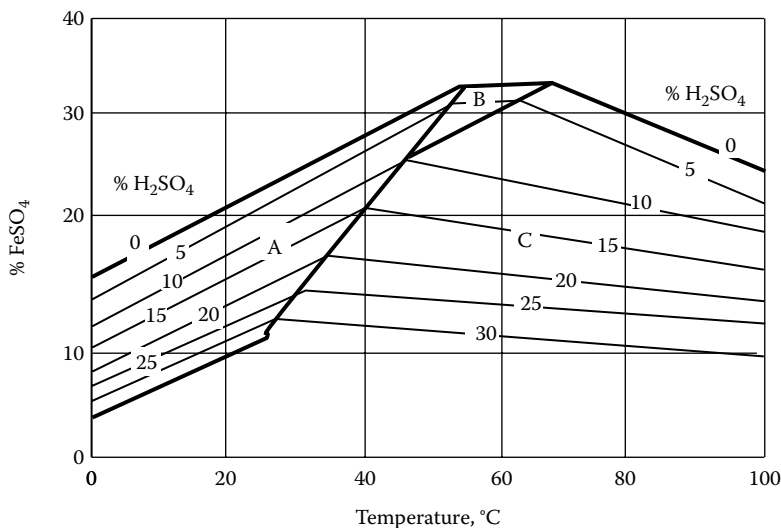


FIGURE 10.2 Solubility of ferrous sulfate FeSO_4 as a function of temperature and sulfuric acid concentration. (Adapted from Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.)

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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is achieved by cooling the acid waters in heat exchangers or by evaporation under vacuum after pickling. 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 to between 0 and 5°C. The crystallized ferric sulfates are recovered by centrifuging. A typical flow diagram for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystallization is shown in Figure 10.3.

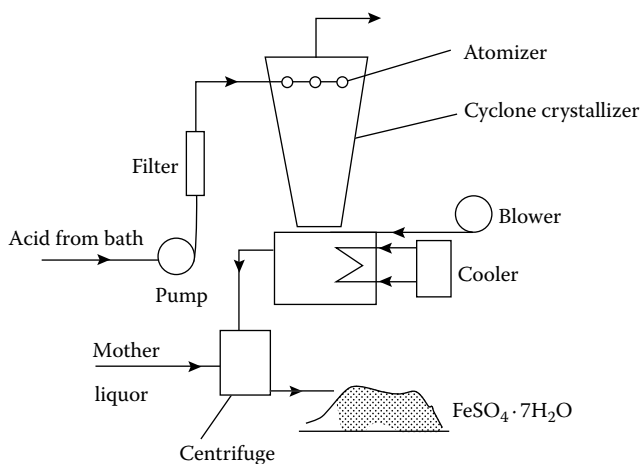


FIGURE 10.3 Flow diagram for ferrous sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystallization. (Adapted from Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.)

The WPL is sprayed above a cyclone crystallizer, and air is blown from the bottom countercurrent to the liquid. Packing material is also present in order to increase the area of contact between the air and the liquid. Acid wastewaters are then cooled, and the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystals are recovered by centrifuging.

In the Ruthner process [1], 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. Ferrous chloride 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; 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 concentrations of dissolved iron and decreasing concentrations of acid.

In the Lurgi system [1], the acid level in the pickling liquor remains 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 preevaporator and heated with gases from the regeneration reactor. Concentrated liquor from the preevaporator 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 preevaporator. 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 preevaporator 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 into the pickle liquor circuit. The regenerated acid contains 12% acid and about 70 g/L of iron. The unabsorbed gases go to a condenser.

10.4 TREATMENT OF WASTEWATER FROM ACID PICKLING TANKS IN A GALVANIZED PIPE MANUFACTURING FACTORY USING SULFURIC ACID

10.4.1 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 the 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 10.4](#).

Acid bath wastewaters are usually discharged once a week. The average flow rate of these wastewaters is 4 m³/hr, with a maximum of 8 m³/hr. The hot and cold water baths are discharged once every 15 days. The quantities and flow rates of these wastewaters are shown in [Table 10.1](#) [1,3].

10.4.2 CHARACTERISTICS OF WASTEWATERS

Wastewater characteristics must be known in order to select a suitable treatment system. For this purpose, wastewater samples taken from the sources were analyzed to determine various parameters.

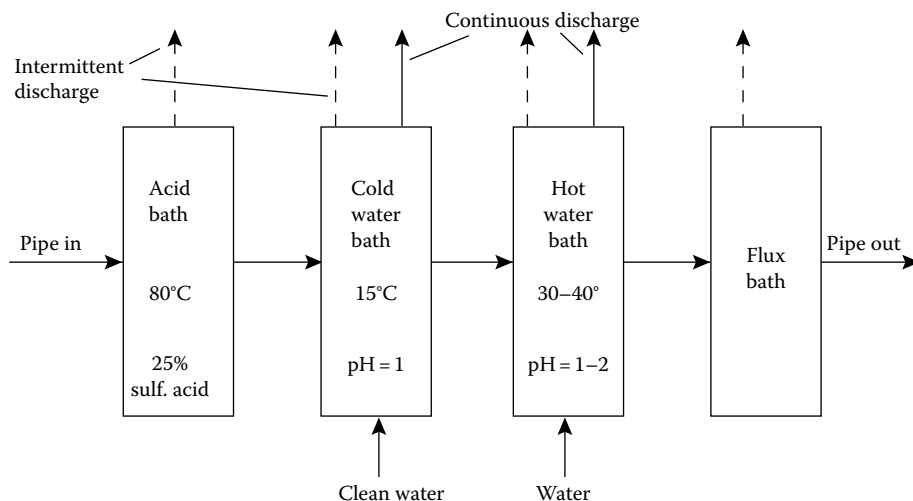


FIGURE 10.4 Flow diagram showing sources of wastewaters in the galvanized pipe manufacturing process. (Adapted from Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.)

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 10.2 [1,3].

Since the continuous discharge quantities are much larger than the batch discharges, they were analyzed separately. Wastewaters from continuous discharge were neutralized with 2 N NaOH. The results are given in Table 10.3 [1,3]. The settling characteristics of continuous discharge wastewaters are shown in Table 10.4 [1,3]. The experimental results for “mixed wastewaters,” the quantities of which are shown in Table 10.2, are given in Table 10.5 [1,3]. The settling characteristics of mixed wastewaters are shown in Table 10.6 [3].

TABLE 10.1
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	8 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 (once every 15 days)	15 m ³	15 m ³
Flux bath	5 m ³	5 m ³

Source: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

TABLE 10.2
Quantities of Wastewater Required for 1000 mL
“Mixed Wastewater”

Source	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: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

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 10.7 [3].

As can be seen from Table 10.7, the required dosage of NaOH does not increase significantly when the lime dosage is more than 20 g/1000 mL. The mixed wastewater, which was treated with the dosages of lime and NaOH shown in Table 10.7, was then aerated for 15 min after a pH of 8.5 was reached. 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 10.8 [3]. The wastewater was treated with 15 g/L of lime and NaOH to attain a pH of 8.5, aerated for 1 hr, mixed for 23 hr, and one additional hour was allowed for clarification. The analysis of the clear clarifier effluent is shown in Table 10.9 [1,3].

TABLE 10.3
Experimental Results for Continuous Discharge

Parameter	Unit	After Neutralization and Separation	
		Original Sample	
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: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*, Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

TABLE 10.4
Settling Characteristics of Continuous Discharge Wastewater

Time	Volume of Clear Phase, <i>h</i> (mL/L)
15 min	20
30 min	50
1.0 hr	90
2.5 hr	240
3.5 hr	400
4.5 hr	460
5.5 hr	500
20 hr	720

Source: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

10.4.3 TREATMENT METHODS

As indicated in the previous section, the concentration of iron in mixed wastewaters ranged from 5980 to 6100 mg/L; its pH was 0.7 and the zinc concentration was 15 µg/L. Since these wastewaters come only from acid baths and not from other processes of the plant, parameters like cadmium and fluoride are not encountered. The discharge standards for metal industry effluents set by the Turkish

TABLE 10.5
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: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

TABLE 10.6
Settling Characteristics of Mixed Wastewaters

Time	Volume of Clear Phase (mL/L)
30 min	40
1 hr	100
2.5 hr	220
3.5 hr	350
4.5 hr	410
5.5 hr	460
20 hr	700

Source: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

Water Pollution Control Regulation (Official Gazette, Table 15.7, September 4, 1988) are shown in [Table 10.10](#) [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 of after dewatering in a filter-press, a horizontal belt filter, or a centrifuge. An equalization tank is required in order to compensate the effects of intermittent discharges. The treated wastewater can then be recycled for use in the process or discharged to the river. The flow diagram of the selected system is shown in [Figure 10.5](#).

TABLE 10.7
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: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

TABLE 10.8**Analysis of Mixed Wastewater after Neutralization, Aeration, and Clarification**

Parameter (mg/L)	Settling Time (min)	Lime + NaOH (g)			
		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
Settleable matter	30	120	280	320	440
	120	400	520	410	480

Source: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

10.5 MANAGEMENT AND TREATMENT OF WASTEWATER AND AIR EMISSIONS FROM ACID PICKLING TANKS USING HYDROCHLORIC ACID

10.5.1 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 on the order of 0.07–0.4 tons per year (tpy) of HCl per tank, depending on tank size and usage. For each million ton of steel processed at

TABLE 10.9**Analysis of Wastewater after Neutralization, Aeration, and Clarification**

Parameter	Concentration (mg/L)
COD	0
Total iron	0
Zinc	0
Sulfate	2100

Source: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.

TABLE 10.10
Effluent Standards for Metal Industry Wastewaters in Turkey

Parameter	2h Composite Sample (mg/L)
COD	200
Suspended solids	125
Oil and grease	20
Ammonium nitrogen	400
Cd	0.1
Fe	3
Fluoride	50
Zn	5
Fish toxicity	10
pH	6–9

Source: Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991.

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 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 that figure up

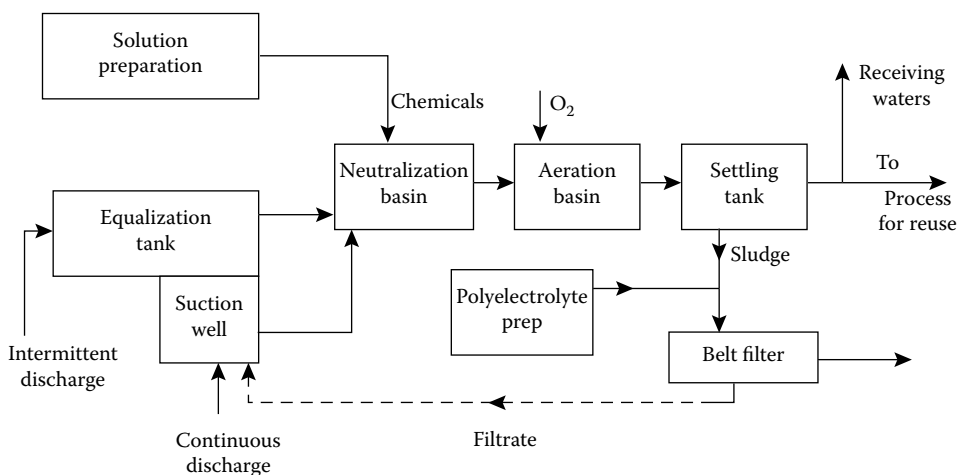


FIGURE 10.5 Flow diagram of the selected treatment system. (Adapted from Eroglu, V. and Erturk, F. In: Wang, L.K. and Wang, M.H.S. (Eds), *Handbook of Industrial Waste Treatment*, Marcel Dekker, Inc., New York, pp. 293–306, 1991; Eroglu, V. et al., *Wastewater Treatment Plant for Cayirova Pipe Factory*. Environmental Engineering Department, Istanbul Technical University, Turkey, 1989.)

to apply to all the materials processed by the same process and under the same conditions. The amount of hydrochloric acid aerosols lost from the pickling tanks is counted 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 of emitting significant amounts of hydrochloric acid aerosols. In ten acid regeneration plants surveyed by the U.S. EPA [6], annual capacities 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 in contact with hot flue gas from the spray roaster, which vaporizes some of the water in the WPL. WPL then becomes concentrated pickling liquor (CPL). CPL is 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,



Flue gas containing HCl goes to a venturi preconcentrator and an absorption column. There 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 in the spent acid, but leave FeCl_2 in the solution, which must be processed or disposed of separately. These acid recovery systems are generally closed-loop processes that do not emit HCl. In their survey, the U.S. EPA compiled data from different types of pickling operations and their estimated emissions [6]. This information is reproduced in Table 10.11.

To estimate emissions from pickling facilities, the U.S. EPA developed 17 model plants to represent five types of pickling operations and one acid regeneration process [6]. The model plants include one

TABLE 10.11
Annual Emission Estimates from Steel Pickling Operations

Type of Facility	Number of Facilities	Number of Operations	Uncontrolled Emission (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 (est.)	41	24

Source: U.S. EPA. *Steel Pickling*. The 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 10.12
Air Emissions and Emission Factors for Model Pickling Plants

Type Facility	Production (tpy) ^a	Hours of Operation (hr)	Uncontrolled		Emission Factor lb HCl/ Tons Processed ^b	
			HCl Emissions (lb/hr)	Control Efficiency (%)	(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*. The 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: S = small; M = medium; L = large; U = uncontrolled; C = controlled.

^a Units of production for acid regeneration facilities are in millions of gallons/yr.

^b Emission factor units for acid regeneration facilities are in lb of HCl per million gallons of HCl produced.

or more size variations for each process model and were developed from information obtained from a survey of steel pickling operations and control technologies. The U.S. EPA estimated emission rates for model facilities. By using these emission rates and the production and hours of operation for the model pickling plants, emission factors were calculated. These are shown in Table 10.12.

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 Mg per year.

10.5.2 A STAINLESS STEEL PIPES AND FITTINGS MANUFACTURER: CASE HISTORY

10.5.2.1 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 hr/yr to produce nearly 30 million pounds of pipe annually.

The 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 the following section.

10.5.2.1.1 Pipe and Fitting Formation

Stainless steel coil and sheet stock is unloaded and stored outdoors under protective cover. When 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 equipment.

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. The pipes are then straightened as necessary and transported to the acid pickling process.

10.5.2.1.2 Acid Pickling

All pipes and fittings are transported to the pickling process. An overhead crane is used to lower them into an acidic pickle liquor solution, which 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.

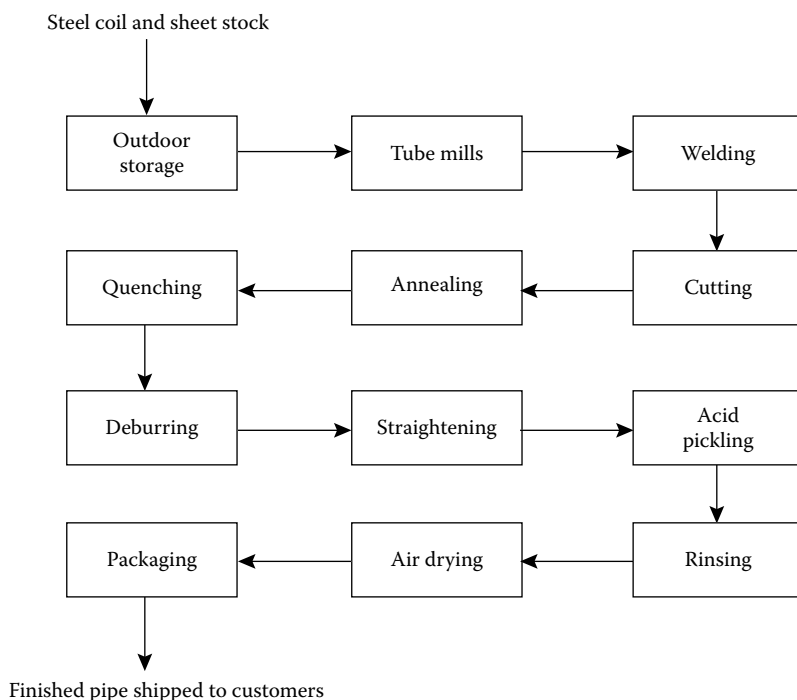


FIGURE 10.6 Flow diagram of a typical stainless steel product manufacturing plant involving acid pickling operation. (Adapted from Jendrucko, R.J. et al., *Pollution Prevention Assessment for Manufacturer of Stainless Steel Pipes and Fittings*. Report no. EPA-600/S-95/017. The U.S. Environmental Protection Agency, Cincinnati, OH, August 1995.)

10.5.2.2 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 onsite wastewater treatment system has been replaced by magnesium hydroxide in order to reduce the volume of sludge generated and shipped offsite.
2. An acid regeneration system has been installed to regenerate spent pickle liquor for reuse onsite.

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 stream identified are given in Figure 10.6 and Table 10.13. Acid pickling appears to be one of many stainless steel product manufacturing operations according to Figure 10.6. However, from Table 10.13, the importance of pickling rinsewater treatment is clearly identified [13]. The toxic waste sludge disposal is the highest, while the miscellaneous solid waste disposal cost is ranked third.

Table 10.14 shows the opportunities for pollution prevention that the U.S. EPA recommended for the plant [13]. The opportunity, type of waste, possible waste reduction and associated savings, and

TABLE 10.13
Summary of Current Waste Generation

Waste Generated	Source of Waste	Waste Management Method	Annual Quantity Generated (lbs/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 onsite WWTP; Sewered to POTW	84,598,000	89,100
Wastewater treatment sludge	Onsite 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: Jendrucko, R.J. et al., *Pollution Prevention Assessment for Manufacturer of Stainless Steel Pipes and Fittings*. Report no. EPA-600/S-95/017. The U.S. Environmental Protection Agency, Cincinnati, OH, August 1995.

^a Included in annual waste management cost for miscellaneous solid waste.

^b Includes specific quantities given for packaging and protective barrier waste, spent abrasive saw blades, and damaged plastic end caps. The majority of this waste stream is cardboard waste.

TABLE 10.14
Summary of Recommended Pollution Prevention Opportunities

Pollution Prevention Opportunity	Annual Waste Reduction					
	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 onsite wastewater treatment system and shipped offsite	Wastewater treatment sludge	928,200	60	\$141,150	\$66,200	0.5
Utilize a trash compactor to reduce the volume of municipal trash shipped offsite 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 onsite wastewater treatment plant in order to reduce caustic purchases and reduce labor costs.	n/a	—	—	12,620	12,600	1.0

Source: Jendrucko, R.J. et al., *Pollution Prevention Assessment for Manufacturer of Stainless Steel Pipes and Fittings*. Report no. EPA-600/S-95/017. The U.S. Environmental Protection Agency, Cincinnati, OH, August 1995.

^a A significant volume reduction would occur.

implementation cost along with 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 the 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.

10.5.2.3 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.

10.5.2.3.1 Copper and Alloys

Straight electrolytic recovery as described earlier is highly effective in many copper pickling and milling solutions, including sulfuric acid, cupric chloride, and ammonium chloride solutions. Solutions based on hydrogen peroxide are generally regenerated best 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 drag-out losses. Regeneration is possible by distillation of nitric acid and removal of copper salts; however, the economics are usually not favorable.

10.5.2.3.2 Sulfuric and Hydrochloric Acids

Both sulfuric and hydrochloric acids are commonly used for cleaning steel. Sulfuric acid can be regenerated by crystallizing ferrous sulfate. Hydrochloric acid can be recovered by distilling off the acid and leaving behind iron oxide. These techniques have been used for many years in large facilities. The economics of these processes, however, are usually not favorable for smaller facilities [14,15].

WPLs from these operations can often be of use in sanitary waste treatment systems for phosphate control and sludge conditioning. Some industrial firms can use spent process waste from the pickling operation. Iron in the waste is used as a coagulant in wastewater treatment systems [14,15].

10.5.2.4 Engineering Calculations for the Determination of Hydrochloric Acid Requirements

On submerging steel in acid, two main reactions take place. Both use hydrogen chloride and both produce ferrous chloride:

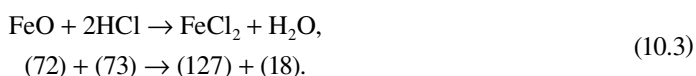


Equation 10.4 shows the chemical reaction where the acid reacts with the base metal (the steel under the scale). This reaction (Equation 10.4) is quite slow and produces hydrogen gas as a by-product, which accounts for the bubbling and foaming in the tank. The ferrous chloride produced is the by-product, which can be sold for cost recovery.

Another reaction shown by Equation 10.3 is the reaction of acid reacts with the scale (FeO) itself. This reaction is faster than the first and produces both ferrous chloride and water as by-products.

It is in the plant's interest to discourage reaction 10.4 from taking place, since the plant is only interested in removing the scale. This is done by leaving the steel in the acid only as long as 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 10.3 and 10.4, an environmental engineer can calculate the acid requirement to pickle 1 ton of steel, assuming an average iron loss of 0.35%, which is typical for pickling strip steel.



73 lb of hydrogen chloride (not acid) is required to react with 56 lb of iron in the scale. Since 1 ton of steel has 0.35% of iron to be removed as scale, which is

$$\frac{2000 \times 0.35}{100} = 7 \text{ lb},$$

it follows that if 56 lb Fe requires 73 lb HCl, then 7 lb Fe requires

$$\frac{73 \times 7}{56} = 9.13 \text{ lb HCl (pure chemical).}$$

The hydrochloric acid commercially available is shipped at 32 lb HCl (gas) per 100 lb of aqueous (in water) solution (32% concentration or 20° Be); it follows then that if 32 lb HCl is dissolved in 100 lb of solution, then 9 lb HCl is dissolved in

$$\frac{100 \times 9.13}{32} = 28.5 \text{ lb of solution.}$$

One gallon of 32% HCl acid weighs approximately 9.7 lb; therefore, the required volume of 32% hydrochloric acid solution is calculated by the following equation:

$$\frac{28.5}{9.7} = 2.94 \text{ gallons of 32\% hydrochloric acid.}$$

The above 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%).

10.5.2.5 Engineering Calculations for the 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 a molecular weight of 56 is equal to 7 lb in the formula ratio, a molecular weight of 127 is equal to $(7 \times 127)/56 = 15.88$ lb. 5.88 lb FeCl₂ is produced per ton of steel pickled. The molecular weight of water is 18. Therefore, $(7 \times 18)/18 = 2.25$ lb of water is produced per ton of steel pickled.

10.6 SUMMARY

1. The basic unit operations/processes required for treating 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 BOD₅, COD, and iron.
2. The iron present in the wastewater appears in the form of ferrous ion (Fe²⁺), which is soluble in water, and can be recovered as a by-product.
3. Ferrous ion can be removed either by oxidation to ferric (Fe³⁺) 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 commonly used 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, a horizontal belt filter, or a centrifuge. An equalization tank is required in order to compensate the effects of intermittent discharges. The treated wastewater can be recycled for use in the process or discharged to the river.
10. A sedimentation clarifier, a DAF clarifier, or a DAFF can be used for the clarification of pickling wastewater [17].
11. Both air emission control and sludge disposal are extremely important in a steel acid pickling plant [18–20].
12. 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 rinsewater is the second most expensive engineering task.

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11 Treatment and Management of Metal Finishing Industry Wastes

Nazih K. Shammam and Lawrence K. Wang

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11.1 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 Wastes Amendments (HSWA) [3]. The metal finishing industry 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].

11.1.1 GENERAL DESCRIPTION

The metal finishing industry consists of 44 unit operations involving the machining, fabrication, and finishing of metal products (SIC groups 34 through 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 manufacture 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 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, whereas a simple product might require only a single operation. Each of the 44 individual unit operations is listed below with a brief description [7].

1. *Electroplating* is the production of a thin coating of one metal on another by electrodeposition.
2. *Electroless plating* is a chemical reduction process that depends on 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 materials.
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. Such operations 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 oxy-acetylene 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 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 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, which are carried in a liquid between the tool and the work and which 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 coating 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 work 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 metallizing* 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 11.1 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 11.1
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 no. EPA-600/2-82-001b. U.S. Environmental Protection Agency, Washington, DC, September 1981.

11.1.2 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 11.2 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.

11.2 WASTEWATER CHARACTERIZATION

In this section, the water uses 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 11.2
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 no. 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 metallizing, and calibration [7].

Table 11.3 displays the ranges of flows in the metal finishing industry. Approximately 81% of the plants have flows of between 1.9 and 57 m³/h (67–2000 ft³/h). For those plants with common metals waste streams, the average contribution of these streams to the total wastewater flow within a particular plant is 62.4% (range of 0.007–100%). All of the plants have a waste stream requiring common metals treatment.

TABLE 11.3
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 no. EPA-600/2-82-001b. U.S. Environmental Protection Agency, Washington, DC, September 1981.

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%).

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 of the samples were performed. The results of these analyses are presented for each subcategory in Tables 11.4 through 11.9. In each table, data are presented 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. The minimum detection limit for the toxic pollutants in the sampling program was 1 µg/L and any value below this is listed in the six tables as BDL (below detection limit).

11.2.1 COMMON METALS SUBCATEGORY

Pollutant parameters found in the common metals subcategory raw waste stream from sampled plants are shown in Table 11.4. The major constituents shown are parameters that originate from process solutions (such as from plating or galvanizing) and then enter wastewaters by drag-out to rinses. These metals appear in waste streams in widely varying concentrations.

TABLE 11.4
Concentrations of Pollutants Found in the Common Metals Subcategory Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Toxic Pollutants (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- <i>n</i> -butyl phthalate	89	79	BDL–10	BDL	BDL
Di- <i>n</i> -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		
<i>N</i> -nitroso-di- <i>n</i> -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		

continued

TABLE 11.4 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
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
Chloroform	65	48	BDL–140	BDL	5
1,1-Dichloroethylene	58	4	BDL–110	BDL	20
1,2- <i>Trans</i> -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		
Alpha-endosulfan	4	1	9		
Endrin aldehyde	4	1	BDL		
Alpha-BHC	4	1	BDL		
Beta-BHC	4	1	4		
Delta-BHC	4	1	BDL		
Concentration (mg/L)					
Classical Pollutants					
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
Phosphorous	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 no. EPA-440/1-80/091. U.S. Environmental Protection Agency, Washington, DC, 1980.

TABLE 11.5
Concentrations of Pollutants Found in the Precious Metals Subcategory Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Concentration (mg/L)					
Classical Pollutants					
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 no. EPA-440/1-80/091. U.S. Environmental Protection Agency, Washington, DC, 1980.

11.2.2 PRECIOUS METALS SUBCATEGORY

Table 11.5 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.

11.2.3 COMPLEXED METALS SUBCATEGORY

The concentrations of metals found in complexed metals subcategory raw waste streams are presented in Table 11.6. 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.

11.2.4 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 11.7. The levels of cyanide range from 0.045 to 500 µg/L. Streams with high cyanide concentrations

TABLE 11.6
Concentrations of Pollutants Found in the Complexed Metals Subcategory Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Concentration (µg/L)					
Toxic Pollutants					
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
Concentration (mg/L)					
Classical Pollutants					
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 no. EPA-440/1-80/091. U.S. Environmental Protection Agency, Washington, DC, 1980.

TABLE 11.7
Concentrations of Pollutants Found in the Cyanide Subcategory Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Concentration (µg/L)					
Toxic Pollutants					
Cyanide	20	20	45–500,000	45,000	110,000
Cyanide, amn.	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 no. EPA-440/1-80/091. U.S. Environmental Protection Agency, Washington, DC, 1980.

normally originate from electroplating and heat-treating processes. Cyanide-bearing waste streams should be segregated and treated before being combined with other raw waste streams.

11.2.5 HEXAVALENT CHROMIUM SUBCATEGORY

Concentrations of hexavalent chromium from metal finishing raw wastes are shown in [Table 11.8](#). 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.

TABLE 11.8
Concentrations of Pollutants Found in the Hexavalent Chromium Subcategory Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Concentration (µg/L)					
Toxic Pollutants					
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 no. EPA-440/1-80/091. U.S. Environmental Protection Agency, Washington, DC, 1980.

11.2.6 OILS SUBCATEGORY

Pollutants and their concentrations found in the oily waste subcategory streams are shown in Table 11.9. 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

TABLE 11.9
Concentrations of Pollutants Found in the Oils Subcategory Raw Wastewater

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Concentration (mg/L)					
Toxic Pollutants					
Phthalates					
Bis(2-ethylhexyl)phthalate	37	20	2–9300	73	820
Butyl benzyl phthalate	37	9	1–10,000	130	1600
Di- <i>n</i> -butyl phthalate	37	13	1–3100	16	270
Di- <i>n</i> -octyl phthalate	37	2	4–120		62
Diethyl phthalate	37	9	1–1900	48	420
Dimethyl phthalate	37	34	1–1200	1	400
Ethers					
Bis(chloroethyl)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	3–12		8
Phenols					
2,4,6-Trichlorophenol	37	3	10–1800	30	610
Parachlorometa cresol	37	8	4–8,00,000	2300	100,000

continued

TABLE 11.9 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
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	10–120	15	120
4-Nitrophenol	37	1	10		
2,4-Dinitrophenol	37	3	10–10,000	13	3300
<i>N</i> -nitrosodiphenylamine	37	5	4–900	750	490
Pentachlorophenol	37	3	10–50,000	5200	18,000
Phenol	37	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	1–9500	12	380
Polynuclear Aromatic Hydrocarbons					
Acenaphthene	37	2	57–5700		2900
2-Chloronaphthalene	37	1	130		
Fluoranthene	37	8	1–55,000	110	6300
Napthalene	37	10	1–260	100	36
Benzo(a)pyrene	37	1	10		
Chrysene	37	3	1–73	2	25
Acenaphthylene	37	3	77–1000	140	410
Anthracene	43	7	3–2000	34	360
Fluorene	37	7	1–760	75	180
Phenanthrene	37	8	8–8000	80	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	6	6–1300	10	330
1,1,2,2-Tetrachloroethane	37	8	6–370		290
Chloroform	37	19	8–690	10	50
1,1-Dichloroethylene	37	18	8–10,000	800	1500
1,2- <i>trans</i> -dichloroethylene	37	9	8–1700	88	510
Methylene chloride	37	89	5–7600	92	600
Methyl chloride	37	4	1–4700	9	1800
Bromoform	37	1	10		
Dichlorobromomethane	37	2	1–10		5
Trichlorofluoromethene	37	8	860–890		800
Chlorodibromomethane	37	3	1–10	8	4

continued

TABLE 11.9 (continued)

Pollutant	Number of Samples	Number of Detections	Range of Detections	Median of Detections	Mean of Detections
Tetrachloroethylene	37	10	1–110,000	10	8900
Trichloroethylene	37	11	1–130,000	110	23,000
<i>Pesticides and Metabolites</i>					
Aldrin	37	2	4–11		7
Dieldrin	37	1	3		
Chlordane	37	8	1–13		7
4,4-DDT	37	8	8–10		6
4,4-DDE	37	4	801–33	8	14
4,4-DDD	37	3	1–10	4	5
Alpha-endosulfan	37	2	6–88		18
Beta-endosulfan	37	8	801–6		3
Endosulfan sulfate	37	4	1–16	11	10
Endrin	37	8	7–10	13	8
Endrin aldehyde	37	8	10–14	7	18
Heptachlor	37	1	801		
Heptachlor epoxide	37	1	801		
Alpha-BHC	37	3	4–18	13	12
Gamma-BHC	37	3	1–9	7	6
Delta-BHC	37	8	4–11		7
<i>Polychlorinated Biphenyls</i>					
Aroclor 1234	37	2	76–1100		590
Aroclor 1248	37	2	160–1800		960

Concentration (mg/L)***Classical Pollutants***

Ammonia	37	10	0.46–270	7.9	46
BOD	37	21	10–17,000	1400	3800
COD	37	16	310–1,900,000	18,000	180,000
Oil and grease	37	17	60–900,000	6100	41,000
Phenols total	37	14	9062–48	624	8.3
Total dissolved solids	37	9	850–4960	1600	8000
Total organic carbon	37	17	1–560,000	1600	88,000
TSS	37	35	35–18,000	600	2700

Source: U.S. EPA. *Development Document for Effluent Limitations Guidelines and Standards for the Metal Finishing Point Source Category*. Report no. EPA-440/1-80/091. U.S. Environmental Protection Agency, Washington, DC, 1980.

levels of the wastes, but oily wastes normally receive specific treatment for oil removal prior to solids removal waste treatment.

The majority of the pollutants listed in Table 11.9 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 organics 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.

11.2.7 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 are predominately comprised of compounds classified by the 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 waste stream.

11.3 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.

11.3.1 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 USD18,400 in equipment costs and USD10/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?

TABLE 11.10
Chemical Substitutes

Polluting	Substitute	Comments
Fire dip (NaCN)	Muriatic acid with additives	Slower acting than + H ₂ O ₂ traditional fire dip Excellent throwing power with a bright, smooth, rapid finish
Heavy copper cyanide plating bath	Copper sulfate	A copper cyanide strike may still be necessary for steel, zinc, or tin-lead base metals Requires good preplate cleaning Noncyanide process eliminates carbonate build-up in tanks
Chromic acid pickles, deoxidizers, and bright dips	Sulfuric acid and hydrogen peroxide	Nonchrome substitute Nonfuming
Chrome-based antitarnish	Benzotriazole (0.1–1.0% solution in methanol) or water-based proprietaries	Nonchrome substitute Extremely reactive, requires ventilation Noncyanide cleaner Good degreasing when hot and in an ultrasonic bath
Cyanide cleaner	Trisodium phosphate or ammonia	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 no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

Based on a survey of chemical suppliers and electroplaters who use nonpolluting chemicals, some commonly used chemical substitutes are summarized in [Table 11.10](#).

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 11.11](#).

11.3.2 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 the 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.

TABLE 11.11
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 no. EPA 625/R-99/009. U.S. Environmental Protection Agency, Cincinnati, OH, December 2000.

11.3.3 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.

11.3.3.1 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%.

11.3.3.2 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 11.1](#) 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.

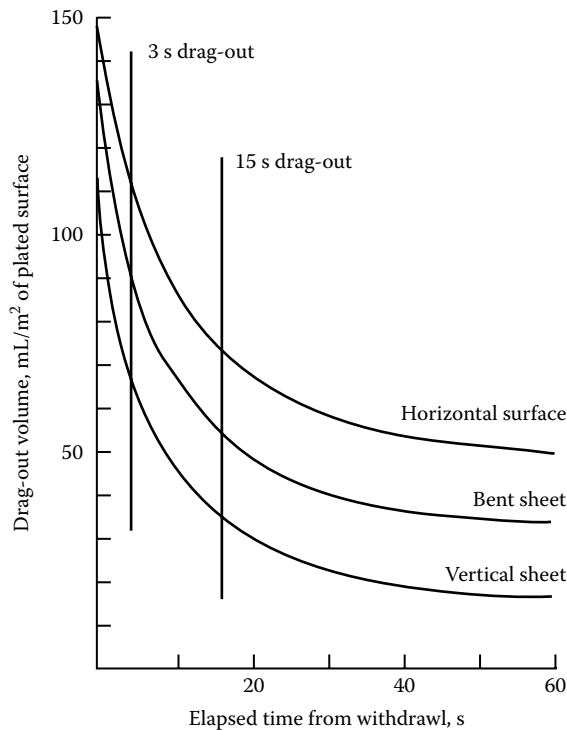


FIGURE 11.1 Typical drag-out drainage rates. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

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 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 ¼ L/h by these techniques.

11.3.3.3 Other Drag-Out Reduction Techniques

11.3.3.3.1 Rinse Elimination

The rinse between a soak cleaner and an electrocleaner may be eliminated if the two baths are compatible.

11.3.3.3.2 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 11.12, the annual cost of chemical replacement, treatment, and disposal is about USD20,700 in terms of 2007 dollars. If the bath is converted to the modified operating condition as shown in the table, the annual cost of chemical replacement, treatment, and

TABLE 11.12
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 ₂ O	300–375	338	308
as NiSO ₄	—	200	182
Nickel chloride			
NiCl ₂ ·6H ₂ O	60–90	75	64
as NiCl ₂	—	41	35
Boric acid H ₃ BO ₃	45–49	47	46

Source: U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

disposal is approximately USD18,700, a savings of about USD2,000 per year. Generally, any percent 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.

11.3.3.3.3 Clean Plating Baths

Contaminated plating baths, for example carbonate build-up 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.

11.3.3.3.4 Low-Viscosity Conducting Salts

Bath viscosity indexes are available from chemical suppliers. As the bath viscosity increases, drag-out volume also increases.

11.3.3.3.5 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.

11.3.3.3.6 No Unnecessary Components

Additional bath components (chemicals) tend to increase both viscosity and drag-out.

11.3.3.3.7 Fog Sprays or Air Knives

Fog sprays or air knives may be used over the bath to remove drag-out from pieces 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.

11.3.3.3.8 Proper Racking

Every piece 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.

11.3.3.4 Capture/Concentration Techniques

11.3.3.4.1 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. In *Water and Waste Control for the Plating Shop* (1972), he describes a “simple waste recovery system,” which 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 which 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 11.2. It is not difficult to automate the direct drag-out recovery process and commercial units are available.

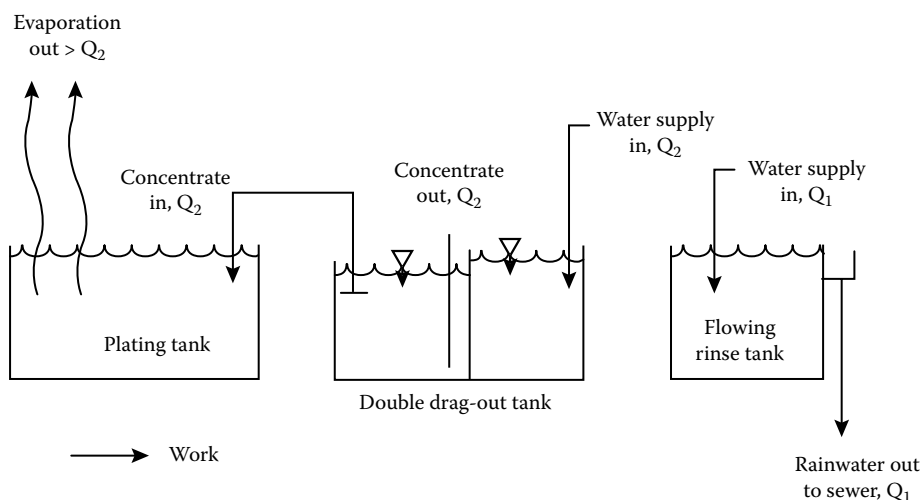


FIGURE 11.2 Kushner method of double drag-out for full reuse. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

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 .

11.3.3.4.2 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 11.3 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.

11.3.4 WASTE REDUCTION COSTS AND BENEFITS

Benefits of waste reduction in the metal finishing shop include

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 generation

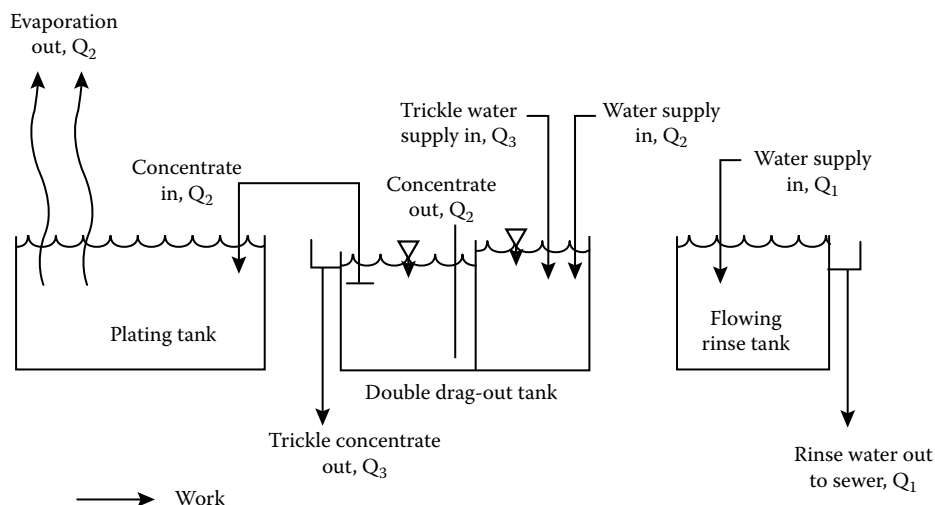


FIGURE 11.3 Modified method of double drag-out for partial reuse. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

TABLE 11.13
Chemical Costs of Treatment and Disposal in 2007 USD

Pollutant	Chemical Cost (2007 USD ^a /kg)	
	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 no. 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 [9].

^b Cost of NaOH at USD 1.00/kg and NaOCl at USD 2.35/kg

^c Cost of disposal at USD 1.84/kg of sludge (USD 400/drum) at 30% solids content

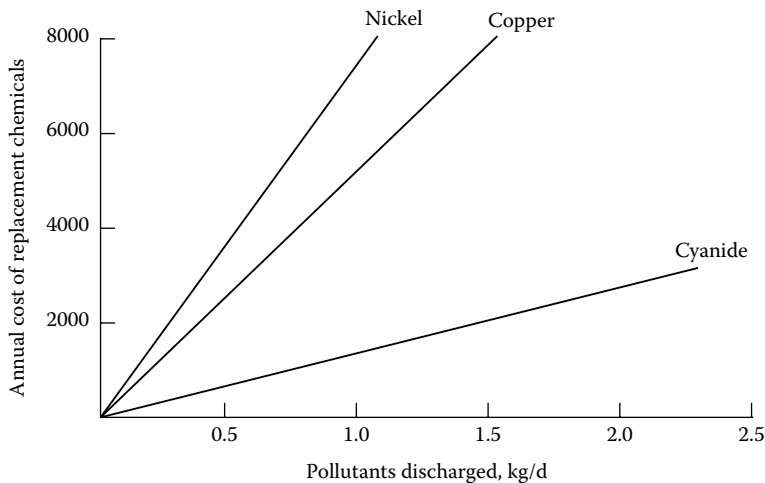


FIGURE 11.4 Annual replacement cost of chemicals in 2007 USD. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

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 11.13 and the annual replacement costs of chemicals are given in Figure 11.4. Calculations of the annual dollar savings are shown in Table 11.14. All costs have been converted into 2007 USD using the U.S. ACE Yearly Average Cost Index for Utilities [9].

11.4 POLLUTANT REMOVABILITY

This section reviews the technologies currently available and used to remove or recover pollutants from the wastewater generated in the metal finishing industry [5–7,10]. Treatment options are

TABLE 11.14
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^d	
Copper	760
Cyanide	0
Nickel	1700
Water and sewer use fee reduction ^d	4360
Total annual savings	20,500

^a Costs were converted from 1979 USD to 2007 USD using U.S. ACE. Yearly average Cost Index for Utilities. (Adapted from 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, 44 pp. A PDF file is available on the Internet at <http://www.nww.usace.army.mil/cost>, 2007.)

^b From Figure 11.4.

^c From Table 11.12 and Figure 11.4.

^d USD 0.77/m³.

Source: U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.

presented for each subcategory within the metal finishing industry. Table 11.15 lists the treatment techniques available for treating wastes from each subcategory.

11.4.1 COMMON METALS

The treatment methods used to treat wastes within the common metals subcategory fall into two groups:

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. This group includes [5–7]

1. Evaporation
2. Ion exchange
3. Electrolytic recovery
4. Electrodialysis
5. Reverse osmosis.

TABLE 11.15
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
Evaporation recovery	63
Ion exchange	11
Electrolysis	3
Reverse osmosis	8
Post adsorption	0
Insoluble starch xanthenes	2
Sulfide precipitation	3
Flotation	29
Membrane flotation	7
Precious Metals	
Evaporation	1
Ion exchange	NR
Electrolytic	NR
Complexed Metals	
High pH precipitation with sedimentation	NR
Membrane filtration	NR
Hexavalent Chromium	
Chemical chrome reduction	343
Electrochemical chromium reduction	2
Electrochemical chromium regeneration	0
Advanced electrodialysis	NR
Evaporation	1
Ion exchange	1
Cyanida	
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	26
Skimming	94
Emulsion breaking and skimming	
Ultrafiltration	20
Reverse osmosis	3

continued

TABLE 11.15 (continued)

Subcategory/Technology	Number of Plants
Carbon adsorption	10
Coalescing	3
Flotation	29
Centrifugation	5
Integrated adsorption	0
Resin adsorption	0
Ozonation	0
Chemical oxidation	0
Aerobic decomposition	14
Thermal emulsion breaking	0
Solvent Wastes	
Segregation	NR
Contract handling	NR
Sludges	
Gravity thickening	76
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 no. EPA-600/2-82-001b. U.S. Environmental Protection Agency, Washington, DC, September 1981.

Note: NR, not reported.

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
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:

The option 1 system consists of hydroxide precipitation [11] followed by sedimentation [12]. This system accomplishes the end-of-pipe metals removal from all common metal-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.

The option 2 system is identical to the option 1 treatment system with the addition of filtration devices [13] 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 [14,15].

The 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 [15].

In addition to these three treatments, there are several alternative treatment technologies applicable to the treatment of common metal wastes. These technologies include electrolytic recovery, electrodialysis, reverse osmosis, peat adsorption, insoluble starch xanthate treatment, sulfide precipitation, flotation, and membrane filtration [14,15].

11.4.2 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.

11.4.3 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 [16] that is primarily used in place of sedimentation for solids removal.

11.4.4 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 [15].

11.4.5 CYANIDE

Cyanides are introduced as metal salts for plating and conversion coating or are 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 [17]. Treatment techniques, which remove cyanide but do not destroy it, include chemical precipitation, reverse osmosis, and evaporation [15,17].

11.4.6 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 [17–19].

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) [20] 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:

- *The option 1* system incorporates the emulsion breaking process followed by surface skimming (gravity separation is adequate if only free oils are present).
- *The option 2* system consists of the option 1 system followed by ultrafiltration.
- *The 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 [17–19].

11.4.7 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.

11.5 TREATMENT TECHNOLOGIES

11.5.1 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. Another 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 to the waste treatment system. This, in effect, neutralizes the acid wastes and eliminates the requirements of manifesting and land disposal.

11.5.2 CYANIDE-CONTAINING WASTES

There are eight methods applicable to the treatment of cyanide wastes for metal finishing [5,21]:

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 most widely used method in the metal finishing industry. A schematic diagram of cyanide reduction via alkaline chlorination is provided in Figure 11.5. 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 at a pH 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, CO₂, ammonia, and amines (Figure 11.6).

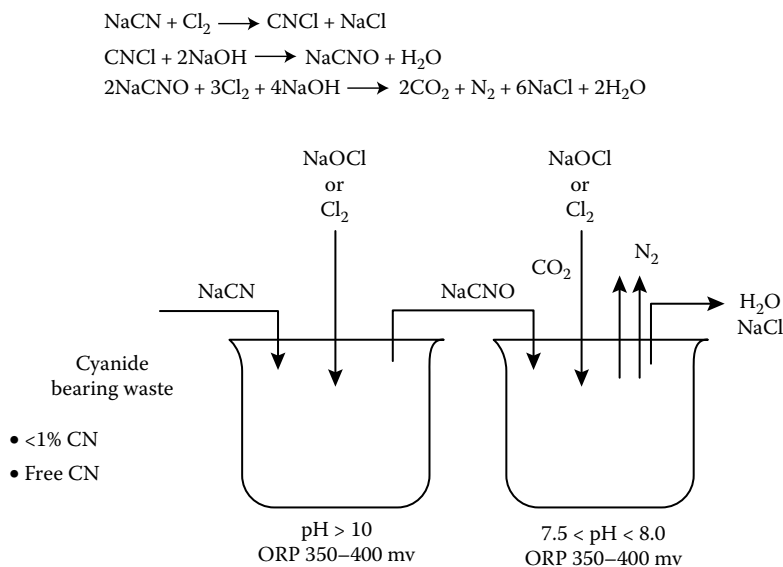


FIGURE 11.5 Cyanide reduction via alkaline chlorination. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

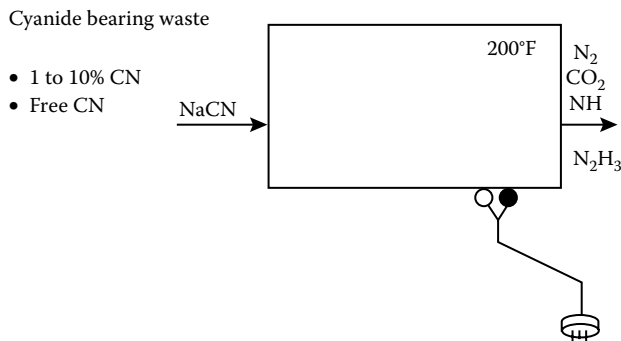


FIGURE 11.6 Cyanide reduction via electrolytic decomposition. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

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 [21]. Cyanide is oxidized to cyanate, with ozone reduced to oxygen as per the following equation:



Then cyanate is hydrolyzed, in the presence of excess ozone, to bicarbonate and nitrogen and oxidized as per the following reaction:

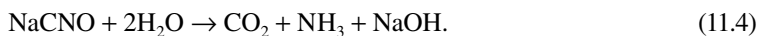
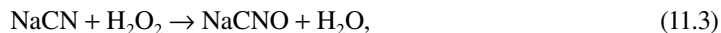


The reaction time for complete cyanide oxidation is rapid in a reactor system with 10–30 min retention time being typical. The second-stage reaction is much slower than the first-stage reaction. The reaction is typically carried out in the pH range 10–12, where the reaction rate is relatively constant. Temperature does not influence the reaction rate significantly.

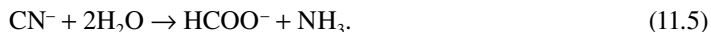
One interesting variation of ozonation technology is augmentation with UV radiation. This is a technology that has been applied on wastes in the coke byproduct manufacturing industry. A significant development has been made that has resulted in significantly less ozone consumption through the use of 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.

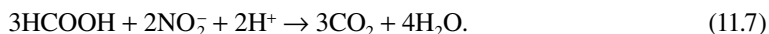
Cyanide reduction with hydrogen peroxide is effective in reducing cyanide. It has been applied on a less frequent basis within this industry, because there are high operating costs associated with hydrogen peroxide generation. The reduction of cyanide with peroxide occurs in two steps and yields CO₂ and ammonia:



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 [22]. 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 [21].



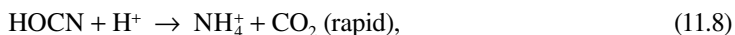
In the presence of nitrates, formate and ammonia can be destroyed in another reactor at 150°C, according to the following equations:



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, whereas at pH 7, cyanate may remain stable for weeks [23]. This treatment process requires specially designed reactors to assure that HCN is properly vented and controlled. The hydrolysis mechanisms are as follows [21]:

In acid medium,



In strongly alkaline medium,



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 range of 2–4 [5].

11.5.3 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.

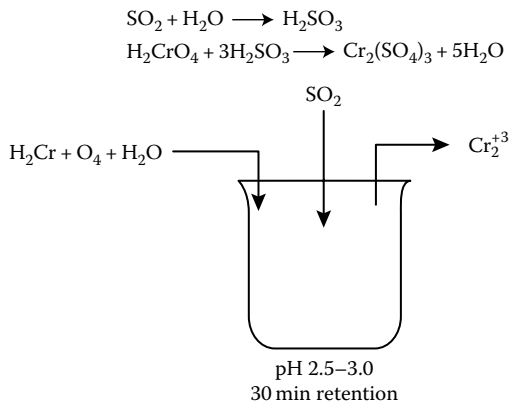


FIGURE 11.7 Hexavalent chromium reduction. (Adapted from U.S. EPA. *Meeting Hazardous Waste Requirements for Metal Finishers*. Report no. EPA/625/4-87/018. U.S. Environmental Protection Agency, Cincinnati, OH, 1987.)

The hexavalent chromium is reduced through the addition of the reductant at a pH range of 2.5–3 with a retention time of approximately 30–40 min (Figure 11.7).

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 technology is that the hexavalent chromium is reduced to trivalent chromium and the ferrous iron is oxidized to ferric iron.

11.5.4 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 1 mg/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 1 mg/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 1 mg/L [21]. The sulfide reacts with the anionic acids to form insoluble sulfides, which are readily separated by means of filtration.

11.5.4.1 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 $\text{Ca}(\text{OH})_2$, 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 [21]:

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 that 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 applications 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.

11.5.4.2 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 by 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 that calcium ions are present in lime. The calcium ions present in solution on the addition of lime are very effective in competing with the ligand for the metal ions. The sodium ions 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 a 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 [21].

11.5.5 OTHER METAL 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 [24]. 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 [24] 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 [24,25]. 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.

11.6 COSTS

The investment cost, operating and maintenance [26,27] 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.

11.6.1 TYPICAL TREATMENT OPTIONS

Many waste treatment options are available [27–31]. 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 the evaporative system.

The flow diagram for suggested option 1 is shown in [Figure 11.8](#). The flow diagram for the other options would be similar.

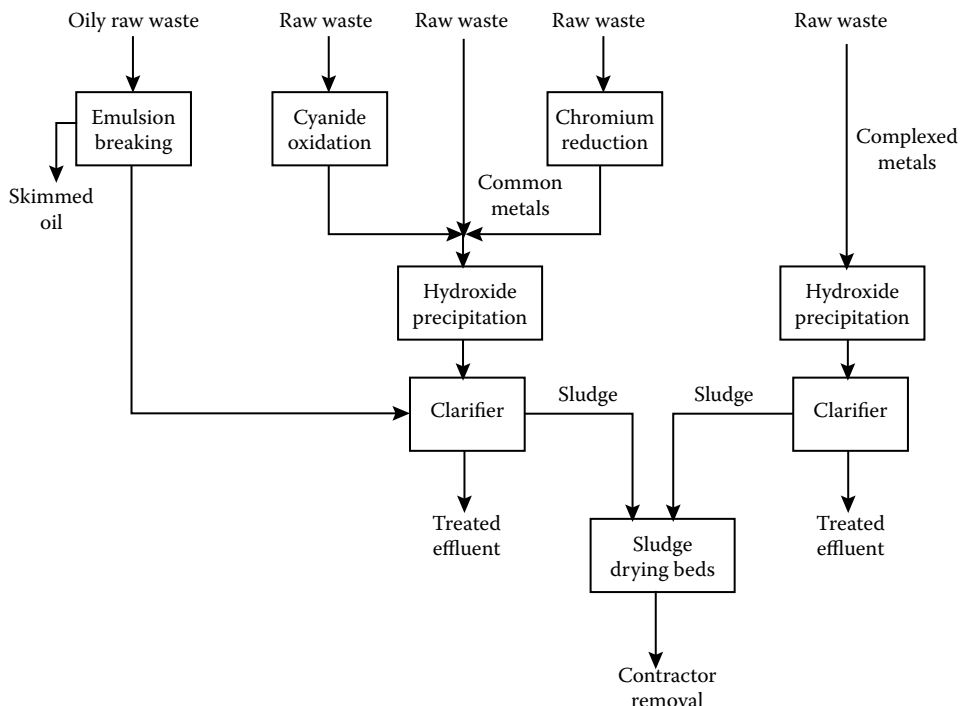


FIGURE 11.8 Metal finishing wastewater treatment flow diagram. (Adapted from U.S. EPA. *Treatability Manual, Volume II. Industrial Descriptions*. Report no. EPA-600/2-82-001b. U.S. Environmental Protection Agency, Washington, DC, September 1981.)

11.6.2 COST ANALYSIS

The cost estimates prepared for the treatment technologies commonly used in this industry are briefly described below. More details of the factors considered in the cost analysis are available in the source [6].

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: 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.

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 aboveground cylindrical tanks with a retention time of 4 h are provided. Chemical storage consists of covered concrete tanks to store 60 d supply of sodium hypochlorite and 90 d supply of sodium hydroxide.

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 condition 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 aboveground concrete tank with a retention time of 45 min is provided. For batch operation, dual aboveground concrete tanks with 4 h retention time are provided.

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/m² and a retention time of 4 h. Batch treatment includes dual reaction-settling tanks sized for 8 h retention time and sludge pumps.

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 [28].

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. Filter beds sized for hydraulic loading of 81 L/min/m² (2 gpm/ft²).

7. Ultrafiltration

Method: 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/m².

8. Carbon adsorption

Method: A packed-bed throwaway system to remove organic pollutants from oily waste stream.

System component: Contactor system, and a pump station designed for a contact time of 30 min and a hydraulic loading of 162 L/min/m² (4 gpm/ft²).

Unit costs shown in Table 11.16 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,
- 52.5% common metals stream, and
- 4.5% complex metal stream.

11.7 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 and 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 (BPT) available; (d) the effluent limitations representing

TABLE 11.16
Total Annual Unit Cost (USD/m³ in 2007 Dollars)^a

Flow (m ³ /h)	Option 1		Option 2		Option 3	
	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 no. 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. (Adapted from U.S. ACE. Yearly Average Cost Index for Utilities. In: 110-2-1304. U.S. Army Corps of Engineers, Washington, DC, 44 pp. A PDF file is available on the Internet at <http://www.nww.usace.army.mil/cost>, 2007.)

the degree of effluent reduction attainable by applying the best available technology (BAT) economically achievable; (e) the pretreatment standards for existing sources (PSES); (f) the new source performance standards (NSPS); and (g) the pretreatment standards for new sources (PSNS).

11.7.1 APPLICABILITY AND 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 metallizing, 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 the following: (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 that are covered by 40 CFR part 413.

11.7.2 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 to 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.

11.7.3 EFFLUENT LIMITATIONS BASED ON THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

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 11.17](#), which represents the degree of effluent reduction attainable by applying the best practicable control technology currently available (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 11.18](#) may apply in place of the total cyanide limit specified in [Table 11.17](#). 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.

11.7.4 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 11.19](#), which represents the degree of effluent

TABLE 11.17**U.S. Best Practicable Control Technology (BPT) Currently Available Effluent Limitations for the Metal Finishing Point Source Category**

Pollutant or Pollutant Property	Maximum for Any 1 day	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 & 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.

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 11.20](#) may apply in place of the total cyanide limit specified in [Table 11.19](#). 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.

11.7.5 PSES

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 part 403 and achieve the PSES. [Table 11.21](#) indicates the PSES for all metal finishing plants except job

TABLE 11.18**Alternative U.S. Best Practicable Control Technology (BPT) Currently Available Effluent Limitations on Cyanide (A) for the Metal Finishing Point Source Category**

Pollutant or Pollutant Property	Maximum for Any 1 day	Monthly Average Shall not Exceed
	(mg/L)	(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 11.19**U.S. BAT Effluent Limitations for the Metal Finishing Point Source Category**

Pollutant or Pollutant Property	Maximum for Any 1 day	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 11.20**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	Monthly Average Shall not Exceed
	(mg/L)	(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 11.21**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	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.

TABLE 11.22**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.

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 11.22 may apply in place of the total cyanide limit specified in Table 11.21. 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.

11.7.6 NSPS

Any new metal finishing point source subject to the 40 CFR part 433 regulations must achieve the NSPS shown in Table 11.23. Alternatively, for the metal finishing industrial facilities with cyanide treatment, and upon agreement between a source subject to those limits and the pollution control

TABLE 11.23**U.S. NSPS for the Metal Finishing Point Source Category**

Pollutant or Pollutant Property	Maximum for Any 1 day	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 & 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 11.24
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.

authority, the amenable cyanide limit shown in Table 11.24 may apply in place of the total cyanide limit specified in Table 11.23. 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.

11.7.7 PSNS

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 PSNS, shown in Table 11.25. 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 11.26 may apply in place of the total cyanide limit specified in Table 11.25.

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.

TABLE 11.25
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
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 11.26
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.

11.8 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 which owns not more than 50% (annual area basis) of the materials undergoing metal finishing.
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 TTO, which is the summation of all quantifiable values greater than 0.01 mg/L for the following toxic organics:

Acenaphthene	1,2-Dichlorobenzene
Acrolein	1,3-Dichlorobenzene
Acrylonitrile	1,4-Dichlorobenzene
Benzene	3,3-Dichlorobenzidine
Benzidine	1,1-Dichloroethylene
Carbon tetrachloride (tetrachloromethane)	1,2- <i>Trans</i> -dichloroethylene
Chlorobenzene	2,4-Dichlorophenol
1,2,4-Trichlorobenzene	1,2-Dichloropropane
Hexachlorobenzene	1,3-Dichloropropylene
1,2,-Dichloroethane	(1,3-dichloropropene)
1,1,1-Trichloroethane	2,4-Dimethylphenol
Hexachloroethane	2,4-Dinitrotoluene
1,1-Dichloroethane	2,6-Dinitrotoluene
1,1,2-Trichloroethane	1,2-Diphenylhydrazine
1,1,2,2-Tetrachloroethane	Ethylbenzene
Chloroethane	Fluoranthene
Bis(2-chloroethyl) ether	4-Chlorophenyl phenyl ether
2-Chloroethyl vinyl ether (mixed)	4-Bromophenyl phenyl ether
2-Chloronaphthalene	Bis(2-chloroisopropyl) ether
2,4,6-Trichlorophenol	Bis(2-chloroethoxy) methane
Parachlorometa cresol	Methylene chloride (dichloromethane)
Chloroform (trichloromethane)	Methyl chloride (chloromethane)
2-Chlorophenol	Methyl bromide (bromomethane)
	Bromoform (tribromomethane)

Dichlorobromomethane	Indeno(1,2,3- <i>cd</i>) pyrene (2,3- <i>o</i> -phenylene pyrene)
Chlorodibromomethane	Pyrene
Hexachlorobutadiene	Tetrachloroethylene
Hexachlorocyclopentadiene	Toluene
Isophorone	Trichloroethylene
Naphthalene	Vinyl chloride (chloroethylene)
Nitrobenzene	Aldrin
2-Nitrophenol	Dieldrin
4-Nitrophenol	Chlordane (technical mixture and metabolites)
2,4-Dinitrophenol	4,4-DDT
4,6-Dinitro- <i>o</i> -cresol	4,4-DDE (<i>p,p</i> -DDX)
<i>N</i> -nitrosodimethylamine	4,4-DDD (<i>p,p</i> -TDE)
<i>N</i> -nitrosodiphenylamine	Alpha-endosulfan
<i>N</i> -nitrosodi- <i>n</i> -propylamine	Beta-endosulfan
Pentachlorophenol	Endosulfan sulfate
Phenol	Endrin
Bis(2-ethylhexyl) phthalate	Endrin aldehyde
Butyl benzyl phthalate	Heptachlor
Di- <i>n</i> -butyl phthalate	Heptachlor epoxide
Di- <i>n</i> -octyl phthalate	(BHC-hexachloro-cyclohexane)
Diethyl phthalate	Alpha-BHC
Dimethyl phthalate	Beta-BHC
1,2-Benzanthracene (Benzo(<i>a</i>)anthracene)	Gamma-BHC
Benzo(<i>a</i>)pyrene (3,4-benzopyrene)	Delta-BHC
3,4-Benzofluoranthene (benzo(<i>b</i>)fluoranthene)	(PCB-polychlorinated biphenyls)
11,12-Benzofluoranthene (benzo(<i>k</i>)fluoranthene)	PCB-1242 (Arochlor 1242)
Chrysene	PCB-1254 (Arochlor 1254)
Acenaphthylene	PCB-1221 (Arochlor 1221)
Anthracene	PCB-1232 (Arochlor 1232)
1,12-Benzoperylene (benzo(<i>ghi</i>)perylene)	PCB-1248 (Arochlor 1248)
Fluorene	PCB-1260 (Arochlor 1260)
Phenanthrene	PCB-1016 (Arochlor 1016)
1,2,5,6-Dibenzanthracene (dibenzo(<i>a,h</i>)anthracene)	Toxaphene
	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin (TCDD)

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12 Recycling and Disposal of Hazardous Solid Wastes Containing Heavy Metals and Other Toxic Substances

Lawrence K. Wang

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12.1 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 only recovered at a justifiable expense 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 for solving the problems of hazardous wastes and universal wastes [1–11].

12.2 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 Switzerland 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]. The Switzerland's Ordinance takes into account the regulations on cooperation between the country's Federal Council and private sectors that 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, 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.

The 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.

12.3 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 the sanitary landfill sites for dismantling, separation, resource recovery, and disposal. Commercial companies are 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 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 polychlorinated biphenyls (PCBs), a carcinogen; most of these ballasts are still in service. Batteries can contain any number of hazardous materials, including cadmium (nickel–cadmium batteries), the explosive lithium (lithium-ion batteries), and lead (lead-acid batteries). Some household

nonrechargeable batteries still in use also contain mercury, although mercury has been phased out of batteries that are in wide circulation.

In the United States, the Universal Waste Regulations so far have streamlined 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 the 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, they also facilitate programs developed to reduce the quantity of these wastes going to MSW landfills or combustors. They also assure 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 disposition 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 universals is 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 may 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 Universals must be handled by a licensed recycler. There are, however, only a few licensed recyclers in the United States available for services.

12.4 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 done 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 only do this provided 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.

12.5 PRACTICAL EXAMPLES

12.5.1 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 as follows: (a) stripping of hazardous substances; (b) reduction of pollutant and metal content 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 disposal of electronic waste appliances are as follows: (a) Appliances may only be broken up (shredded) if the components containing particularly hazardous substances have previously been removed. (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 for disposal of electronic waste appliances include the following steps:

1. *Stripping of hazardous components:* In an initial step, 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, turbo-rotor, sink-float, eddy current, or magnetic separation. The separated fractions are handed on in 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 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. *Handling and processing of CRTs:* CRTs are handed on 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.

12.5.2 GENERAL MANAGEMENT AND DISPOSAL OF LARGE ELECTRICAL WASTE APPLIANCES

Large electrically powered domestic waste appliances, such as cookers, ovens, washing machine, and other cleaning appliances, mobile electrical heaters, and ventilators (see List of appliances) 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 (see separate fact sheet). They may contain particularly hazardous components (accumulators, batteries, condensers, mercury switches, etc.).

The objectives for management and disposal of large electrical waste appliances are as follows: (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 only be shredded if the particularly hazardous components have previously been removed.

Older appliances (such as ovens) still sometimes contain asbestos. Waste from which asbestos fibers may be released is classified as 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 for management and disposal of large electrical waste appliances include the following steps:

1. *Stripping of hazardous substances:* In an initial step, 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, cement works, or they are recycled.

12.5.3 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 disposal of small electrical waste appliances is that appliances may be shredded 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 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, 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, turbo-rotor, sink-float, eddy current, or magnetic separation. The separated fractions are handed on in 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 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, cement works, or they are recycled.

12.5.4 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 of disposal of refrigeration and air-conditioning waste appliances are as follows: (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 to be the priority in metal recycling.

The requirements for 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) Ninety percent 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/m³ 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 direct 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 sent to be destroyed.
5. *Shredding and fractionation of the main unit:* It 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 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 12.1](#) shows the flow diagram for management, separation, recycle, and disposal of used refrigeration appliances [4].

12.5.5 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 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 as follows: (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 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 as much as 3 g of liquid mercury and are located in almost any building, including commercial,

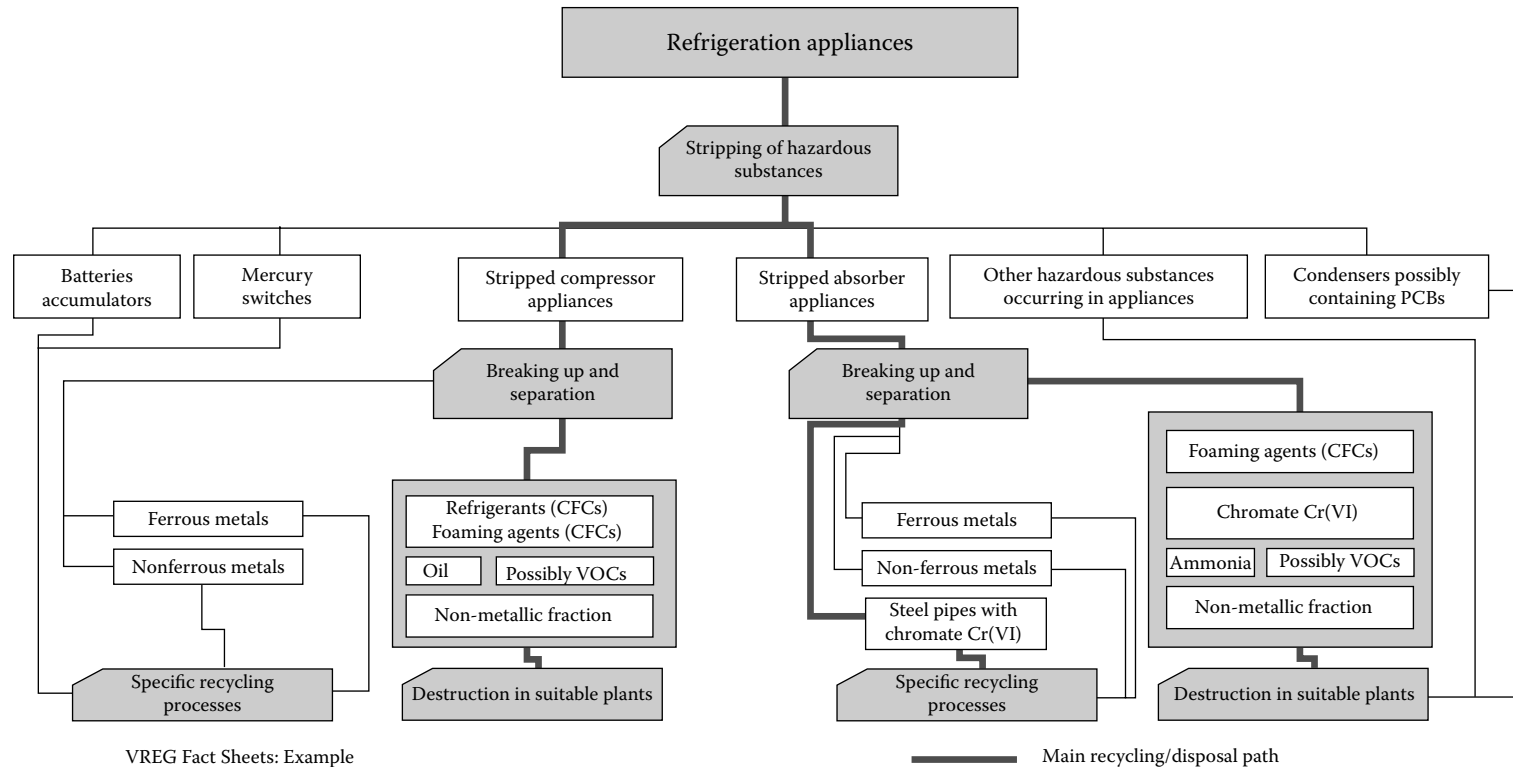


FIGURE 12.1 Flow diagram for management, separation, recycling, and disposal of waste refrigeration appliances. (Adapted from SAEFL. *Waste Management Guidelines for the Ordinance on the Return, the Taking Back and the Disposal of Electrical and Electronic Appliances (ORDEA)*, p. 76. Swiss Agency for the Environment, Forests and Landscape Bern, Switzerland, 2000.)

industrial, agricultural, community, and household buildings; (d) lamps that are the bulb or tube portion of electric lighting devices that have a hazardous component [*Note:* 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 system.

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 they can make them more stringent by adding their own universal wastes (such as antifreeze, for instance).
4. *Universal waste battery:* Battery means a device consisting of one or more electrically connected electrochemical cells that 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 plant regulator, defoliant, or desiccant.
6. *Universal waste thermostat:* Thermostat means a temperature-controlling device that contains metallic mercury in an ampoule 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 as follows: (a) a business that generated (needs to dispose of) a universal waste (fluorescent lights for instance); (b) a take-back program; and (c) a collection program.
9. *Small quantity handlers of universal waste (SQHUW):* A handler that accumulates less than 5000 kg (11,000 lbs) of universal waste at any one time.
10. *Large quantity handlers of universal waste (LQHUW):* A handler that accumulates 5000 kg (11,000 lbs) 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*: This does not include facilities that only store universal waste since those facilities qualify as a universal waste handler.)

12.5.6 MANAGEMENT AND DISPOSAL OF A SPECIFIC ELECTRONIC WASTE: CRTs

CRTs, as shown in Figure 12.2, are the video 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

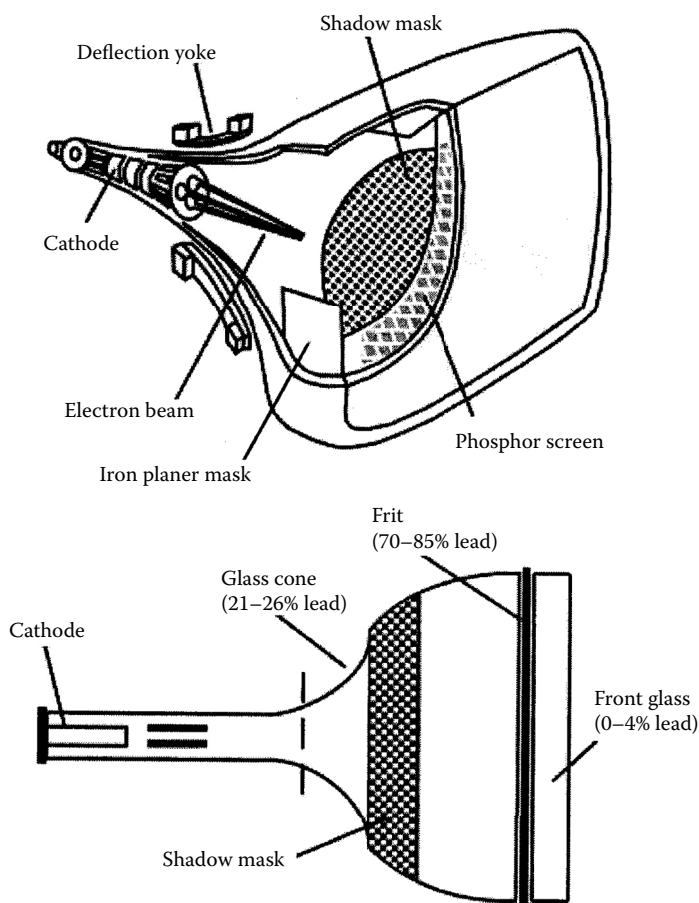


FIGURE 12.2 Schematic diagram of a CRT. (Adapted from RSC. Royal Society of Chemistry, London, 2009. Available at: www.rsc.org/ej/GC/2001/b102671m/b102671m-f1.gif)

containerized and labeled when stored or shipped before recycling, they resemble commodities more than wastes.

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 12.3](#) shows a flow diagram for management, separation, recycle, and disposal of CRTs [4].

12.5.7 MANAGEMENT AND DISPOSAL OF MERCURY-CONTAINING EQUIPMENT INCLUDING LAMPS

Mercury is present in several types of instruments that are commonly used by electric utilities, municipalities, and households. Among others, these devices include barometers, meters, temperature gauges, pressure gauges, sprinkler system contacts, and parts of coal conveyor systems. The 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 equipments.

The 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 the awareness of the proper disposal methods of these lamps in compliance with the 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 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 20–40% by 2005, and to 80% by 2009.

The 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 one cooperative agreements are developing outreach materials such as fact sheets, recycling database, websites, public service announcements, and educational materials.

Although phase one cooperative agreement recipients focused on developing outreach materials, the recently selected phase two 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 one to target-specific audiences (i.e., industry-specific lamp users or lamp users within a certain geographic location).

12.5.8 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, and 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. Though batteries generally make up only a tiny portion of MSWs, less than 1%, they account for a disproportionate amount of the toxic heavy metals in MSWs. For example, the U.S. EPA has reported that, as of 1995, nickel–cadmium batteries accounted for 75% of the cadmium found in MSWs. When MSW

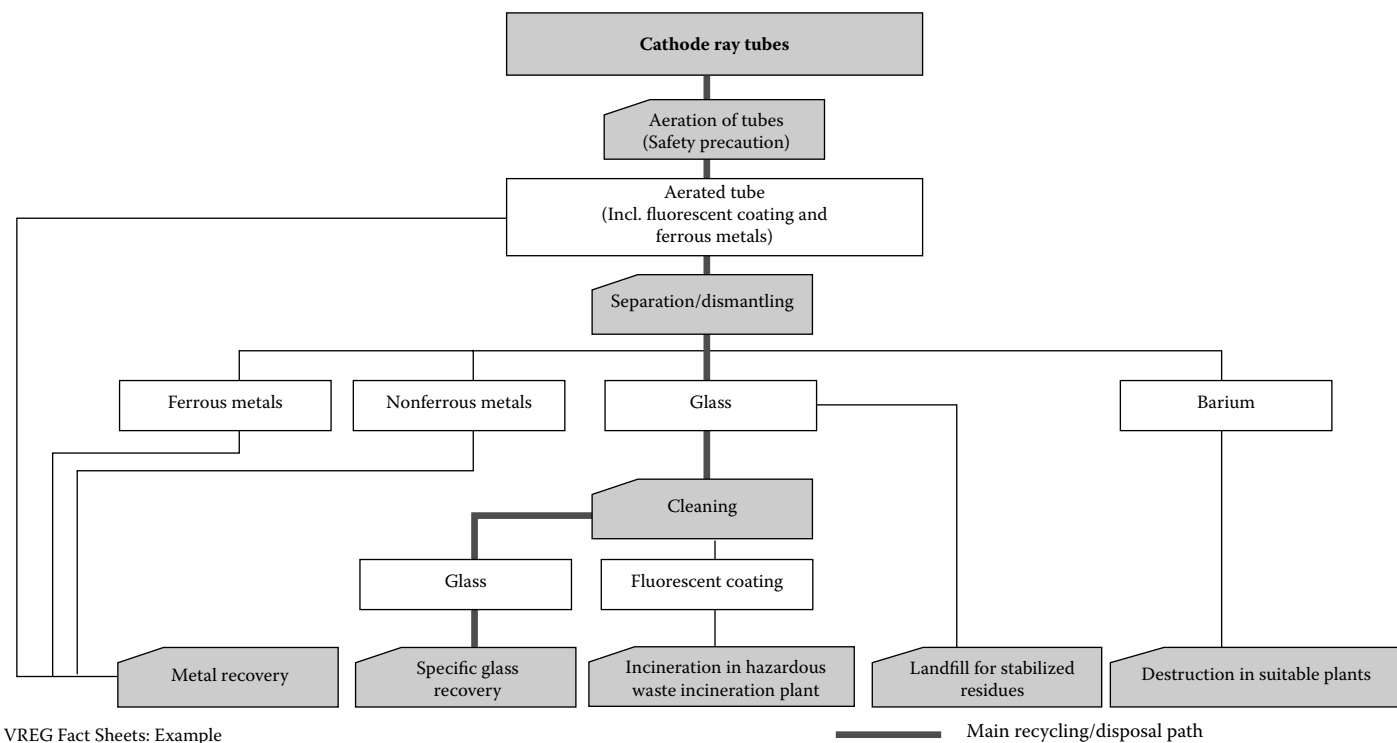


FIGURE 12.3 Flow diagram for management, separation, recycling, and disposal of waste CRTs. (Adapted from SAEFL. *Waste Management Guidelines for the Ordinance on the Return, the Taking Back and the Disposal of Electrical and Electronic Appliances (ORDEA)*, p. 76. Swiss Agency for the Environment, Forests and Landscape Bern, Switzerland, 2000.)

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 pounds 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.

The environmental hazards of batteries are briefly summarized below. 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 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 with a new 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 away from children and sources of sparks. All old batteries should be recycled.

Prolonging battery life is another method for environmental protection. 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, if the following procedures can be followed: (a) check the battery for adequate water level if the battery is not a sealed battery, and check the battery and the vehicle charge system if the battery is low on water; (b) do not overfill a battery; (c) make sure all connections are clean; (d) if the vehicle is seldom used, charge the battery at least every two months to maintain the battery charge, because in a discharge state, the battery might freeze; (e) if the battery must be stored out of the vehicle, store 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 positive cable on the battery to be jumped, and the negative cable to a solid ground on the vehicle (e.g., bracket on alternator). This avoids 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 for 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, United States, has adopted legislation that requires retailers to either (a) accept a used battery upon sale of a new battery, or (b) collect a USD 10 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 more than 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.

12.5.9 MANAGEMENT, REUSE, RECYCLE, AND DISPOSAL OF HOUSEHOLD BATTERIES

More and more household batteries are being used today. The average 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 12.1 shows the typical types of household batteries.

Battery manufacturers are producing more rechargeable batteries each year. The National Electrical Manufacturers Association has estimated that the USA'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 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 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 is 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

TABLE 12.1
Typical Types of Household Batteries

Primary Cells (Nonrechargeable)	Common Uses
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)	Common uses
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.

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, a battery used as a backup power source for memory or program, nor as a rechargeable alkaline battery.

The term “rechargeable consumer product” (a) means a product that, when sold at retail, includes a regulated battery as a primary energy supply, and that is primarily intended 1 kW personal or household use; but (b) does not include a product that only uses a battery solely as a source of backup power for memory or program instruction storage, time keeping, or any similar purpose that requires uninterrupted electrical power in order to function if the primary energy supply fails or fluctuates momentarily.

The term “regulated battery” (a) means a rechargeable battery that 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 and 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 and (rechargeable) include lead–acid, nickel–cadmium, and potentially nickel–hydrogen.

Mercury reduction in household batteries began in 1984 and continues today. During the last 5 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 technology 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 system are being researched, but nickel–cadmium 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 the nickel–cadmium batteries for recycling.

To reduce waste, start with pollution prevention. Starting with prevention creates less or no leftover waste to become potentially hazardous wastes. Rechargeable batteries result in a longer life span and use fewer batteries. However, rechargeable batteries still contain heavy metals such as nickel–cadmium. When disposing of rechargeable batteries, recycle 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 in 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 for information on battery recycling.

Mercury oxide and silver oxide button batteries are sometimes collected by jewelers, pharmacies, hospitals, and electronic or hearing aid stores for shipping to companies that reclaim mercury or silver. Some batteries cannot be recycled. If recycling is not possible, batteries should be saved for a hazardous waste collection. Battery recycling and button battery collection may be a good option 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, 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 area permitted landfill, 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 the metals they contain 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.

In the United States, Federal and State initiatives are assisting the business 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 rulemaking.

The Mercury-Containing and Rechargeable Battery Management Act (the "Battery Act"), which was signed into 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 are 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. States 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) Northeast Waste Management Officials' Association (NEWMOA); and (b) New England Governors' Conference.

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 phase-outs 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 phase-outs, product labeling, disposal bans, and collection and recycling programs. Certain types of mercury-containing batteries are among the products targeted by the model legislation.

12.5.10 MANAGEMENT OF ELECTRONIC WASTES: WASTE COMPUTERS

In the early 1980s, the world witnessed the sale of the first personal computer. The 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 5 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 used in a typical computer and cause potential harm if they are released 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, which separates the salvageable components for reuse, removes the special metals/materials that have recyclable value, and only disposes of the remaining waste materials. The Town charges the residents a fee, USD 10 per computer system (monitor, CPU, printer, keyboard, and mouse, 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.

12.5.11 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 2 ppb, 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 byproducts or secondary wastes. 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," which is critically important in constantly changing industries and the environment. It has broad applications in environmental cleanup where mercury contamination is prevalent, or for mercury removal in 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 ranging from 2 nm (nanometer) to 20 nm, with high surface areas (about 600 to 1000 m²/g) are functionalized with a self-assembled monolayer, resulting in an extremely high density of 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, whereas 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 reduced by about 99.5%. Estimates indicate that it will cost about USD 200 (October 2004 cost), including material, analysis, and labor, to treat similar volumes of this waste solution, resulting in a savings of USD 3200 over more traditional polymeric adsorbent (resin) or activated carbon disposal methods.

12.5.12 SOLIDIFICATION (CEMENTATION) TECHNOLOGY FOR HAZARDOUS e-WASTE DISPOSAL

Cementation technology is one of the solidification technologies, involving the use of a solidifying agent (i.e., cement, in this case) for solidifying the hazardous solid e-wastes (such as mercury-containing batteries or equipment). Conventional cementation technology has the following problems: (a) the solidified cement or concrete is still porous, and eventually the hazardous substances may leak out; and (b) the solidified cement or concrete block are not strong enough, and may break upon impact or earth quake.

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 friendly to the environment, 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 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) a 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 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 byproducts of cement hydration (calcium hydroxide, mineral salts, mineral oxides, and unhydrated and partially hydrated cement particles). The end result is crystallization and, ultimately, a nonsoluble crystalline structure that plugs the pores and capillary tracts of the concrete 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 variety 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 3–11.

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13 Management and Removal of Heavy Metals from Contaminated Soil

Nazih K. Shammam

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13.1 INTRODUCTION

Metals account for much of the contamination found at hazardous waste sites. They are present in the soil and groundwater at approximately 65% of the Superfund or CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act [1] sites for which the U.S. Environmental Protection Agency (U.S. EPA) has signed records of decisions [2]. The metals most frequently identified are lead, arsenic, chromium, cadmium, nickel, and zinc. Other metals often identified as contaminants include copper and mercury. In addition to the Superfund program, metals make up a significant portion of the contamination requiring remediation under the Resource Conservation and Recovery Act (RCRA) [3] and contamination present at federal facilities, notably those that are the responsibility of the Department of Defense (DoD) and the Department of Energy (DOE).

This chapter provides remedial project managers, engineers, on-scene coordinators, contractors, and other state or private remediation managers and their technical support personnel with information to facilitate the selection of appropriate remedial alternatives for soil contaminated with arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb) [4–6].

Common compounds, transport, and fate are discussed for each of the five elements. A general description of metal-contaminated Superfund soils is provided. The technologies covered are containment (immobilization), solidification/stabilization (S/S), vitrification, soil washing, soil flushing, pyrometallurgy, electrokinetics, and phytoremediation. Use of treatment trains and remediation costs are also addressed.

It is assumed that users of this chapter will, as necessary, familiarize themselves with (1) applicable or relevant and appropriate regulations pertinent to the site of interest, (2) applicable health and safety regulations and practices relevant to the metals and compounds discussed, and (3) relevant sampling, analysis, and data interpretation methods. Information on Pb battery (Pb, As), wood preserving (As, Cr), pesticide (Pb, As, Hg), and mining sites has been addressed in U.S. EPA Superfund documents [7–12]. The greatest emphasis is on remediation of inorganic forms of the metals of interest. Organometallic compounds, organic-metal mixtures, and multimetal mixtures are briefly addressed.

13.2 OVERVIEW OF METALS AND THEIR COMPOUNDS

This section provides a brief, qualitative overview of the physical characteristics and mineral origins of the five metals and factors affecting their mobility. More comprehensive and quantitative reviews of the behavior of these five metals in soil can be found in readily available U.S. EPA Superfund documents [4,13,14].

13.2.1 OVERVIEW OF PHYSICAL CHARACTERISTICS AND MINERAL ORIGINS

Arsenic is a semimetallic element or metalloid that has several allotropic forms. The most stable allotrope is a silver-gray, brittle, crystalline solid that tarnishes in air. As compounds, mainly As_2O_3 , can be recovered as a by-product of processing complex ores mined mainly for copper, lead, zinc, gold, and silver. As occurs in a wide variety of mineral forms, including arsenopyrite, FeAsS_4 , which is the main commercial ore of As worldwide.

Cadmium is a bluish-white, soft, ductile metal. Pure Cd compounds are rarely found in nature, although occurrences of greenockite (CdS) and otavite (CdCO_3) are known. The main sources of Cd are sulfide ores of lead, zinc, and copper. Cd is recovered as a by-product when these ores are processed.

Chromium is a lustrous, silver-gray metal. It is one of the less common elements in the earth's crust, and occurs only in compounds. The chief commercial source of Cr is the mineral chromite, FeCr_2O_4 . Cr is mined as a primary product and is not recovered as a by-product of any other mining operation. There are no chromite-ore reserves, nor any primary production of chromite in the United States.

Mercury is a silvery, liquid metal. The primary source of Hg is cinnabar (HgS), a sulfide ore. In a few cases, Hg occurs as the principal ore product; it is more commonly obtained as the by-product of processing complex ores that contain mixed sulfides, oxides, and chloride minerals (these are usually associated with base and precious metals, particularly gold). Native or metallic Hg is found in very small quantities in some ore sites. The current demand for Hg is met by secondary production (i.e., recycling and recovery).

Lead is a bluish-white, silvery, or gray metal that is highly lustrous when freshly cut but tarnishes when exposed to air. It is very soft and malleable, has a high density (11.35 g/cm^3) and low melting point (327.4°C), and can be cast, rolled, and extruded. The most important Pb ore is galena, PbS. Recovery of Pb from the ore typically involves grinding, flotation, roasting, and smelting. Less common forms of the mineral are cerussite, PbCO_3 , anglesite, PbSO_4 , and crocoite, PbCrO_4 .

13.2.2 OVERVIEW OF BEHAVIOR OF AS, CD, CR, PB, AND HG

Since metals cannot be destroyed, remediation of metal-contaminated soil consists primarily of manipulating (i.e., exploiting, increasing, decreasing, or maintaining) the mobility of metal contaminant(s) to produce a treated soil that has an acceptable total or leachable metal content. Metal mobility depends on numerous factors. Metal mobility in soil-waste systems is determined by the following [13]:

1. Type and quantity of soil surfaces present.
2. Concentration of metal of interest.
3. Concentration and type of competing ions and complexing ligands, both organic and inorganic.
4. pH.
5. Redox status.

“Generalization can only serve as rough guides of the expected behavior of metals in such systems. Use of literature or laboratory data that do not mimic the specific site soil and waste system will not be adequate to describe or predict the behavior of the metal. Data must be site specific. Long-term effects must also be considered. As organic constituents of the waste matrix degrade, or as pH or redox conditions change, either through natural processes of weathering or human manipulation, the potential mobility of the metal will change as soil conditions change” [13].

Cd, Cr(III), and Pb are present in cationic forms under natural environmental conditions [13]. These cationic metals generally are not mobile in the environment and tend to remain relatively close to the point of initial deposition. The capacity of soil to adsorb cationic metals increases with increasing pH, cation exchange capacity, and organic carbon content. Under the neutral to basic conditions typical of most soils, cationic metals are strongly adsorbed on the clay fraction of soils and can be adsorbed by hydrous oxides of iron, aluminum, or manganese present in soil minerals. Cationic metals will precipitate as hydroxides, carbonates, or phosphates. In acidic, sandy soils, the cationic metals are more mobile. Under conditions that are atypical of natural soils (e.g., $\text{pH} < 5$ or > 9 elevated concentrations of oxidizers or reducers; high concentrations of soluble organic or inorganic complexing or colloidal substances), but may be encountered as a result of waste disposal or remedial processes, the mobility of these metals may be substantially increased. Also, competitive adsorption between various metals has been observed in experiments involving various solids with oxide surfaces ($\gamma\text{-FeOOH}$, $\alpha\text{-SiO}_2$, and $\gamma\text{-Al}_2\text{O}_3$). In several experiments, Cd adsorption was decreased by the addition of Pb or Cu for all three of these solids. The addition of zinc resulted in the greatest decrease of Cd adsorption. Competition for surface sites occurred when only a few percent of all surface sites were occupied [15].

As, Cr(VI), and Hg behaviors differ considerably from Cd, Cr(III), and Pb. As and Cr(VI) typically exist in anionic forms under environmental conditions. Hg, although it is a cationic metal, has unusual properties (e.g., liquid at room temperature and easily transforms among several possible valence states).

In most As-contaminated sites, As appears as As_2O_3 or as anionic As species leached from As_2O_3 , oxidized to As(V), and then sorbed onto iron-bearing minerals in the soil. As may also be present in organometallic forms, such as methylarsenic acid, $\text{H}_2\text{AsO}_3\text{CH}_3$, and dimethylarsenic acid, $(\text{CH}_3)_2\text{AsO}_2\text{H}$, which are active ingredients in many pesticides, as well as the volatile compounds arsine (AsH_3) and its methyl derivatives [i.e., dimethylarsine $\text{HAs}(\text{CH}_3)_2$ and trimethylarsine, $\text{As}(\text{CH}_3)_3$]. These As forms illustrate the various oxidation states that As commonly exhibits (—III, 0, III, and V) and the resulting complexity of its chemistry in the environment.

As(V) is less mobile and less toxic than As(III). As(V) exhibits anionic behavior in the presence of water, and hence its aqueous solubility increases with increasing pH, and it does not complex or precipitate with other anions. As(V) can form low-solubility metal arsenates. Calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, is the most stable metal arsenate in well-oxidized and alkaline environments, but it is unstable in acidic environments. Even under initially oxidizing and alkaline conditions, absorption of CO_2 from the air will result in the formation of CaCO_3 and release of arsenate. In sodic soils, sufficient sodium is available, such that the mobile compound Na_3AsO_4 can form. The slightly less stable manganese arsenate, $\text{Mn}_2(\text{AsO}_4)_2$, forms in both acidic and alkaline environments, while iron arsenate is stable under acidic soil conditions. In aerobic environments, HAsO_4 predominates at $\text{pH} < 2$ and is replaced by H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} as pH increases to about 2, 7, and 11.5, respectively. Under mildly reducing conditions, H_3AsO_3 is a predominant species at low pH, but is replaced by H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-} as pH increases. Under still more reducing conditions and in the presence of sulfide, As_2S_3 can form. As_2S_3 is a low-solubility, stable solid. AsS_2 and AsS_2^- are thermodynamically unstable with respect to As_2S_3 [16]. Under extreme reducing conditions, elemental As and volatile arsine, AsH_3 , can form. Just as competition between cationic metals affects mobility in soil, competition between anionic species (chromate, arsenate, phosphate, sulfate, and so on) affects anionic fixation processes and may increase mobility.

The most common valence states of Cr in the earth's surface and near-surface environment are +3 (trivalent or Cr(III)) and +6 (hexavalent or Cr(VI)). Trivalent Cr (discussed above) is the most thermodynamically stable form under common environmental conditions. Except in leather tanning, industrial applications of Cr generally use the Cr(VI) form. Due to kinetic limitations, Cr(VI) does not always readily reduce to Cr(III) and can remain present over an extended period of time.

Cr(VI) is present as the chromate, CrO_4^{2-} , or dichromate, $\text{Cr}_2\text{O}_7^{2-}$, anion, depending on pH and concentration. Cr(VI) anions are less likely to be adsorbed to solid surfaces than Cr(III). Most solids in soils carry negative charges that inhibit Cr(VI) adsorption. Although clays have a high capacity to adsorb cationic metals, they interact little with Cr(VI) because of the similar charges carried by the anion and clay in the common pH range of soil and groundwater. The only common soil solid that adsorbs Cr(VI) is iron oxyhydroxide. Generally, a major portion of Cr(VI) and other anions adsorbed in soils can be attributed to the presence of iron oxyhydroxide. The quantity of Cr(VI) adsorbed onto the iron solids increases with decreasing pH.

At metal-contaminated sites, Hg can be present in mercuric form (Hg^{2+}), mercurous form (Hg_2^{2+}), elemental form (Hg), or alkylated form (e.g., methyl and ethyl Hg). Hg_2^{2+} and Hg^{2+} are more stable under oxidizing conditions. Under mildly reducing conditions, both organically bound Hg and inorganic Hg compounds can be converted to elemental Hg, which can then be readily converted to methyl or ethyl Hg by biotic and abiotic processes. Methyl and ethyl Hg are mobile and toxic forms.

Hg is moderately mobile, regardless of the soil. Both the mercurous and mercuric cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption of cationic forms of Hg increases with increasing pH. Mercurous and mercuric Hg are also immobilized by forming various precipitates. Mercurous Hg precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of Hg commonly found in soil, only the phosphate precipitate is stable. In alkaline soils, mercuric Hg precipitates with carbonate and hydroxide to form a stable (but not exceptionally insoluble) solid phase. At lower pH and high chloride concentration, soluble HgCl_2 is formed. Mercuric Hg also forms complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility [13]. In strong reducing conditions, HgS , a very low-solubility compound is formed.

13.3 DESCRIPTION OF SUPERFUND SOILS CONTAMINATED WITH METALS

Soils can become contaminated with metals from direct contact with industrial plant waste discharges, fugitive emissions, or leachate from waste piles, landfills, or sludge deposits. The specific type of metal contaminant expected at a particular Superfund site would obviously be directly related to the type of operation that had occurred there. Table 13.1 lists the types of operations that are directly associated with each of the five metal contaminants [5].

Wastes at CERCLA sites are frequently heterogeneous on a macro- and microscale. The contaminant concentration and the physical and chemical forms of the contaminant and matrix are usually complex and variable. Of these, waste disposal sites collect the widest variety of waste types; therefore, concentration profiles vary by orders of magnitude through a pit or pile. Limited volumes of high-concentration “hot spots” may develop due to variations in the historical waste disposal patterns or local transport mechanisms. Similar radical variations frequently occur on the particle-size scale as well. The waste often consists of a physical mixture of very different solids, for example, paint chips in spent abrasive.

Industrial processes may result in a variety of solid metal-bearing waste materials, including slags, fumes, mold sand, fly ash, abrasive wastes, spent catalysts, spent activated carbon, and refractory bricks [17]. These process solids may be found above ground as waste piles or below ground in landfills. Solid-phase wastes can be dispersed by well-intended but poorly controlled reuse projects. Waste piles can be exposed to natural disasters or accidents, causing further dispersion.

13.4 SOIL CLEANUP GOALS AND TECHNOLOGIES FOR REMEDIATION

Table 13.2 provides an overview of cleanup goals (actual and potential) for both total and leachable metals. Based on inspection of the total metals cleanup goals, one can see that they vary considerably both within the same metal and between metals.

Similar variation is observed in the actual or potential leachate goals. The observed variation in cleanup goals has at least two implications with regard to technology alternative evaluation and selection. Firstly, the importance of identifying the target metal(s), contaminant state (leachable versus total metal), the specific type of test and conditions, and the numerical cleanup goals early in the remedy evaluation process is made apparent. Depending on which cleanup goal is selected, the required removal or leachate reduction efficiency of the overall remediation can vary by several orders of magnitude [5,18]. Secondly, the degree of variation in goals both within and between metals, plus the many factors that affect mobility of the metals, suggest that generalizations about effectiveness of a technology for meeting total or leachable treatment goals should be viewed with some caution.

Technologies that are potentially applicable to the remediation of soils contaminated with the five metals or their inorganic compounds are listed below [2,5]:

Technology Class	Specific Technology
Containment	Caps
	Vertical barriers
	Horizontal barriers
S/S	Cement-based
	Polymer microencapsulation
	Vitrification
Separation/concentration	Soil washing
	Soil flushing
	Pyrometallurgy
	Electrokinetics
	Phytoremediation

TABLE 13.1
Principal Sources of As, Cd, Cr, Hg, and Pb Contaminated Soils

Contaminant	Principal Sources
As	Wood preserving As-waste disposal Pesticide production and application Mining
Cd	Plating Ni–Cd battery manufacturing Cd-waste disposal
Cr	Plating Textile manufacturing Leather tanning Pigment manufacturing Wood preserving Cr-waste disposal
Hg	Chloralkali manufacturing Weapons production Copper and zinc smelting Gas line manometer spills Paint application Hg-waste disposal
Pb	Ferrous/nonferrous smelting Pb-acid battery breaking Ammunition production Leaded paint waste Pb-waste disposal Secondary metals production Waste oil recycling Firing ranges Ink manufacturing Mining Pb-acid battery manufacturing Leaded glass production Tetraethyl Pb production Chemical manufacturing

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

The Best Demonstrated Available Technology (BDAT) status refers to the determination under the RCRA of the BDAT for various industry-generated hazardous wastes that contain the metals of interest. Whether the characteristics of a Superfund metal-contaminated soil (or fractions derived from it) are similar enough to the RCRA waste to justify serious evaluation of the BDAT for a specific Superfund soil must be made on a site specific basis. Other limitations relevant to BDATs include the following: (a) the regulatory basis for BDAT standards focus BDATs on proven, commercially available technologies at the time of the BDAT determination; (b) a BDAT may be

TABLE 13.2
Cleanup Goals (Actual and Potential) for Total and Leachable Metals

Description	As	Cd	Cr (Total)	Hg	Pb
Total Metals Goals (mg/kg)					
Background (mean)	5	0.06	100	0.03	10
Background (range)	1–50	0.01–0.70	1–1000	0.01–0.30	2–200
Superfund site goals from TRD	5–65	3–20	6.7–375	1–21	200–500
Theoretical minimum total metals to ensure TCLP Leachate < threshold (i.e., TCLP × 20)	100	20	100	4	100
California total threshold limit concentration	500	100	500	20	1000
Leachable Metals (µg/L)					
TCLP threshold for RCRA waste	5000	1000	5000	200	5000
Extraction procedure toxicity test	5000	1000	5000	200	5000
Synthetic Precipitate Leachate	—	—	—	—	—
Multiple extraction procedure	—	—	—	—	—
California soluble threshold leachate concentration	5000	1000	5000	200	5000
Maximum contaminant level ^a	50	5	100	2	15
Superfund site goals from TRD	50	—	50	0.05–2	50

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

^a Maximum contaminant level = The maximum permissible level of contaminant in water delivered to any user of a public system.

— No specified level and no example cases identified.

identified, but that does not necessarily preclude the use of other technologies; and (c) a technology identified as BDAT may not necessarily be the current technology of choice in the RCRA hazardous waste treatment industry.

The U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program evaluates many emerging and demonstrated technologies to promote the development and use of innovative technologies to clean up Superfund sites across the country. The major focus of SITE is the Demonstration Program, which is designed to provide engineering and cost data for selected technologies.

Cost is not discussed in each technology narrative; however, a summary table is provided at the end of the technology discussion section that illustrates technology cost ranges and treatment train options.

13.5 CONTAINMENT

Containment technologies for application at Superfund sites include landfill covers (caps), vertical barriers, and horizontal barriers [4]. For metal remediation, containment is considered an established technology except for *in situ* installation of horizontal barriers.

13.5.1 PROCESS DESCRIPTION

Containment ranges from a surface cap that limits infiltration of uncontaminated surface water to subsurface vertical or horizontal barriers that restrict lateral or vertical migration of contaminated groundwater. The material provided here is primarily from U.S. EPA [5,9].

13.5.1.1 Caps

Capping systems reduce surface water infiltration, control gas and odor emissions, improve aesthetics, and provide a stable surface over the waste. Caps can range from a simple native soil cover to a full RCRA subtitle C, composite cover.

Cap construction costs depend on the number of components in the final cap system (i.e., costs increase with the addition of barrier and drainage components). Additionally, cost escalates as a function of topographic relief. Side slopes steeper than 3 horizontal to 1 vertical can cause stability and equipment problems that dramatically increase the unit cost [4,19].

13.5.1.2 Vertical Barriers

Vertical barriers minimize the movement of contaminated groundwater off-site or limit the flow of uncontaminated groundwater on-site. Common vertical barriers include slurry walls in excavated trenches; grout curtains formed by injecting grout into soil borings; vertically injected, cement-bentonite grout-filled borings or holes formed by withdrawing beams driven into the ground; and sheet-pile walls formed of driven steel.

Certain compounds can affect cement-bentonite barriers. The impermeability of bentonite may significantly decrease when it is exposed to high concentrations of creosote, water-soluble salts (copper, Cr, and As), or fire-retardant salts (borates, phosphates, and ammonia). The specific gravity of salt solutions must be greater than 1.2 to impact bentonite [20,21]. In general, soil-bentonite blends resist chemical attack best if they contain only 1% bentonite and 30–40% natural soil fines. Treatability tests should evaluate the chemical stability of the barrier if adverse conditions are suspected.

Carbon steel used in pile walls quickly corrodes in dilute acids, slowly corrodes in brines or salt water, and remains mostly unaffected by organic chemicals or water. Salts and fire retardants can reduce the service life of a steel sheet pile; corrosion-resistant coatings can extend their anticipated life. Major steel suppliers will provide site-specific recommendations for cathodic protection of piling.

The construction costs for vertical barriers are influenced by the soil profile of the barrier material used and by the method of placing it. The most economical shallow vertical barriers are soil-bentonite trenches excavated with conventional backhoes; the most economical deep vertical barriers consist of a cement-bentonite wall placed by a vibrating beam.

13.5.1.3 Horizontal Barriers

In situ horizontal barriers can underlie a sector of contaminated materials on-site without removing the hazardous waste or soil. Established technologies use grouting techniques to reduce the permeability of underlying soil layers. Studies performed by the U.S. Army Corps of Engineers [22] indicate that conventional grout technology cannot produce an impermeable horizontal barrier because it cannot ensure uniform lateral growth of the grout. These same studies found greater success with jet grouting techniques in soils that contain fines sufficient to prevent collapse of the wash hole and that present no large stones or boulders that could deflect the cutting jet.

Since few *in situ* horizontal barriers have been constructed, accurate costs have not been established. Work performed by the Corps of Engineers for U.S. EPA has shown that it is very difficult to form effective horizontal barriers. The most efficient barrier installation used a jet wash to create a cavity in sandy soils into which cement-bentonite grouting was injected. The costs relate to the number of borings required. Each boring takes at least one day to drill.

13.5.2 SITE REQUIREMENTS

In general, the site must be suitable for a variety of heavy construction equipment, including bulldozers, graders, backhoes, multi-shaft drill rigs, various rollers, vibratory compactors, forklifts, and seaming devices [23,24]. When capping systems are being utilized, on-site storage areas are necessary for the materials to be used in the cover. If site soils are adequate for use in the cover, a borrow area needs to be identified and the soil tested and characterized. If site soils are not suitable, it may

be necessary to truck in other low-permeability soils [23]. In addition, an adequate supply of water may also be needed to achieve optimum soil density.

The construction of vertical containment barriers, such as slurry walls, requires knowledge of the site, the local soil and hydrogeologic conditions, and the presence of underground utilities [25]. Preparation of the slurry requires batch mixers, hydration ponds, pumps, hoses, and an adequate supply of water. Therefore, on-site water storage tanks and electricity are necessary. In addition, areas adjacent to the trench need to be available for the storage of trench spoils (which could potentially be contaminated) and the mixing of backfill. If excavated soils are not acceptable for use as backfill, suitable backfill must be trucked onto the site [25].

13.5.3 APPLICABILITY

Containment is most likely to be applicable to the following [5]:

1. Wastes that are low hazard (e.g., low toxicity or low concentration) or immobile.
2. Wastes that have been treated to produce low-hazard or low-mobility wastes for on-site disposal.
3. Wastes whose mobility must be reduced as a temporary measure to mitigate risk until a permanent remedy can be tested and implemented.

Situations where containment would not be applicable include the following:

1. Wastes for which there is a more permanent and protective remedy that is cost-effective.
2. Where effective placement of horizontal barriers below existing contamination is difficult.
3. Where drinking water sources will be adversely affected if containment fails, and if there is inadequate confidence in the ability to predict, detect, or control harmful releases due to containment failure.

Important advantages of containment are [5] the following:

1. Surface caps and vertical barriers are relatively simple and rapid to implement at low cost and can be more economical than excavation and removal of waste.
2. Caps and vertical barriers can be applied to large areas or volumes of waste.
3. Engineering control (containment) is achieved, and may be a final action if metals are well immobilized and potential receptors are distant.
4. A variety of barrier materials are available commercially.
5. In some cases, it may be possible to create a land surface that can support vegetation and/or be applicable for other purposes.

Disadvantages of containment include [5] the following:

1. Design life is uncertain.
2. Contamination remains on-site, available to migrate should containment fail.
3. Long-term inspection, maintenance, and monitoring is required.
4. The site must be amenable to effective monitoring.
5. Placement of horizontal barriers below existing waste is difficult to implement successfully.

13.5.4 PERFORMANCE AND BDAT STATUS

Containment is widely accepted as a means of controlling the spread of contamination and preventing the future migration of waste constituents. Table 13.3 shows a list of selected sites where containment has been selected for remediating metal-contaminated solids.

TABLE 13.3
Containment Applications at Selected Superfund Sites with Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology
Ninth Avenue Dump, IN	Containment-slurry wall	Pb	Slurry wall/capping
Industrial Waste Control, AK	Containment-slurry wall	As, Cd, Cr, Pb	Capping/French drain
E.H. Shilling Landfill, OH	Containment-slurry wall	As	Capping/clay berm
Chemtronic, NC	Capping	Cr, Pb	Capping
Ordnance Works Disposal, WV	Capping	As, Pb	Capping
Industriplex, MA	Capping	As, Pb, Cr	Capping

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

The performance of capping systems, once installed, may be difficult to evaluate [23]. Monitoring well systems or infiltration monitoring systems can provide some information, but it is often not possible to determine whether the water or leachate originated as surface water or groundwater.

With regard to slurry walls and other vertical containment barriers, performance may be affected by a number of variables, including geographic region, topography, and material availability. A thorough characterization of the site and a compatibility study are highly recommended [25].

Containment technologies are not considered “treatment technologies” and hence no BDATs involving containment have been established.

13.5.5 SITE PROGRAM DEMONSTRATION PROJECTS

Ongoing SITE demonstrations applicable to soils contaminated with the metals of interest include

- Morrison Knudsen Corporation (high clay grouting technology) and
- RKK, Ltd. (frozen soil barriers).

13.6 SOLIDIFICATION/STABILIZATION TECHNOLOGIES

The term “solidification/stabilization (S/S)” refers to a general category of processes that are used to treat a wide variety of wastes, including solids and liquids. Solidification and stabilization are each distinct technologies, as described below [26]:

Solidification—refers to processes that encapsulate a waste to form a solid material and to restrict contaminant migration by decreasing the surface area exposed to leaching and/or by coating the waste with low-permeability materials. Solidification can be accomplished by a chemical reaction between a waste and binding (solidifying) reagents or by mechanical processes. Solidification of fine waste particles is referred to as microencapsulation, whereas solidification of a large block or container of waste is referred to as macroencapsulation.

Stabilization—refers to processes that involve chemical reactions that reduce the leachability of a waste. Stabilization chemically immobilizes hazardous materials (such as heavy metals) or reduces their solubility through a chemical reaction. The physical nature of the waste may or may not be changed by this process.

S/S aims to accomplish one or more of the following objectives [4]:

1. Improve the physical characteristics of the waste by producing a solid from liquid or semi-liquid wastes.
2. Reduce the contaminant solubility by formation of sorbed species or insoluble precipitates (e.g., hydroxides, carbonates, silicates, phosphates, sulfates, or sulfides).

3. Decrease the exposed surface area across which mass transfer loss of contaminants may occur by the formation of a crystalline, glassy, or polymeric framework that surrounds the waste particles.
4. Limit the contact between transport fluids and contaminants by reducing the material's permeability.

S/S technology is usually applied by mixing contaminated soils or treatment residuals with a physical binding agent to form a crystalline, glassy, or polymeric framework surrounding the waste particles. In addition to the microencapsulation, some chemical fixation mechanisms may improve the waste's leach resistance. Other forms of S/S treatment rely on macroencapsulation, where the waste is unaltered but macroscopic particles are encased in a relatively impermeable coating [27], or on specific chemical fixation, where the contaminant is converted to a solid compound resistant to leaching. S/S treatment can be accomplished primarily through the use of either inorganic binders (e.g., cement, fly ash, and/or blast furnace slag) or organic binders such as bitumen [4]. Additives may be used, for example, to convert the metal to a less mobile form or to counteract adverse effects of the contaminated soil on the S/S mixture (e.g., accelerated or retarded setting times and low physical strength). The form of the final product from S/S treatment can range from a crumbly, soil-like mixture to a monolithic block. S/S is more commonly carried out as an *ex situ* process, but the *in situ* option is available. The full range of inorganic binders, organic binders, and additives is too broad. The emphasis in this chapter is on *ex situ*, cement-based S/S, which is widely used; *in situ*, cement-based S/S, which has been applied to metals at full-scale; and polymer microencapsulation, which appears applicable to certain wastes that are difficult to treat via cement-based S/S.

Additional information and references on S/S of metals can be found in U.S. EPA documents [4,28–30]. Innovative S/S technologies (e.g., sorption and surfactant processes, bituminization, emulsified asphalt, modified sulfur cement, polyethylene extrusion, soluble silicate, slag, lime, and soluble phosphates) are addressed in U.S. EPA reports [31–36].

13.6.1 PROCESS DESCRIPTION

13.6.1.1 *Ex Situ*, Cement-Based S/S

Ex situ, cement-based S/S is performed on contaminated soil that has been excavated and classified to reject oversize. Cement-based S/S involves mixing contaminated materials with an appropriate ratio of cement or similar binder/stabilizer, and possibly water and other additives. A system is also necessary for delivering the treated wastes to molds, surface trenches, or subsurface injection. Off-gas treatment (if volatiles or dust are present) may be necessary. The fundamental materials used to perform this technology are Portland-type cements and pozzolanic materials. Portland cements are typically composed of calcium silicates, aluminates, aluminoferrites, and sulfates. Pozzolans are very small spheroidal particles that are formed in combustion of coal (fly ash) in lime and cement kilns, for example. Pozzolans of high silica content are found to have cement-like properties when mixed with water. Cement-based S/S treatment may involve using only Portland cement, only pozzolanic materials, or blends of both. The composition of the cement and pozzolan, together with the amount of water, aggregate, and other additives, determines the set time, cure time, pour characteristics, and material properties (e.g., pore size and compressive strength) of the resulting treated waste. The composition of cements and pozzolans, including those commonly used in S/S applications, is classified according to American Society for Testing and Materials (ASTM) standards. S/S treatment usually results in an increase (>50% in some cases) in the treated waste volume. *Ex situ* treatment provides high throughput (100–200 m³/d/mixer).

Cement-based S/S reduces the mobility of inorganic compounds by formation of insoluble hydroxides, carbonates, or silicates; substitution of the metal into a mineral structure; sorption; physical encapsulation; and perhaps other mechanisms. Cement-based S/S involves a complex series of reactions, and there are many potential interferences (e.g., coating of particles by organics,

excessive acceleration or retardation of set times by various soluble metal and inorganic compounds; excessive heat of hydration; pH conditions that solubilize anionic species of metal compounds, and so on) that can prevent the attainment of S/S treatment objectives for physical strength and leachability. While there are many potential interferences, Portland cement is widely used and studied, and a knowledgeable vendor may be able to identify, and confirm via treatability studies, approaches to counteract adverse effects by the use of appropriate additives or other changes in formulation.

13.6.1.2 *In Situ*, Cement-Based S/S

In situ, cement-based S/S has only two steps: (1) mixing and (2) off-gas treatment. The processing rate for *in situ* S/S is typically much lower than that for *ex situ* processing. *In situ* S/S is demonstrated to depths of 10m and may be able to extend to 50m. The most significant challenge in applying S/S *in situ* for contaminated soils is achieving complete and uniform mixing of the binder with the contaminated matrix [37]. Three basic approaches are used for *in situ* mixing of the binder with the matrix [5]:

1. Vertical auger mixing.
2. In-place mixing of binder reagents with waste by conventional earthmoving equipment, such as draglines, backhoes, or clamshell buckets.
3. Injection grouting, which involves forcing a binder containing dissolved or suspended treatment agents into the subsurface, allowing it to permeate the soil. Grout injection can be applied to contaminated formations lying well below the ground surface. The injected grout cures in-place to produce an *in situ* treated mass.

13.6.1.3 Polymer Microencapsulation S/S

Polymer microencapsulation S/S can include application of thermoplastic or thermosetting resins. Thermoplastic materials are the most commonly used organic-based S/S treatment materials. Potential candidate resins for thermoplastic encapsulation include bitumen, polyethylene and other polyolefins, paraffins, waxes, and sulfur cement. Of these candidate thermoplastic resins, bitumen (asphalt) is the least expensive and by far the most commonly used [38]. The process of thermoplastic encapsulation involves heating and mixing the waste material and the resin at elevated temperature, typically 130–230°C in an extrusion machine. Any water or volatile organics in the waste boil off during extrusion and are collected for treatment or disposal. Because the final product is a stiff, yet plastic resin, the treated material is typically discharged from the extruder into a drum or other container.

S/S process quality control requires information on the range of contaminant concentrations; potential interferences in waste batches awaiting treatment; and treated product properties such as compressive strength, permeability, leachability, and in some instances toxicity [28].

13.6.2 SITE REQUIREMENTS

The site must be prepared for the construction, operation, maintenance, decontamination, and decommissioning of the equipment. The size of the area required for the process equipment depends on several factors, including the type of S/S process involved, the required treatment capacity of the system, and site characteristics, especially soil topography and load-bearing capacity. A small mobile *ex situ* unit occupies space for two, standard flatbed trailers. An *in situ* system requires a larger area to accommodate a drilling rig as well as a larger area for auger decontamination.

13.6.3 APPLICABILITY

This section addresses expected applicability based on the chemistry of the metal and the S/S binders. The soil–contaminant–binder equilibrium and kinetics are complicated, and many factors influence metal mobility; hence there may be exceptions to the generalizations presented below.

13.6.3.1 Cement-Based S/S

For cement-based S/S, if a single metal is the predominant contaminant in soil, then Cd and Pb are the most amenable to cement-based S/S. The predominant mechanism for immobilization of metals in Portland and similar cements is precipitation of hydroxides, carbonates, and silicates. Both Pb and Cd tend to form insoluble precipitates in the pH ranges found in cured cement. They may resolubilize, however, if the pH is not carefully controlled. For example, Pb in aqueous solutions tends to resolubilize as $\text{Pb}(\text{OH})_3^-$ around pH 10 and above. Hg, though it is a cationic metal like Pb and cadmium, does not form low-solubility precipitates in cement; hence it is difficult to stabilize reliably by cement-based processes, and this difficulty would be expected to be greater with increasing Hg concentration and with organomercury compounds. As, due to its formation of anionic species, also does not form insoluble precipitates in the high pH cement environment, and cement-based solidification is generally not expected to be successful. Cr(VI) is difficult to stabilize in cement due to the formation of anions that are soluble at high pH. However, Cr(VI) can be reduced to Cr(III), which does form insoluble hydroxides. Although Hg and As (III and V) are particularly difficult candidates for cement-based S/S, this should not necessarily eliminate S/S (even cement-based) from consideration since (a) as with Cr(VI), it may be possible to devise a multistep process that will produce an acceptable product for cement-based S/S; (b) a non-cement-based S/S process (e.g., lime and sulfide for Hg; oxidation to As(V); and coprecipitation with iron) may be applicable; or (c) the leachable concentration of the contaminant may be sufficiently low that a highly efficient S/S process may not be required to meet treatment goals.

The above discussion on applicability also applies to *in situ* cement-based S/S. If *in situ* treatment introduces chemical agents into the ground, this chemical addition may cause a pollution problem in itself, and may be subject to additional requirements under the Land Disposal Restrictions.

13.6.3.2 Polymer Microencapsulation

Polymer microencapsulation has been mainly used to treat low-level radioactive wastes. However, organic binders have been tested or applied to wastes containing chemical contaminants such as As, metals, inorganic salts, polychlorinated biphenyls, and dioxins [38]. Polymer microencapsulation is particularly well suited for treating water-soluble salts such as chlorides or sulfates that are generally difficult to immobilize in a cement-based system [39]. Characteristics of the organic binder and extrusion system impose compatibility requirements on the waste material. The elevated operating temperatures place a limit on the quantity of water and volatile organic chemicals (VOCs) in the waste feed. Low-volatility organics will be retained in the bitumen but may act as solvents causing the treated product to be too fluid. Bitumen is a potential fuel source, so the waste should not contain oxidizers such as nitrates, chlorates, or perchlorates. Oxidants present the potential for rapid oxidation, causing immediate safety concerns, as well as slow oxidation, which results in waste form degradation.

Cement-based S/S of multiple metal wastes is particularly difficult if a set of treatment and disposal conditions that simultaneously produce low-mobility species for all the metals of concern cannot be found. For example, the relatively high pH conditions that favor Pb immobilization would tend to increase the mobility of As. On the other hand, the various metal species in a multiple metal waste may interact (e.g., the formation of low-solubility compounds by the combination of Pb and arsenate) to produce a low-mobility compound.

Organic contaminants are often present with inorganic contaminants at metal-contaminated sites. S/S treatment of organic-contaminated waste with cement-based binders is more complex than treatment of inorganics alone. This is particularly true with VOCs, where the mixing process and heat generated by cement hydration reactions can increase vapor losses [40–43]. However, S/S can be applied to wastes that contain lower levels of organics, particularly when inorganics are present and/or the organics are semivolatile or nonvolatile. Also, recent studies indicate that the addition of silicates or modified clays to the binder system may improve S/S performance with organics [27].

13.6.4 PERFORMANCE AND BDAT STATUS

Information about the use of S/S at Superfund remedial sites in 2000 indicates that S/S has been used at 167 sites since FY 1982 [34]. Figure 13.1 shows the number of projects by status for the following stages: predesign/design, design completed/being installed, operational, and completed. Data are shown for the *in situ* and *ex situ* S/S projects. In addition, information about all source control technologies is provided. With respect to S/S projects, the majority of both *in situ* and *ex situ* projects (62%) are completed, followed by projects in the predesign/design stage (21%). Overall, completed S/S projects represent 30% of all completed Superfund projects in which treatment technologies have been used for source control.

Figure 13.2 shows the types of binder materials used for S/S projects at Superfund remedial sites, including inorganic binders, organic binders, and combination organic and inorganic binders. Many of the binders used include one or more proprietary additives. Examples of inorganic binders include cement, fly ash, lime, soluble silicates, and sulfur-based binders, whereas organic binders include asphalt, epoxide, polyesters, and polyethylene. More than 90% of the S/S projects used inorganic binders. In general, inorganic binders are less expensive and easier to use than organic binders. Organic binders are generally used to solidify radioactive wastes or specific hazardous organic compounds.

Figure 13.3 shows the types of contaminant groups and combination of contaminant groups treated by S/S at Superfund remedial sites. S/S was used to treat metals only in 56% of the projects, and used to treat metals alone or in combination with organics or radioactive metals at approximately 90% of the sites. S/S was used to treat organics only at 6% of the sites [34]. Figure 13.4 provides a further breakdown of the metals treated by S/S at Superfund remedial sites. The top five metals treated by S/S are Pb, Cr, As, Cd, and Cu.

S/S with cement-based and pozzolan binders is a commercially available, established technology [5]. Table 13.4 shows a selected list of sites where S/S has been selected for remediating metal-contaminated solids. Note that S/S has been used to treat all five metals (Cr, Pb, As, Hg, and Cd). Although it would not generally be expected that cement-based S/S would be applied to As- and Hg-contaminated soils, it was beyond the scope of the project to examine in detail the characterization data, S/S formulations, and performance data upon which the selections were based; hence the selection/implementation data are presented without further comment.

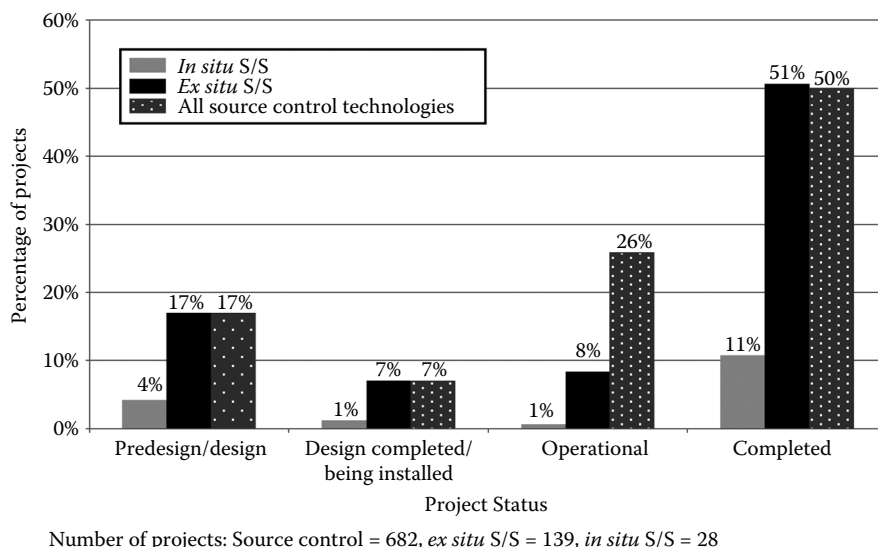


FIGURE 13.1 Percentage of Superfund remedial projects by status. (Adapted from U.S. EPA. *Solidification/Stabilization Use at Superfund Sites*. EPA-542-R-00-010, U.S. Environmental Protection Agency, Washington, DC, September 2000.)

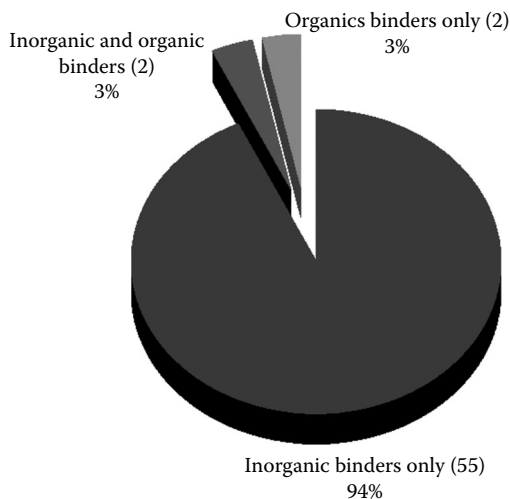


FIGURE 13.2 Binder materials used for S/S projects. (Adapted from U.S. EPA. *Solidification/Stabilization Use at Superfund Sites*. EPA-542-R-00-010, U.S. Environmental Protection Agency, Washington, DC, September 2000.)

Applications of polymer microencapsulation have been limited to special cases where specific performance features are required for the waste matrix, and contaminants allow reuse of the treated waste as a construction material [44].

S/S is a BDAT for the following waste types [5]:

- Cd non-wastewaters other than Cd-containing batteries,
- Cr non-wastewaters following reduction to Cr(III),
- Pb non-wastewaters,
- wastes containing low concentrations (<260 mg/kg) of elemental Hg-sulfide precipitation, and
- plating wastes and steelmaking wastes.

Although vitrification, not S/S, was selected as BDAT for RCRA As-containing non-wastewaters, U.S. EPA does not preclude the use of S/S for the treatment of As (particularly inorganic As) wastes but recommends that its use be determined on a case-by-case basis. A variety of stabilization

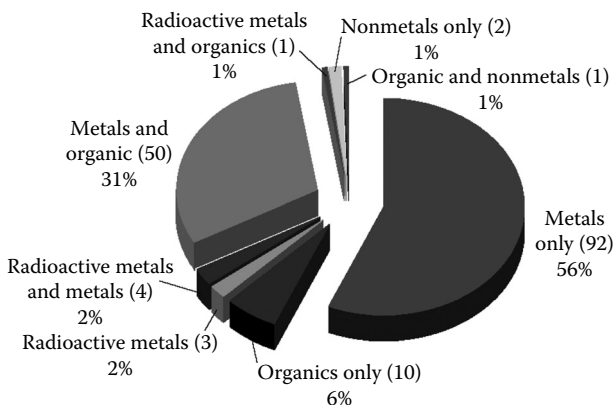


FIGURE 13.3 Contaminant types treated by S/S. (Adapted from U.S. EPA. *Solidification/Stabilization Use at Superfund Sites*. EPA-542-R-00-010, U.S. Environmental Protection Agency, Washington, DC, September 2000.)

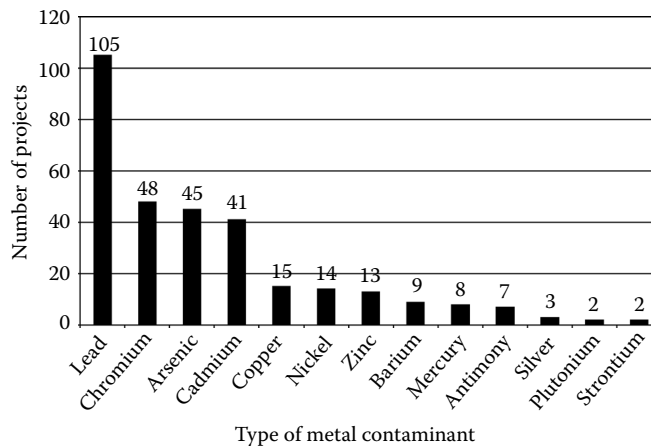


FIGURE 13.4 Number of S/S projects treating specific metals. (Adapted from U.S. EPA. *Solidification/Stabilization Use at Superfund Sites*. EPA-542-R-00-010, U.S. Environmental Protection Agency, Washington, DC, September 2000.)

TABLE 13.4
S/S Applications at Superfund Sites with Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology
DeRewal Chemical, NJ	Solidification	Cr, Cd, Pb	GW pump and treatment
Marathon Battery Co., NY	Chemical fixation	Cd, Ni	Dredging, off-site disposal
Nascolite, Millville, NJ	Stabilization of wetland soils	Pb	On-site disposal of stabilized soils; excavation and off-site disposal of wetland soils
Roebbling Steel, NJ	S/S	As, Cr, Pb	Capping
Waldick Aerospace, NJ	S/S	Cd, Cr	Off-site disposal
Aladdin Plating, PA	Stabilization	Cr	Off-site disposal
Palmerton Zinc, PA	Stabilization, fly ash, lime, potash	Cd, Pb	—
Tonolli Corp., PA	S/S	As, Pb	<i>In situ</i> chemical limestone barrier
Whitmoyer Laboratories, PA	Oxidation/fixation	As	GW pump and treatment, capping, grading, and revegetation
Bypass 601, NC	S/S	Cr, Pb	Capping, regrading, revegetation, GW pump and treatment
Flowood, MS	S/S	Pb	Capping
Independent Nail, SC	S/S	Cd, Cr	Capping
Pepper's Steel and Alloys, FL	S/S	As, Pb	On-site disposal
Gurley Pit, AR	<i>In situ</i> S/S	Pb	—
Pesses Chemical, TX	Stabilization	Cd	Concrete capping
E.I. Dupont de Nemours, IA	S/S	Cd, Cr, Pb	Capping, regrading, and revegetation
Shaw Avenue Dump, IA	S/S	As, Cd	Capping, groundwater monitoring
Frontier Hard Chrome, WA	Stabilization	Cr	—
Gould Site, OR	S/S	Pb	Capping, regrading, and revegetation

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

techniques, including cement, silicate, pozzolan, and ferric coprecipitation, were evaluated as candidate BDATs for As. Due to concerns about long-term stability and waste volume increase, particularly with ferric coprecipitation, stabilization was not accepted as BDAT.

13.6.5 SITE PROGRAM DEMONSTRATION PROJECTS

Completed SITE demonstrations applicable to soils contaminated with the metals of interest include [5]

- Advanced Remediation Mixing, Inc. (*ex situ* S/S),
- Funderburk and Associates (*ex situ* S/S),
- Geo-Con, Inc. (*in situ* S/S),
- Soliditech, Inc. (*ex situ* S/S),
- STC Omega, Inc. (*ex situ* S/S),
- WASTECH Inc. (*ex situ* S/S),
- Separation and Recovery Systems, Inc. (*ex situ* S/S), and
- Wheelabrator Technologies Inc. (*ex situ* S/S).

13.6.6 COST OF S/S

Information about the cost of using S/S to treat wastes at Superfund remedial sites was reported by U.S. EPA for 29 completed projects in 2000 [34]. Total costs in terms of 2007 USD [45] for S/S projects ranged from USD 86,000 to USD 18,000,000 including the cost of excavation, treatment, and disposal (if *ex situ*). The cost ranged from USD 12/m³ to approximately USD 1800/m³. The average cost for these projects was USD 396/m³, including two projects with relatively high costs (approximately USD 1800/m³). Excluding those two projects, the average cost per cubic meter was USD 291 [34].

13.7 VITRIFICATION

Vitrification applies high-temperature treatment aimed primarily at reducing the mobility of metals by incorporation into a chemically durable, leach-resistant, vitreous mass. Vitrification can be carried out on excavated soils as well as *in situ*.

13.7.1 PROCESS DESCRIPTION

During the vitrification process, organic wastes are pyrolyzed (*in situ*) or oxidized (*ex situ*) by the melt front, whereas inorganics, including metals, are incorporated into the vitreous mass. Off-gases released during the melting process, containing volatile components and products of combustion and pyrolysis, must be collected and treated [4,46,47]. Vitrification converts contaminated soils to a stable glass and crystalline monolith [47]. With the addition of low-cost materials such as sand, clay, and/or native soil, the process can be adjusted to produce products with specific characteristics, such as chemical durability. Waste vitrification may be able to transform the waste into useful, recyclable products such as clean fill, aggregate, or higher valued materials such as erosion-control blocks, paving blocks, and road dividers.

13.7.1.1 Ex Situ Vitrification

Ex situ vitrification (ESV) technologies apply heat to a melter through a variety of sources such as combustion of fossil fuels (coal, natural gas, and oil) or input of electric energy by direct joule heat, arcs, plasma torches, and microwaves. Combustion or oxidation of the organic portion of the waste can contribute significant energy to the melting process, thus reducing energy costs. The particle size of the waste may need to be controlled for some of the melting technologies. For wastes containing refractory compounds that melt above the unit's nominal processing temperature, such as

quartz or alumina, size reduction may be required to achieve acceptable throughputs and a homogeneous melt. For high-temperature processes using arcing or plasma technologies, size reduction is not a major factor. For the intense melters using concurrent gas-phase melting or mechanical agitation, size reduction is needed for feeding the system and for achieving a homogeneous melt.

13.7.1.2 *In Situ* Vitrification

In situ vitrification (ISV) technology is based on electric melter technology, and the principle of operation is joule heating, which occurs when an electrical current is passed through a region that behaves as a resistive heating element. Electrical current is passed through the soil by means of an array of electrodes inserted vertically into the surface of the contaminated soil zone. Because dry soil is not conductive, a starter path of flaked graphite and glass frit is placed in a small trench between the electrodes to act as the initial flow path for electricity. Resistance heating in the starter path transfers heat to the soil that then begins to melt. Once molten, the soil becomes conductive. The melt grows outward and downward as power is gradually increased to the full constant operating power level. A single melt can treat a region of up to 1000T. The maximum treatment depth has been demonstrated to be about 6 m. Large contaminated areas are treated in multiple settings that fuse the blocks together to form one large monolith [4]. Further information on ISV can be found in the following references [48–51].

13.7.2 SITE REQUIREMENTS

The site must be prepared for the mobilization, operation, maintenance, and demobilization of the equipment. Site activities such as clearing vegetation, removing overburden, and acquiring backfill material are often necessary for ESV as well as ISV. *Ex situ* processes will require areas for the storage of excavated, treated, and possibly pretreated materials. The components of one ISV system are contained in three transportable trailers: an off-gas and process control trailer, a support trailer, and an electrical trailer. The trailers are mounted on wheels sufficient for transportation to and over a compacted ground surface [52].

The field-scale ISV system evaluated in the SITE program required three-phase electrical power at either 12,500 or 13,800 V, which is usually taken from a utility distribution system [53]. Alternatively, the power may be generated on-site by means of a diesel generator. Typical applications require 800–1000 kWh/T [48].

13.7.3 APPLICABILITY

Setting cost and implementability aside, vitrification should be most applicable where nonvolatile metal contaminants have glass solubilities exceeding the level of contamination in the soil. Cr-contaminated soil should pose the least difficulties for vitrification, since it has low volatility, and glass solubility between 1% and 3%. Vitrification may or may not be applicable for Pb, As, and Cd, depending on the level of difficulty encountered in retaining the metals in the melt, and controlling and treating any volatile emissions that may occur. Hg clearly poses problems for vitrification due to high volatility and low glass solubility (<0.1%), but may be allowable at very low concentrations.

Chlorides present in the waste in excess of about 0.5% by weight (wt) typically will not be incorporated into and discharged with the glass but will fume off and enter the off-gas treatment system. If chlorides are excessively concentrated, salts of alkali, alkaline earths, and heavy metals will accumulate in solid residues collected by off-gas treatment. Separation of the chloride salts from the other residuals may be required before or during the return of residuals to the melter. When excess chlorides are present, there is also a possibility that dioxins and furans may form and enter the off-gas treatment system.

Waste matrix composition affects the durability of the treated waste. Sufficient glass-forming materials, SiO₂ (>30 wt%), and combined alkali, Na + K (>1.4 wt%), are required for vitrification of wastes. If these conditions are not met, frit and/or flux additives are typically needed. Vitrification is also potentially applicable to soils contaminated with mixed metals and metal-organic wastes.

Specific situations where ESV would not be applicable or would face additional implementation problems include the following [5]:

1. Wastes containing >25% moisture content cause excessive fuel consumption.
2. Wastes where size reduction and classification are difficult or expensive.
3. Volatile metals, particularly Cd and Hg, will vaporize and must be captured and treated separately.
4. Arsenic-containing wastes may require pretreatment to produce less volatile forms.
5. Metal concentrations in soil that exceed their solubility in glass.
6. Sites where commercial capacity is not adequate or transportation cost to a fixed facility is unacceptable.

Specific situations, in addition to those cited above, where ISV would not be applicable or would face additional implementation problems include the following [5]:

1. Metal-contaminated soil where a less costly and adequately protective remedy exists.
2. Projects that cannot be undertaken because of limited commercial availability.
3. Contaminated soil <2 m and >6 m below the ground surface.
4. Presence of an aquifer with high hydraulic conductivity (e.g., soil permeability $>1 \times 10^{-5}$ cm/s) limits economic feasibility due to the excessive energy required.
5. Contaminated soil mixed with buried metal that can result in a conductive path causing short circuiting of electrodes.
6. Contaminated soil mixed with loosely packed rubbish or buried coal can start underground fires and overwhelm off-gas collection and the treatment system.
7. Volatile heavy metals near the surface can be entrained in combustion product gases and not retained in the melt.
8. Sites where the surface slope is >5% may cause the melt to flow.
9. *In situ* voids >150 m³ interrupt conduction and heat transfer.
10. Underground structures and utilities <6 m from the melt zone must be protected from heat or avoided.

Where it can be successfully applied, the advantages of vitrification include the following [5]:

1. Vitrified product is an inert, impermeable solid that should reduce leaching for long periods of time.
2. The volume of vitrified product will typically be smaller than initial waste volume.
3. Vitrified product may be usable.
4. A wide range of inorganic and organic wastes can be treated.
5. There is both an *ex situ* and an *in situ* option available.

A particular advantage of *ex situ* treatment is its better control of processing parameters. Also, fuel costs may be reduced for ESV by the use of combustible waste materials. This fuel cost-saving option is not directly applicable for ISV, since combustibles would increase the design and operating requirements for gas capture and treatment.

13.7.4 PERFORMANCE AND BDAT STATUS

ISV has been implemented at metal-contaminated Superfund sites and was evaluated under the SITE Program [54]. Some improvements are needed for melt containment and air emission control systems. ISV has been operated at a large scale 10 times, including two demonstrations on radioactively contaminated sites at the DOE's Hanford Nuclear Reservation [46,55]. Pilot-scale tests have been conducted at Oak Ridge National Laboratory, Idaho National Engineering Laboratory,

TABLE 13.5
ISV Applications at Superfund Sites with Metal Contamination

Site Name/State	Key Metal Contaminants
Parsons Chemical, MI	Hg (low)
Rocky Mountain Arsenal, CO	As, Hg

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

and Arnold Engineering Development Center. More than 150 tests and demonstrations at various scales have been performed on a broad range of waste types in soils and sludges. The technology has been selected as a preferred remedy at 10 private, Superfund, and DoD sites [56]. Table 13.5 provides a summary of ISV technology selection/application at metal-contaminated Superfund sites. A number of ESV systems are under development. The technical resource document identified one full-scale *ex situ* melter that was reported to be operating on RCRA organics and inorganics.

Vitrification is a BDAT for the As-containing wastes.

13.7.5 SITE PROGRAM DEMONSTRATION PROJECTS

Completed SITE demonstrations applicable to soils contaminated with the metals of interest include [5]

- Babcock & Wilcox Co. (cyclone furnace—ESV),
- Retech, Inc. (plasma arc—ESV),
- Geosafe Corporation (ISV), and
- Vortec Corporation (*ex situ* oxidation and vitrification process).

13.8 SOIL WASHING

Soil washing is an *ex situ* remediation technology that uses a combination of physical separation and aqueous-based separation unit operations to reduce contaminant concentrations to site-specific remedial goals [57]. Although soil washing is sometimes used as a stand-alone treatment technology, more often it is combined with other technologies to complete site remediation. Soil washing technologies have successfully remediated sites contaminated with organic, inorganic, and radioactive contaminants [57]. The technology does not detoxify or significantly alter the contaminant but transfers the contaminant from the soil into the washing fluid or mechanically concentrates the contaminants into a much smaller soil mass [58] for subsequent treatment (see [Figure 13.5](#)).

Further information on soil washing can be found in U.S. EPA innovative technology reports and programs [59,60].

13.8.1 PROCESS DESCRIPTION

Soil washing systems are quite flexible in terms of the number, type, and order of processes involved. Soil washing is performed on excavated soil and may involve some or all of the following, depending on the contaminant–soil matrix characteristics, cleanup goals, and the specific process employed [5,58]:

1. Mechanical screening to remove various oversized materials.
2. Crushing to reduce applicable oversize to suitable dimensions for treatment.

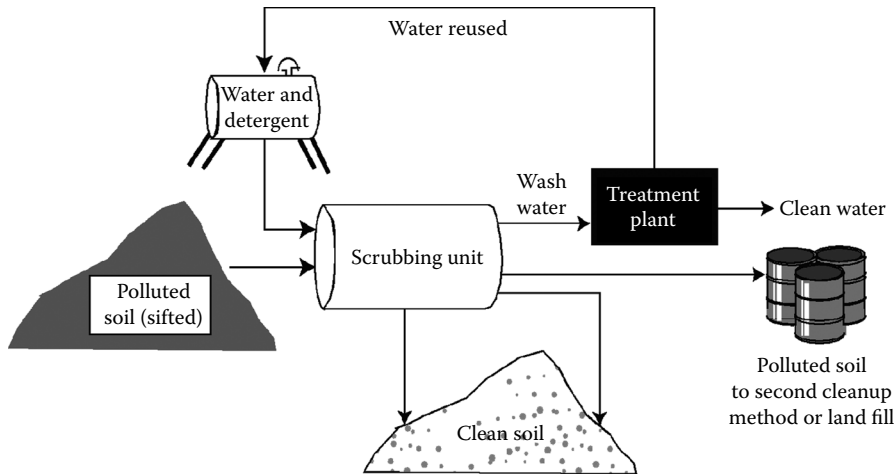


FIGURE 13.5 Soil washing operation. (Adapted from U.S. EPA. *A Citizen's Guide to Soil Washing*. EPA 542-F-01-008, U.S. Environmental Protection Agency, Washington, DC, May 2001.)

3. Physical processes (e.g., soaking, spraying, tumbling, and attrition scrubbing) to liberate weakly bound agglomerates (e.g., silts and clays bound to sand and gravel) followed by size classification to generate coarse-grained and fine-grained soil fraction(s) for further treatment.
4. Treatment of the coarse-grained soil fraction(s).
5. Treatment of the fine-grained fraction(s).
6. Management of the generated residuals.

Treatment of the coarse-grained soil fraction typically involves additional application of physical separation techniques and possibly aqueous-based leaching techniques. Physical separation techniques (e.g., sorting, screening, elutriation, hydrocyclones, spiral concentrators, flotation) exploit physical differences (e.g., size, density, shape, color, wettability) between contaminated particles and soil particles to produce a clean (or nearly clean) coarse fraction and one or more metal-concentrated streams. Many of the physical separation processes listed above involve the use of water as a transport medium, and if the metal contaminant has significant water solubility, then some of the coarse-grained soil cleaning will occur as a result of transfer to the aqueous phase. If the combination of physical separation and unaided transfer to the aqueous phase cannot produce the desired reduction in the soil's metal content, which is frequently the case for metal contaminants, then solubility enhancement is an option for meeting cleanup goals for the coarse fraction. Solubility enhancement can be accomplished in several ways [5,61,62]:

1. Converting the contaminant into a more soluble form (e.g., oxidation/reduction and conversion to soluble metal salts).
2. Using an aqueous-based leaching solution (e.g., acidic, alkaline, oxidizing, or reducing) in which the contaminant has enhanced solubility.
3. Incorporating a specific leaching process into the system to promote increased solubilization via increased mixing, elevated temperatures, higher solution/soil ratios, efficient solution/soil separation, multiple stage treatment, and so on.
4. A combination of the above.

After the leaching process is completed on the coarse-grained fraction, it will be necessary to separate the leaching solution and the coarse-grained fraction by settling. A soil rinsing step may be necessary to reduce the residual leachate in the soil to an acceptable level. It may also be necessary to

readjust soil parameters such as pH or redox potential before replacement of the soil on the site. The metal-bearing leaching agent must also be treated further to remove the metal contaminant and permit reuse in the process or discharge, and this topic is discussed below under management of residuals.

The treatment of fine-grained soils is similar in concept to the treatment of coarse-grained soils, but the production rate would be expected to be lower and hence more costly than for the coarse-grained soil fraction. The reduced production rate arises from factors including (a) the tendency of clays to agglomerate, thus requiring time, energy, and high water/clay ratios to produce leachable slurry; and (b) slow-settling velocities that require additional time and/or capital equipment to produce acceptable soil/water separation for multibatch or countercurrent treatment, or at the end of treatment. A site-specific determination needs to be made on whether the fines should be treated to produce clean fines or whether they should be handled as a residual waste stream.

Management of generated residuals is an important aspect of soil washing. The effectiveness, implementability, and cost of treating each residual stream are important to the overall success of soil washing for the site. Perhaps the most important of the residual streams is the metal-loaded leachant that is generated, particularly if the leaching process recycles the leaching solution. Furthermore, it is often critical to the economic feasibility of the project that the leaching solution be recycled. For these closed or semiclosed loop leaching processes, successful treatment of the metal-loaded leachant is imperative to the successful cleaning of the soil. The leachant must (a) have adequate solubility for the metal so that the metal reduction goals can be met without using excessive volumes of leaching solution; and (b) be readily, economically, and repeatedly adjustable (e.g., pH adjustment) to a form in which the metal contaminant has very low solubility so that the recycled aqueous phase retains a favorable concentration gradient compared to the contaminated soil. Also, efficient soil–water separation is important prior to recovering metal from the metal-loaded leachant in order to minimize contamination of the metal concentrate. Recycling the leachant reduces logistical requirements and costs associated with makeup water, storage, permitting, compliance analyses, and leaching agents. It also reduces external coordination requirements and eliminates the dependence of the remediation on the ability to meet Publicly Owned Treatment Works (POTW) discharge requirements.

Other residual streams that may be generated and require proper handling include the following [5]:

1. Untreatable and uncrushable oversize.
2. Recyclable metal-bearing particulates, concentrates, or sludges from physical separation or leachate treatment.
3. Nonrecyclable metal-bearing particulates, concentrates, soils, sludges, or organic debris that fail toxicity characteristic leaching procedure (TCLP) thresholds for RCRA hazardous waste.
4. Soils or sludges that are neither RCRA hazardous wastes nor sufficiently clean to permit return to the site.
5. Metal-loaded leachant from systems where leachant is not recycled.
6. Rinsate from treated soil.

13.8.2 SITE REQUIREMENTS

The area required for a unit at a site will depend on the vendor system selected, the amount of soil storage space, and/or the number of tanks or ponds needed for washwater preparation and wastewater storage and treatment. Typical utilities required are water, electricity, steam, and compressed air; the quantity of each is vendor- and site-specific. It may be desirable to control the moisture content of contaminated soil for consistent handling and treatment by covering the excavation, storage, and treatment areas. Climatic conditions such as annual or seasonal precipitation cause surface runoff and water infiltration; therefore, runoff control measures may be required. Since soil washing is an aqueous-based process, cold weather impacts include freezing as well as potential effects on leaching rates.

13.8.3 APPLICABILITY

Soil washing is potentially applicable to soils contaminated with all five metals of interest. Conditions that particularly favor soil washing include the following [5]:

1. A single principal contaminant metal that occurs in dense, insoluble particles that report to a specific, small mass fraction of the soil.
2. A single contaminant metal and species that is very water or aqueous leachant soluble and has a low soil/water partition coefficient.
3. Soil containing a high proportion (e.g., >80%) of soil particles >2 mm, which is desirable for efficient contaminant–soil and soil–water separation.

Conditions that clearly do not favor soil washing include the following [5]:

1. Soils with a high (i.e., >40%) silt and clay fraction.
2. Soils that vary widely and frequently in significant characteristics such as soil type, contaminant type, and concentration, and where blending for homogeneity is not feasible.
3. Complex mixtures (e.g., multicomponent, solid mixtures where access of leaching solutions to contaminant is restricted; mixed anionic and cationic metals where the pH values of solubility maximums are not close).
4. High clay content, cation exchange capacity, or humic acid content, which would tend to interfere with contaminant desorption.
5. The presence of substances that interfere with the leaching solution (e.g., carbonaceous soils would neutralize extracting acids; similarly, high humic acid content will interfere with an alkaline extraction).
6. Metal contaminants in a very low solubility, stable form (e.g., PbS) may require long contact times and excessive amounts of reagent to solubilize.

13.8.4 PERFORMANCE AND BDAT STATUS

Soil washing has been used at waste sites in Europe, especially in Germany, the Netherlands, and Belgium [63]. Table 13.6 lists selected Superfund sites where soil washing has been selected and/or implemented.

Acid leaching, which is a form of soil washing, is the BDAT for Hg.

TABLE 13.6
Soil Washing Applications at Selected Superfund Sites with Metal Contamination

Site Name/State	Specific Technology	Key Metal Contaminants	Associated Technology
Ewan Property, NJ	Water washing	As, Cr, Cu, Pb	Pretreatment by solvent extraction to remove organics
GE Wiring Devices, PR	Water with KI solution additive	Hg	Treated residues disposed on-site and covered with clean soil
King of Prussia, NJ	Water with washing agent additives	Ag, Cr, Cu	Sludges to be land disposed
Zanesville Well Field, OH	Soil washing	Hg, Pb	SVE to remove organics
Twin Cities Army Ammunition Plant, MN	Soil washing	Cd, Cr, Cu, Hg, Pb	Soil leaching
Sacramento Army Depot Sacramento, CA	Soil washing	Cr, Pb	Off-site disposal of wash liquid

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

13.8.5 SITE DEMONSTRATIONS AND EMERGING TECHNOLOGIES PROGRAM PROJECTS

SITE demonstrations applicable to soils contaminated with the metals of interest include [5]

- Bergmann USA (physical separation/leaching) BioGenesisSM (physical separation/leaching),
- Biotrol, Inc. (physical separation),
- Brice Environmental Services Corp. (physical separation),
- COGNIS, Inc. (leaching), and
- Toronto Harbor Commission (physical separation/leaching).

Four SITE Emerging Technologies Program projects have been completed that are applicable to soils contaminated with the metals of interest.

13.9 SOIL FLUSHING

Soil flushing is the *in situ* extraction of contaminants from the soil via an appropriate washing solution. Water or an aqueous solution is injected into or sprayed onto the area of contamination, and the contaminated elutriate is collected and pumped to the surface for removal, recirculation, or onsite treatment and reinjection. The technology is applicable to both organic and inorganic contaminants, and metals in particular [4]. For the purpose of metals remediation, soil flushing has been operated at full scale, but for a small number of sites.

13.9.1 PROCESS DESCRIPTION

Soil flushing uses water, a solution of chemicals in water, or an organic extractant to recover contaminants from the *in situ* material. The contaminants are mobilized by solubilization, formation of emulsions, or a chemical reaction with the flushing solutions. After passing through the contamination zone, the contaminant-bearing fluid is collected by strategically placed wells or trenches and brought to the surface for disposal, recirculation, or on-site treatment and reinjection. During elutriation, the flushing solution mobilizes the sorbed contaminants by dissolution or emulsification.

One key to efficient operation of a soil flushing system is the ability to reuse the flushing solution, which is recovered along with groundwater. Various water treatment techniques can be applied to remove the recovered metals and render the extraction fluid suitable for reuse. Recovered flushing fluids may need treatment to meet appropriate discharge standards prior to their release to a POTW or receiving waters. The separation of surfactants from recovered flushing fluid, for reuse in the process, is a major factor in the cost of soil flushing. Treatment of the flushing fluid results in process sludges and residual solids, such as spent carbon and spent ion exchange resin, which must be appropriately treated before disposal. Air emissions of volatile contaminants from recovered flushing fluids should be collected and treated, as appropriate, to meet applicable regulatory standards. Residual flushing additives in the soil may be a concern and should be evaluated on a site-specific basis [64]. Subsurface containment barriers can be used in conjunction with soil flushing technology to help control the flow of flushing fluids.

Further information on soil flushing can be found in references [59,64–66].

13.9.2 SITE REQUIREMENTS

Stationary or mobile soil flushing systems are located on-site. The exact area required will depend on the vendor system selected and the number of tanks or ponds needed for washwater preparation and wastewater treatment. Certain permits may be required for operation, depending on the system being utilized. Slurry walls or other containment structures may be needed along with hydraulic

controls to ensure capture of contaminants and flushing additives. Impermeable membranes may be necessary to limit infiltration of precipitation, which could cause dilution of the flushing solution and loss of hydraulic control. Cold weather freezing must also be considered for shallow infiltration galleries and aboveground sprayers [67].

13.9.3 APPLICABILITY

Soil flushing may be easy or difficult to apply, depending on the ability to wet the soil with the flushing solution and to install collection wells or subsurface drains to recover all the applied liquids. The achievable level of treatment varies and depends on the contact of the flushing solution with the contaminants and the appropriateness of the solution for contaminants, and the hydraulic conductivity of the soil. Soil flushing is most applicable to contaminants that are relatively soluble in the extracting fluid, and that will not tend to sorb onto soil as the metal-laden flushing fluid proceeds through the soil to the extraction point. Based on the earlier discussion of metal behavior, some potentially promising scenarios for soil flushing would include Cr(VI), As (III or V) in permeable soil with low iron oxide, low clay, and high pH; Cd in permeable soil with low clay, low cation exchange capacity, and moderately acidic pH; and Pb in acid sands. A single target metal would be preferable to multiple metals, due to the added complexity of selecting a flushing fluid that would be reasonably efficient for all contaminants. Also, the flushing fluid must be compatible with not only the contaminant, but also the soil. Soils that counteract the acidity or alkalinity of the flushing solution will decrease its effectiveness. If precipitants occur due to interaction between the soil and the flushing fluid, then this could obstruct the soil pore structure and inhibit the flow to and through sectors of the contaminated soil. It may take long periods of time for soil flushing to achieve cleanup standards.

A key advantage of soil flushing is that contaminant is removed from the soil. Recovery and reuse of the metal from the extraction fluid may be possible in some cases, although the value of the recovered metal would not be expected to fully offset the costs of recovery. The equipment used for the technology is relatively easy to construct and operate. It does not involve excavation, treatment, and disposal of the soil, which avoids the expense and hazards associated with these activities.

13.9.4 PERFORMANCE AND BDAT STATUS

Table 13.7 lists the Superfund sites where soil flushing has been selected and/or implemented. Soil flushing has a more established history for removal of organics but has been used for Cr removal (e.g., United Chrome Products Superfund Site, near Corvallis, Oregon). *In situ* technologies, such as soil flushing, are not considered RCRA BDAT for any of the five metals [5].

TABLE 13.7
Soil Flushing Applications at Selected Superfund Sites with Metal Contamination

Site Name/State	Specific Technology	Key Metal	
		Contaminants	Associated Technology
Lipari Landfill, NJ	Soil flushing of soil and wastes contained by slurry wall and cap;	Cr, Hg, Pb	Slurry wall and cap
United Chrome Products, OR	Excavation from impacted wetlands	Cr	Electrokinetic Pilot test, Considering <i>in situ</i> reduction

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

Soil flushing techniques for mobilizing contaminants can be classified as conventional and unconventional. Conventional applications employ only water as the flushing solution. Unconventional applications that are currently being researched include the enhancement of flushing water with additives, such as acids, bases, and chelating agents, to aid in the desorption/dissolution of target contaminants from the soil matrix to which they are bound.

Researchers are also investigating the effects of numerous soil factors on heavy metal sorption and migration in the subsurface. Such factors include pH, soil type, soil horizon, particle size, permeability, specific metal type and concentration, and type and concentrations of organic and inorganic compounds in solutions. Generally, as soil pH decreases, cationic metal solubility and mobility increase. In most cases, metal mobility and sorption are likely to be controlled by the organic fraction in topsoils and the clay content in subsoils.

13.9.5 SITE DEMONSTRATION AND EMERGING TECHNOLOGIES PROGRAM PROJECTS

There are no *in situ* soil flushing projects reported to be completed either as SITE demonstration or as Emerging Technologies Program Projects [67].

13.10 PYROMETALLURGY

Pyrometallurgy is used here as a broad term encompassing elevated temperature techniques for the extraction and processing of metals for use or disposal. High-temperature processing increases the rate of reaction and often makes the reaction equilibrium more favorable, lowering the required reactor volume per unit output [4]. Some processes that clearly involve both metal extraction and recovery include roasting, retorting, or smelting. While these processes typically produce a metal-bearing waste slag, metal is also recovered for reuse. A second class of pyrometallurgical technologies included here is a combination of high-temperature extraction and immobilization. These processes use thermal means to cause volatile metals to separate from the soil and report to the fly ash, but the metal in the fly ash is then immobilized, instead of recovered, and no metal is recovered for reuse. A third class of technologies are those that are primarily incinerators for mixed organic–inorganic wastes, but that have the capability of processing wastes containing the metals of interest by either capturing volatile metals in the exhaust gases or immobilizing the nonvolatile metals in the bottom ash or slag. Since some of these systems may have applicability to some cases where metal contamination is the primary concern, a few technologies of this type are noted that are in the SITE program. Vitrification is addressed in a previous section. It is not considered pyrometallurgical treatment, since there is typically neither a metal extraction nor a metal recovery component in the process.

13.10.1 PROCESS DESCRIPTION

Pyrometallurgical processing is usually preceded by physical treatment [5] to produce a uniform feed material and upgrade the metal content.

Solids treatment in a high-temperature furnace requires efficient heat transfer between the gas and solid phases while minimizing particulate in the off-gas. The particle-size range that meets these objectives is limited and is specific to the design of the process. The presence of large clumps or debris slows heat transfer; hence pretreatment to either remove or pulverize oversized material is normally required. Fine particles are also undesirable because they become entrained in the gas flow, increasing the volume of dust to be removed from the flue gas. The feed material is sometimes pelletized to give uniform size. In many cases, a reducing agent and flux may be mixed in prior to pelletization to ensure good contact between the treatment agents and the contaminated material and to improve the gas flow in the reactor [4].

Due to its relatively low boiling point (357°C) and ready conversion at elevated temperature to its metallic form, Hg is commonly recovered through roasting and retorting at much lower temperatures

than the other metals. Pyrometallurgical processing to convert compounds of the other four metals to elemental metal requires a reducing agent, fluxing agents to facilitate melting and to slag off impurities, and a heat source. The fluid mass often is called a melt, but the operating temperature, although quite high, often is still below the melting points of the refractory compounds being processed. The fluid forms as a lower-melting-point material due to the presence of a fluxing agent such as calcium. Depending on processing temperatures, volatile metals such as Cd and Pb may fume off and be recovered from the off-gas as oxides. Nonvolatile metals, such as Cr or nickel, are tapped from the furnace as molten metal. Impurities are scavenged by the formation of slag [4]. The effluents and solid products generated by pyrometallurgical technologies typically include solid, liquid, and gaseous residuals. Solid products include debris, oversized rejects, dust, ash, and the treated medium. Dust collected from particulate control devices may be combined with the treated medium or, depending on analyses for carryover contamination, recycled through the treatment unit.

13.10.2 SITE REQUIREMENTS

Few pyrometallurgical systems are available in mobile or transportable configurations. Since this is typically an off-site technology, the distance of the site from the processing facility has an important influence on transportation costs. Off-site treatment must comply with U.S. EPA's off-site treatment policies and procedures. The off-site facility's environmental compliance status must be acceptable, and the waste must be of a type allowable under their operating permits. In order for pyrometallurgical processing to be technically feasible, it must be possible to generate a concentrate from the contaminated soil that will be acceptable to the processor. The processing rate of the off-site facility must be adequate to treat the contaminated material in a reasonable amount of time. Storage requirements and responsibilities must be determined. The need for air discharge and other permits must be determined on a site-specific basis.

13.10.3 APPLICABILITY

With the possible exception of Hg, or a highly contaminated soil, pyrometallurgical processing where metal recovery is the goal would not be applied directly to the contaminated soil, but rather to a concentrate generated via soil washing. Pyrometallurgical processing in conventional rotary kilns, rotary furnaces, or arc furnaces is most likely to be applicable to large volumes of material containing metal concentrations (particularly Pb, Cd, or Cr) higher than 5–20%. Unless a very concentrated feed stream can be generated (e.g., approximately 60% for Pb), there will be a charge, in addition to transportation, for processing the concentrate. Lower metal concentrations can be acceptable if the metal is particularly easy to reduce and vaporize (e.g., Hg) or is particularly valuable (e.g., gold or platinum). Arsenic is the weakest candidate for pyrometallurgical recovery, since there is almost no recycling of arsenic in the United States. Arsenic is also the least valuable of the metals. The price ranges for the five metals [4] are reported here in terms of 2007 USD [45]:

	2007 USD/T
As	300–600 (as As trioxide)
Cd	7320
Cr	9630
Pb	860–950
Hg	6500–11,000

13.10.4 PERFORMANCE AND BDAT STATUS

The U.S. EPA technical document [4] contains a list of approximately 35 facilities/addresses/contacts that may accept concentrates of the five metals of interest for pyrometallurgical processing. Sixteen

of the 35 facilities are Pb recycling operations, seven facilities recover Hg, and the remainder address a range of RCRA wastes that contain the metals of interest. Due to the large volume of electric arc furnace emission control waste, extensive processing capability has been developed to recover Cd, Pb, and Zn from solid waste matrices. The available process technologies include the following [5]:

- A Waelz kiln process (Horsehead Resource Development Company, Inc.).
- A Waelz kiln and calcination process (Horsehead Resource Development Company, Inc.).
- A flame reactor process (Horsehead Resource Development Company, Inc.).
- An inclined rotary kiln (Zia Technology).

Plasma arc furnaces are successfully treating waste at two steel plants. These are site-dedicated units that do not accept outside material for processing.

Pyrometallurgical recovery is a BDAT for the following waste types [5]:

- Cd-containing batteries,
- Pb non-wastewaters in the noncalcium sulfate subcategory,
- Hg wastes prior to retorting,
- Pb acid batteries,
- Zn non-wastewaters, and
- Hg from wastewater treatment sludge.

13.10.5 SITE DEMONSTRATION AND EMERGING TECHNOLOGIES PROGRAM PROJECTS

SITE demonstrations applicable to soils contaminated with the metals of interest include [5]

- RUST Remedial Services, Inc. (X-Trax thermal desorption) and
- Horsehead Resource Development Company, Inc. (flame reactor).

13.11 ELECTROKINETICS

Electrokinetic remediation relies on the application of low-intensity direct current between electrodes placed in the soil. Contaminants are mobilized in the form of charged species, particles, or ions [2]. Attempts to leach metals from soils by electro-osmosis date back to the 1930s. In the past, research focused on removing unwanted salts from agricultural soils. Electrokinetics has been used for dewatering of soils and sludges since the first recorded use in the field in 1939 [68]. Electrokinetic extraction has been used in the former Soviet Union since the early 1970s to concentrate metals and to explore for minerals in deep soils. By 1979, research had shown that the content of soluble ions increased substantially in electro-osmotic consolidation of polluted dredgings, while metals were not found in the effluent [69]. By the mid-1980s, numerous researchers had realized independently that electrokinetic separation of metals from soils was a potential solution to contamination [70].

Several organizations are developing technologies for the enhanced removal of metals by transporting contaminants to the electrodes where they are removed and subsequently treated above-ground. A variation of the technique involves treatment without removal by transporting contaminants through specially designed treatment zones that are created between electrodes. Electrokinetics can also be used to slow or prevent migration of contaminants by configuring cathodes and anodes in a manner that causes contaminants to flow toward the center of a contaminated area of soil. Performance data illustrate the potential for achieving removals greater than 90% for some metals [2].

The range of potential metals is broad. The commercial applications in Europe treated copper, lead, zinc, arsenic, cadmium, chromium, and nickel. There is also potential applicability for radionuclides and some types of organic compounds. The electrode spacing and duration of remediation is site-specific. The process requires adequate soil moisture in the vadose zone; hence the addition of a conducting pore fluid may be required (particularly due to a tendency for soil drying near the anode).

TABLE 13.8
Overview of Electrokinetic Remediation Technology

General characteristics

- Depth of soil that is amenable to treatment depends on electrode placement
- Best used in homogeneous soils with high moisture content and high permeability

Approach #1

Enhanced removal

Description:

Electrokinetic transport of contaminants toward the polarized electrodes to concentrate the contaminants for subsequent removal and *ex situ* treatment

Status:

Demonstration projects using full-scale equipment are reported in Europe. Bench- and pilot-scale laboratory studies are reported in the United States and at least two full-scale field studies are ongoing in the United States

Applicability:

Pilot scale: lead, arsenic, nickel, mercury, copper, zinc

Lab scale: lead, cadmium, chromium, mercury, zinc, iron, magnesium, uranium, thorium, radium

Comments:

Field studies are under evaluation by U.S. EPA, DOE, DoD, and EPRI

The technique primarily would require addition of water to maintain the electric current and facilitate migration; however, there is ongoing work in the application of the technology in partially saturated soils

Approach #2

Treatment without removal

Description:

Electro-osmotic transport of contaminants through treatment zones placed between the electrodes. The polarity of the electrodes is reversed periodically, which reverses the direction of the contaminants back and forth through treatment zones. The frequency with which electrode polarity is reversed is determined by the rate of transport of contaminants through the soil

Status:

Demonstrations are ongoing

Applicability:

Technology developed for organic species and metals

Comments:

This technology is being developed for deep clay formations

Source: U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997.

Specially designed pore fluids are also added to enhance the migration of target contaminants. The pore fluids are added at either the anode or the cathode, depending on the desired effects.

Table 13.8 presents an overview of two variations of electrokinetic remediation technology. Geokinetics International, Inc.; Battelle Memorial Institute; Electrokinetics, Inc.; and Isotron Corporation are all developing variations of technologies categorized under Approach #1, Enhanced Removal. The consortium of Monsanto, E.I. du Pont de Nemours and Company (DuPont), General Electric (GE), DOE, and the U.S. EPA Office of Research and Development is developing the Lasagna Process, which is categorized under Approach #2, Treatment without Removal [2].

13.11.1 PROCESS DESCRIPTION

Electrokinetic remediation, also referred to as electrokinetic soil processing, electromigration, electrochemical decontamination, or electroreclamation, can be used to extract radionuclides, metals,

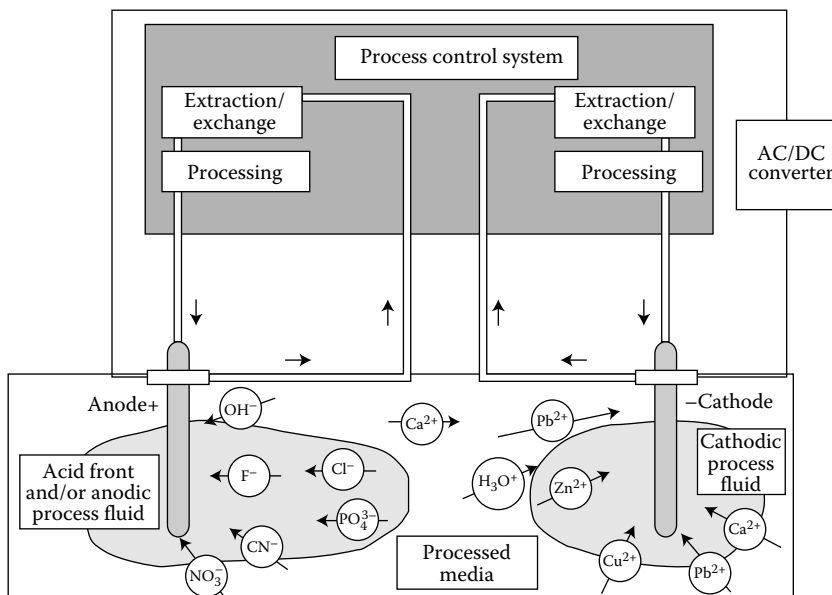


FIGURE 13.6 Diagram of one electrode configuration used in field implementation of electrokinetics. (Adapted from U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997.)

and some types of organic wastes from saturated or unsaturated soils, slurries, and sediments [71]. This *in situ* soil processing technology is primarily a separation and removal technique for extracting contaminants from soils.

The principle of electrokinetic remediation relies upon application of a low-intensity direct current through the soil between two or more electrodes. Most soils contain water in the pores between the soil particles and have an inherent electrical conductivity that results from salts present in the soil [72]. The current mobilizes charged species, particles, and ions in the soil by the following processes [73]:

1. Electromigration (transport of charged chemical species under an electric gradient),
2. Electro-osmosis (transport of pore fluid under an electric gradient).
3. Electrophoresis (movement of charged particles under an electric gradient).
4. Electrolysis (chemical reactions associated with the electric field).

Figure 13.6 presents a schematic diagram of a typical conceptual electrokinetic remediation application.

Electrokinetics can be efficient in extracting contaminants from fine-grained, high-permeability soils. A number of factors determine the direction and extent of the migration of the contaminant. Such factors include the type and concentration of the contaminant, the type and structure of the soil, and the interfacial chemistry of the system [74]. Water or some other suitable salt solution may be added to the system to enhance the mobility of the contaminant and increase the effectiveness of the technology. (For example, buffer solutions may change or stabilize pore fluid pH.) Contaminants arriving at the electrodes may be removed by any of several methods, including electroplating at the electrode, precipitation or coprecipitation at the electrode, pumping of water near the electrode, or complexing with ion exchange resins [74].

Electrochemistry associated with this process involves an acid front that is generated at the anode if water is the primary pore fluid present. The variation of pH at the electrodes results from the electrolysis of the water. The solution becomes acidic at the anode because hydrogen ions are produced and oxygen gas is released, and the solution becomes basic at the cathode, where hydroxyl

ions are generated and hydrogen gas is released [75]. At the anode, the pH could drop to below 2, and it could increase at the cathode to above 12, depending on the total current applied. The acid front eventually migrates from the anode to the cathode. Movement of the acid front by migration and advection results in the desorption of contaminants from the soil [71]. The process leads to temporary acidification of the treated soil, and there are no established procedures for determining the length of time needed to reestablish equilibrium. Studies have indicated that metallic electrodes may dissolve as a result of electrolysis and introduce corrosion products into the soil mass. However, if inert electrodes, such as carbon, graphite, or platinum, are used, no residue will be introduced in the treated soil mass as a result of the process [2].

13.11.2 SITE REQUIREMENTS

Before electrokinetic remediation is undertaken at a site, a number of different field and laboratory screening tests must be conducted to determine whether the particular site is amenable to the treatment technique.

1. *Field conductivity surveys:* The natural geologic spatial variability should be delineated because buried metallic or insulating material can induce variability in the electrical conductivity of the soil and, therefore, the voltage gradient. In addition, it is important to assess whether there are deposits that exhibit very high electrical conductivity, at which the technique may be inefficient.
2. *Chemical analysis of water:* The pore water should be analyzed for major dissolved anions and cations, as well as for the predicted concentration of the contaminant(s). In addition, electrical conductivity and pH of the pore water should be measured.
3. *Chemical analysis of soil:* The buffering capacity and geochemistry of the soil should be determined at each site.
4. *pH effects:* The pH values of the pore water and the soil should be determined because they have a great effect on the valence, solubility, and sorption of contaminant ions.
5. *Bench-scale test:* The dominant mechanism of transport, removal rates, and amounts of contamination left behind can be examined for different removal scenarios by conducting bench-scale tests. Because many of these physical and chemical reactions are interrelated, it may be necessary to conduct bench-scale tests to predict the performance of electrokinetics remediation at the field scale [70,71].

13.11.3 APPLICABILITY AND DEMONSTRATION PROJECTS

Various methods, developed by combining electrokinetics with other techniques, are being applied for remediation. This section describes different types of electrokinetic remediation methods for their use at contaminated sites. The methods discussed were developed by Electrokinetics, Inc.; Geokinetics International, Inc.; Isotron Corporation; Battelle Memorial Institute; a consortium effort; and P&P Geotechnik GmbH [2].

13.11.3.1 Electrokinetics, Inc.

Electrokinetics, Inc. operates under a licensing agreement with Louisiana State University (LSU). The technology is patented by and assigned to LSU [76] and a complementing process patent is assigned to Electrokinetics, Inc. [77]. As depicted in [Figure 13.5](#), groundwater and/or a processing fluid (supplied externally through the boreholes that contain the electrodes) serves as the conductive medium. The additives in the processing fluid, the products of electrolysis reactions at the electrodes, and the dissolved chemical entities in the contaminated soil are transported across the contaminated soil by conduction under electric fields. This transport, when coupled with sorption, precipitation/dissolution, and volatilization/complexation, provides the fundamental mechanism that can affect the electrokinetic remediation process. Electrokinetics, Inc. accomplishes extraction

and removal by electrodeposition, evaporation/condensation, precipitation, or ion exchange, either at the electrodes or in a treatment unit that is built into the system that pumps the processing fluid to and from the contaminated soil. Pilot-scale testing was carried out with a support from the U.S. EPA that also developed a design and analysis package for the process [78].

13.11.3.2 Geokinetics International, Inc.

Geokinetics International, Inc. (GII) obtained a patent for an electroreclamation process. The key claims in the patent are the use of electrode wells for both anodes and cathodes and the management of the pH and electrolyte levels in the electrolyte streams of the anode and the cathode. The patent also includes claims for the use of additives to dissolve different types of contaminants [79]. Fluor Daniel is licensed to operate GII's metal removal process in the United States.

GII has developed and patented electrically conductive ceramic material (EBONEX[®]) that has an extremely high resistance to corrosion. It has a lifetime of at least 45 years in soil and is self-cleaning. GII has also developed a batch electrokinetic remediation (BEK[®]) process. The process, which incorporates electrokinetic technology, normally requires 24–48 h for complete remediation of the substrate. BEK[®] is a mobile unit that remediates *ex situ* soils on-site. GII has also developed a solution treatment technology (EIX[®]) that allows removal of contamination from anode and cathode solutions up to a thousand times faster than can be achieved through conventional means [2].

13.11.3.3 Isotron Corporation

Isotron Corporation participated in a pilot-scale demonstration of electrokinetic extraction supported by DOE's Office of Technology Development. The demonstration took place at the Oak Ridge K-25 facility in Tennessee. Completed laboratory tests showed that the Isotron process could affect the movement and capture of uranium present in soil from the Oak Ridge site [80].

Isotron Corporation was also involved with Westinghouse Savannah River Company in a demonstration of electrokinetic remediation. The demonstration, supported by DOE's Office of Technology Development, took place at the old TNX basin at the Savannah River site in South Carolina. Isotron used the Electrosorb[®] process with a patented cylinder to control buffering conditions *in situ*. An ion exchange polymer matrix called Isolock[®] was used to trap metal ions. The process was tested for the removal of lead and chromium [80].

13.11.3.4 Battelle Memorial Institute

Another method that uses electrokinetic technology is electroacoustical soil decontamination. This technology combines electrokinetics with sonic vibration. Through the application of mechanical vibratory energy in the form of sonic or ultrasonic energy, the properties of a liquid contaminant in soil can be altered in a way that increases the level of removal of the contaminant. Battelle Memorial Institute of Columbus, OH developed the *in situ* treatment process that uses both electrical and acoustical forces to remove floating contaminants, and possibly metals, from subsurface zones of contamination. The process was selected for U.S. EPA's SITE program [81].

13.11.3.5 Consortium Process

Monsanto Company has coined the name Lasagna to identify its products and services that are based on the integrated *in situ* remediation process developed by a consortium. The proposed technology combines electro-osmosis with treatment zones that are installed directly in the contaminated soils to form an integrated *in situ* remedial process, as Figure 13.7 shows. The consortium consists of Monsanto, DuPont, and GE, with participation by the U.S. EPA Office of Research and Development and DOE.

The *in situ* decontamination process occurs as follows [2]:

1. Creates highly permeable zones in close proximity sectioned through the contaminated soil region and turns them into sorption-degradation zones by introducing appropriate materials (sorbents, catalytic agents, microbes, oxidants, buffers, and others).

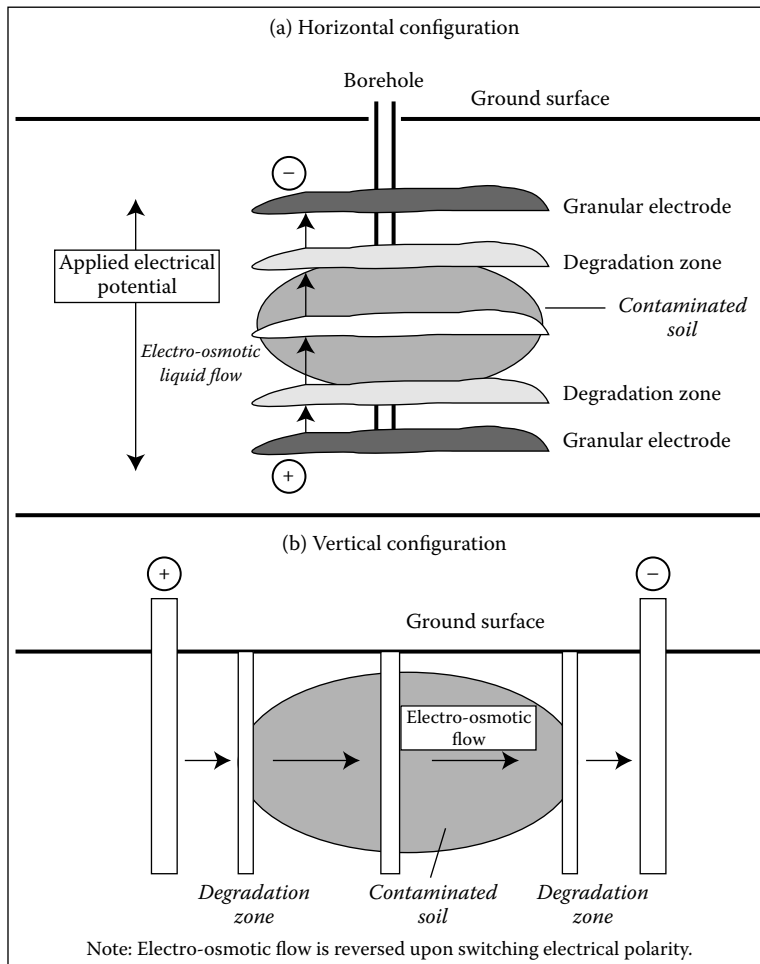


FIGURE 13.7 Schematic diagram of the Lasagna™ process. (Adapted from U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997.)

2. Uses electro-osmosis as a liquid pump to flush contaminants from the soil into the treatment zones of degradation.
3. Reverses liquid flow, if desired, by switching electrical polarity, a mode that increases the efficiency with which contaminants are removed from the soil; allows repeated passes through the treatment zones for complete sorption.

Initial field tests of the consortium process were conducted at DOE's gaseous diffusion plant in Paducah, Kentucky. The experiment tested the combination of electro-osmosis and *in situ* sorption in treatment zones. Technology development for the degradation processes and their integration into the overall treatment scheme were carried out at bench and pilot scales, followed by field experiments of the full-scale process [82].

13.11.4 PERFORMANCE AND COST

Work sponsored by U.S. EPA, DOE, the National Science Foundation, and private industry, when coupled with the efforts of researchers from academic and public institutions, have demonstrated

the feasibility of moving electrokinetics remediation to pilot-scale testing and demonstration stages [71].

This section describes testing and cost summary results reported by LSU, Electrokinetics, Inc., GII, Battelle Memorial Institute, and the consortium [2].

13.11.4.1 LSU-Electrokinetics, Inc.

The LSU-Electrokinetics, Inc. group has conducted bench-scale testing on radionuclides and on organic compounds. Test results have been reported for lead, cadmium, chromium, mercury, zinc, iron, and magnesium. The radionuclides tested include uranium, thorium, and radium.

In collaboration with U.S. EPA, the LSU-Electrokinetics, Inc. group has completed pilot-scale studies of electrokinetic soil processing in the laboratory. Electrokinetics, Inc. carried out a site-specific pilot-scale study of the Electro-Klean™ electrical separation process. Pilot field studies have also been reported in the Netherlands on soils contaminated with lead, arsenic, nickel, mercury, copper, and zinc.

A pilot-scale laboratory study investigating the removal of 2000 mg/kg of lead loaded onto kaolinite was completed. Removal efficiencies of 90–95% were obtained. The electrodes were placed one inch apart in a 2 ton kaolinite specimen for 4 months, at a total energy cost of about 2007 USD 22/T [81].

With the support of DoD, Electrokinetics, Inc. carried out a comprehensive demonstration study of lead extraction from a creek bed at a U.S. Army firing range in Louisiana. U.S. EPA took part in independent assessments of the results of that demonstration study under the SITE program. The soils are contaminated with levels as high as 4500 mg/kg of lead; pilot-scale studies have demonstrated that concentrations of lead decreased to less than 300 mg/kg in 30 weeks of processing. The TCLP values dropped from more than 300 mg/L to less than 40 mg/L within the same period. At the site of the demonstration study, Electrokinetics, Inc. used the CADEX™ electrode system that promotes transport of species into the cathode compartment, where they are precipitated and/or electrodeposited directly. Electrokinetics, Inc. used a special electrode material that is cost-effective and does not corrode. Under the supervision and support of the Electric Power Research Institute (EPRI) and power companies in the southern USA a treatability and a pilot-scale field testing study of soils in sites contaminated with arsenic has been performed, in a collaborative effort between Southern Company Services Engineers and Electrokinetics, Inc. [2].

The processing cost of a system designed and installed by Electrokinetics, Inc. consists of energy cost, conditioning cost, and fixed costs associated with installation of the system. Power consumption is related directly to the conductivity of the soil across the electrodes. Electrical conductivity of soils can span orders of magnitude, from 30 mho/cm to more than 3000 μ mho/cm, with higher values being in saturated, high-plasticity clays. A mean conductivity value is 500 μ mho/cm. The voltage gradient is held to approximately 1 V/cm in an attempt to prevent adverse effects of temperature increases and for other practical reasons [71]. It may be cost-prohibitive to attempt to remediate high-plasticity soils that have high electrical conductivities. However, for most deposits having conductivities of 500 μ mho/cm, the daily energy consumption will be approximately 12 kWh/m³/d or about USD 1.20/m³/d (USD 0.10/kWh) and USD 36/m³/month. The processing time will depend on several factors, including spacing of the electrodes and type of conditioning scheme that will be used. If an electrode spacing of 4 m is selected, it may be necessary to process the site over several months.

Pilot-scale studies using “real-world” soils indicate that energy expenditures in the extraction of metals from soils may be 500 kWh/m³ or more at electrode spacings of 1.0–1.5 m [78]. The vendor estimates that the direct cost of about USD 50/m³ (USD 0.10/kWh) suggested for this energy expenditure, together with the cost of enhancement, could result in direct costs of USD 100/m³. If no other efficient *in situ* technology is available to remediate fine-grained and heterogeneous subsurface deposits contaminated with metals, this technique would remain potentially competitive.

13.11.4.2 Geokinetics International, Inc.

GII has successfully demonstrated *in situ* electrochemical remediation of metal-contaminated soils at several sites in Europe. Geokinetics, a sister company of GII, has also been involved in the

TABLE 13.9
Performance of Electrochemical Soil Remediation Applied at Five Field Sites in Europe

Site Description	Soil Volume (m ³)	Soil Type	Contaminant	Initial Concentration (mg/kg)	Final Concentration (mg/kg)
Former paint factory	230	Peat/clay soil	Cu	1220	<200
			Pb	>3780	<280
Operational galvanizing plant	40	Clay soil	Zn	>1400	600
Former timber plant	190	Heavy clay soil	As	>250	<30
Temporary landfill	5440	Argillaceous sand	Cd	>180	<40
Military air base	1900	Clay	Cd	660	47
			Cr	7300	755
			Cu	770	98
			Ni	860	80
			Pb	730	108
			Zn	2600	289

Source: U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997.

electrokinetics arena in Europe. Table 13.9 summarizes the physical characteristics of five of the sites, including size, contaminant(s) present, and overall performance of the technology at each site. GII that estimates its typical costs for “turn key” remediation projects, which are in the range of 2007 USD 160–260/m³ [2].

13.11.4.3 Battelle Memorial Institute

The technology demonstration through the SITE program was completed [81]. The results indicate that the electroacoustical technology is technically feasible for the removal of inorganic species from clay soils [83].

13.11.4.4 Consortium Process

The Phase I field test of the LasagnaTM process has been completed. Scale-up from laboratory units was successfully achieved with respect to electrical parameters and electro-osmotic flow. Soil samples taken throughout the test site before and after the test indicate a 98% removal of trichloroethylene (TCE) from a tight clay soil (i.e., hydraulic conductivity less than 1×10^{-7} cm/s). TCE soil levels were reduced from the 100 to the 500 mg/kg range to an average concentration of 1 mg/kg [84]. Various treatment processes are being investigated in the laboratory to address other types of contaminants, including heavy metals [84].

13.11.5 SUMMARY OF ELECTROKINETIC REMEDIATION

Electrokinetic remediation may be applied to both saturated and partially saturated soils. One problem to overcome when applying electrokinetic remediation to the vadose zone is the drying of soil near the anode. When an electric current is applied to soil, water will flow by electro-osmosis in the soil pores, usually toward the cathode. The movement of the water will deplete soil moisture adjacent to the anode, and moisture will collect near the cathode. However, processing fluids may be circulated at the electrodes. The fluids can serve both as a conducting medium and as a means to extract or exchange the species and introduce other species. Another use of processing fluids is to

control, depolarize, or modify either or both electrode reactions. The advance of the process fluid (acid or the conditioning fluid) across the electrodes assists in desorption of species and dissolution of carbonates and hydroxides. Electro-osmotic advection and ionic migration lead to the transport and subsequent removal of contaminants. The contaminated fluid is then recovered at the cathode.

Spacing of the electrode will depend on the type and level of contamination and the selected current voltage regime. When higher voltage gradients are generated, the efficiency of the process might decrease because of increases in temperature. A spacing that will generate a potential gradient in the order of 1V/cm is preferred. The spacing of electrodes will generally be as much as 3m. The duration of the remediation will be site-specific. The remediation process should be continued until the desired removal is achieved. However, it should be recognized that, in cases in which the duration of treatment is reduced by increasing the electrical potential gradient, the efficiency of the process will decrease [85,86].

The advantage of the technology is its potential for cost-effective use for both *in situ* and *ex situ* applications. The fact that the technique requires the presence of a conducting pore fluid in a soil mass may have site-specific implication. Also, heterogeneities or anomalies found at sites, such as submerged foundations, rubble, large quantities of iron or iron oxides, large rocks or gravel, or submerged cover material (such as seashells), are expected to reduce removal efficiencies [71].

13.12 PHYTOREMEDIATION

This technology is in the stage of commercialization for the treatment of soils contaminated with metals, and in the future may provide a low-cost option under specific circumstances. At the current stage of development, this process is best suited for sites with widely dispersed contamination at low concentrations where only treatment of soils at the surface (in other words, within depth of the root zone) is required [2].

Phytoremediation is the use of plants to remove, contain, or render harmless environmental contaminants. This definition applies to all biological, chemical, and physical processes that are influenced by plants and that aid in the cleanup of contaminated substances [87]. Plants can be used in site remediation, both to mineralize and immobilize toxic organic compounds at the root zone and to accumulate and concentrate metals and other inorganic compounds from soil into aboveground shoots [88]. Although phytoremediation is a relatively new concept in the waste management community, techniques, skills, and theories developed through the application of well-established agro-economic technologies are easily transferable. The development of plants for restoring sites contaminated with metals will require the multidisciplinary research efforts of agronomists, toxicologists, biochemists, microbiologists, pest management specialists, engineers, and other specialists [87,88]. Table 13.10 presents an overview of phytoremediation technology.

Two basic approaches for metal remediation include phytoextraction and phytostabilization. Phytoextraction relies on the uptake of contaminants from the soil and their translocation into aboveground plant tissue, which is harvested and treated. Although hyperaccumulating trees, shrubs, herbs, grasses, and crops have potential, crops seem to be most promising because of their greater biomass production. Nickel and zinc appear to be the most easily absorbed, although tests with copper and cadmium are encouraging [2]. Significant uptake of lead, a commonly occurring contaminant, has not been demonstrated on a large scale. However, some researchers are experimenting with soil amendments that would facilitate the uptake of lead by plants.

13.12.1 PROCESS DESCRIPTION

Metals that are considered essential for at least some forms of life include vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and molybdenum (Mo) [88]. Because many metals are toxic in concentrations above minute levels, an organism must regulate the cellular concentrations of such metals. Consequently, organisms have evolved transport systems to regulate the uptake and distribution of metals. Plants have remarkable metabolic and

TABLE 13.10
Overview of Phytoremediation Technology

General characteristics

- Best used at sites with low to moderate disperse metals content and with soil media that will support plant growth
- Applications limited to depth of the root zone
- Longer times required for remediation compared with other technologies
- Different species have been identified to treat different metals

Approach #1

Phytoextraction (harvest)

Description:

Uptake of contaminants from soil into aboveground plant tissue, which is periodically harvested and treated

Status:

Field testing for effectiveness on radioactive metals is ongoing in the vicinity of the damaged nuclear reactor in Chernobyl, Ukraine

Field testing also is being conducted in Trenton, NJ and Butte, MT and by the Idaho National Engineering Laboratory (INEL) in Fernald, OH

Applicability:

Potentially applicable for many metals. Nickel and zinc appear to be most easily absorbed. Preliminary results for absorption of copper and cadmium are encouraging

Comments:

Cost affected by volume of biomass produced that may require treatment before disposal. Cost affected by concentration and depth of contamination and number of harvests required

Approach #2

Phytostabilization (root-fixing)

Description:

Production of chemical compounds by the plant to immobilize contaminants at the interface of roots and soil. Additional stabilization can occur by raising the pH level in the soil.

Status:

Research is ongoing

Applicability:

Potentially applicable for many metals, especially lead, chromium, and mercury

Comments:

Long-term maintenance is required

Source: U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997.

absorption capabilities, as well as transport systems that can take up ions selectively from the soil. Plants have evolved a great diversity of genetic adaptations to handle potentially toxic levels of metals and other pollutants that occur in the environment. In plants, the uptake of metals occurs primarily through the root system, in which the majority of mechanisms to prevent metal toxicity are found [89]. The root system provides an enormous surface area that absorbs and accumulates the water and nutrients essential for growth. In many ways, living plants can be compared to solar-powered pumps that can extract and concentrate certain elements from the environment [90].

Plant roots cause changes at the soil–root interface as they release inorganic and organic compounds (root exudates) in the area of the soil immediately surrounding the roots (the rhizosphere) [91]. Root exudates affect the number and activity of microorganisms, the aggregation and stability of soil particles around the root, and the availability of elements. They can increase (mobilize) or decrease (immobilize) directly or indirectly the availability of elements in the rhizosphere. Mobilization and immobilization of elements in the rhizosphere can be caused by the following [92,93]:

1. Changes in soil pH.
2. Release of complexing substances, such as metal-chelating molecules.

3. Changes in oxidation–reduction potential.
4. Increase in microbial activity.

Phytoremediation technologies can be developed for different applications in environmental cleanup and are classified into three types:

1. Phytoextraction
2. Phytostabilization
3. Rhizofiltration.

13.12.1.1 Phytoextraction

Phytoextraction technologies use hyperaccumulating plants to transport metals from the soil and concentrate them in the roots and aboveground shoots that can be harvested [87,88,91]. A plant containing more than 0.1% of Ni, Co, Cu, Cr, or 1% Zn and Mn in its leaves on a dry weight basis is called a hyperaccumulator, regardless of the concentration of metals in the soil [88,94,95].

Almost all metal-hyperaccumulating species known today were discovered on metal-rich soils, either natural or artificial, often growing in communities with metal excluders [88,96]. Actually, almost all metal-hyperaccumulating plants 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. The majority of hyperaccumulating species discovered so far are restricted to a few specific geographical locations [88,94]. For example, Ni hyperaccumulators are found in New Caledonia, the Philippines, Brazil, and Cuba. Ni and Zn hyperaccumulators are found in southern and central Europe and Asia Minor.

Dried or composted plant residues or plant ashes that are highly enriched with metals can be isolated as hazardous waste or recycled as metal ore [98]. The goal of phytoextraction is to recycle as “bio-ores” metals reclaimed from plant ash in the feed stream of smelting processes. Even if the plant ashes do not have enough concentration of metal to be useful in smelting processes, phytoextraction remains beneficial because it reduces the amount of hazardous waste to be landfilled [2] by as much as 95%. Several research efforts in the use of trees, grasses, and crop plants are being pursued to develop phytoremediation as a cleanup technology. The following paragraphs briefly discuss these three phytoextraction techniques.

The use of trees can result in the extraction of significant amounts of metal because of their high biomass production. However, the use of trees in phytoremediation requires long-term treatment and may create additional environmental concerns about falling leaves. When leaves containing metals fall or blow away, recirculation of metals to the contaminated site and migration to off-site by wind transport or through leaching can occur [2].

Some grasses accumulate surprisingly high levels of metals in their shoots without exhibiting toxic effects. However, their low biomass production results in a relatively low yield of metals. Genetic breeding of hyperaccumulating plants that produce relatively large amounts of biomass could make the extraction process highly effective [99].

It is known that many crop plants can accumulate metals in their roots and aboveground shoots, potentially threatening the food chain. For example, in May 1980 regulations proposed under RCRA for hazardous waste included limits on the amounts of cadmium and other metals that can be applied to crops. Recently, however, the potential use of crop plants for environmental remediation has been under investigation. Using crop plants to extract metals from the soil seems practical because of their high biomass production and relatively fast rate of growth. Other benefits of using crop plants are that they are easy to cultivate and exhibit genetic stability [97].

13.12.1.2 Phytostabilization

Phytostabilization uses plants to limit the mobility and bioavailability of metals in soils. Ideally, phytostabilizing plants should be able to tolerate high levels of metals and to immobilize them in the

soil by sorption, precipitation, complexation, or the reduction of metal valences. Phytostabilizing plants should also exhibit low levels of accumulation of metals in shoots to eliminate the possibility that residues in harvested shoots might become hazardous wastes [90]. In addition to stabilizing metals present in the soil, phytostabilizing plants can also stabilize the soil matrix to minimize erosion and migration of sediment. Dr Gary Pierzynski of Kansas State University is studying phytostabilization in poplar trees, which were selected for the study because they can be deep-planted and may be able to form roots below the zone of maximum contamination [2].

Since most sites contaminated with metals lack established vegetation, metal-tolerant plants are used to revegetate such sites to prevent erosion and leaching [100]. However, that approach is a containment rather than a remediation technology. Some researchers consider phytostabilization as an interim measure to be applied until phytoextraction becomes fully developed. However, other researchers are developing phytostabilization as a standard protocol of metal remediation technology, especially for sites at which the removal of metals does not seem to be economically feasible. After field applications conducted by a group in Liverpool, England, three varieties of grasses were made commercially available for phytostabilization [90]:

- *Agrostis tenuis*, cv *Parys* for copper wastes,
- *Agrostis tenuis*, cv *Coginan* for acid lead and zinc wastes, and
- *Festuca rubra*, cv *Merlin* for calcareous lead and zinc wastes.

13.12.1.3 Rhizofiltration

One type of rhizofiltration uses plant roots to absorb, concentrate, and precipitate metals from wastewater [90], which may include leachate from soil. Rhizofiltration uses terrestrial plants instead of aquatic plants because the terrestrial plants develop much longer, fibrous root systems covered with root hairs that have extremely large surface areas. This variation of phytoremediation uses plants that remove metals by sorption, which does not involve biological processes. The use of plants to translocate metals to shoots is a slower process than phytoextraction [100].

Another type of rhizofiltration, which is more fully developed, involves the construction of wetlands or reed beds for the treatment of contaminated wastewater or leachate. The technology is cost-effective for the treatment of large volumes of wastewater that have low concentrations of metals [100]. Since rhizofiltration focuses on the treatment of contaminated water, it is not discussed further in this chapter.

Table 13.11 presents the advantages and disadvantages of each of the types of phytoremediation currently being researched that are categorized as either phytoextraction or phytostabilization [90].

13.12.1.4 Future Development

Faster uptake of metals and higher yields of metals in harvested plants may become possible through the application of genetic engineering and/or selective breeding techniques. Recent laboratory-scale testing has revealed that a genetically altered species of mustard weed can uptake mercuric ions from the soil and convert them to metallic mercury, which is transpired through the leaves [2]. Improvements in phytoremediation may be attained through research and a better understanding of the principles governing the processes by which plants affect the geochemistry of their soils. In addition, future testing of plants and microflora may lead to the identification of plants that have metal accumulation qualities that are far superior to those currently known.

13.12.2 APPLICABILITY

Plants have been used to treat wastewater for more than 300 years, and plant-based remediation methods for slurries of dredged material and soils contaminated with metals have been proposed since the mid-1970s [87,101]. Reports of successful remediation of soils contaminated with metals are rare, but the suggestion of such application is more than two decades old, and progress is being

TABLE 13.11**Types of Phytoremediation Technology: Advantages and Disadvantages**

Type of Phytoremediation	Advantages	Disadvantages
Phytoextraction by trees	High biomass production	Potential for off-site migration and leaf transportation of metals to surface Metals are concentrated in plant biomass and must be disposed of eventually
Phytoextraction by grasses	High accumulation	Low biomass production and slow growth rate Metals are concentrated in plant biomass and must be disposed of eventually
Phytoextraction by crops	High biomass and increased growth rate	Potential threat to the food chain through ingestion by herbivores Metals are concentrated in plant biomass and must be disposed of eventually
Phytostabilization	No disposal of contaminated biomass required	Remaining liability issues, including maintenance for indefinite period of time (containment rather than removal)
Rhizofiltration	Readily absorbs metals	Applicable for treatment of water only Metals are concentrated in plant biomass and must be disposed of eventually

Source: U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997.

made at a number of pilot test sites [96]. Successful phytoremediation must meet cleanup standards in order to be approved by regulatory agencies.

No full-scale applications of phytoremediation have been reported. One vendor, Phytotech, Inc., is developing phytostabilization for soil remediation applications. Phytotech has also patented strategies for phytoextraction and is conducting several field tests in Trenton, New Jersey and in Chernobyl, Ukraine [97]. Also, as previously mentioned, a group in Liverpool, England has made three grasses commercially available for the stabilization of lead, copper, and zinc wastes [90].

13.12.3 PERFORMANCE AND COST

A variety of new research approaches and tools are expanding an understanding of the molecular and cellular processes that can be employed through phytoremediation [102].

13.12.3.1 Performance

Potential for phytoremediation (phytoextraction) can be assessed by comparing the concentration of contaminants and volume of soil to be treated with the particular plant's seasonal productivity of biomass and ability to accumulate contaminants. Table 13.6 lists selected examples of plants identified as metal hyperaccumulators and their native countries [94,103]. If plants are to be effective remediation systems, 1 ton of plant biomass, costing from several hundred to a few thousand dollars to produce, must be able to treat large volumes of contaminated soil. For metals that are removed from the soil and accumulated in aboveground biomass, the total amount of biomass per hectare required for soil cleanup is determined by dividing the total weight of metal per hectare to be remediated by the accumulation factor, which is the ratio of the accumulated weight of the metal to the weight of the biomass containing the metal. The total biomass per hectare (T/ha) can then be divided by the productivity of the plant (T/ha/yr) to determine the number of years required to achieve cleanup standards—a major determinant of the overall cost and feasibility of phytoremediation [102].

As discussed earlier, the amount of biomass is one of the factors that determine the practicality of phytoremediation. Under the best climatic conditions, with irrigation, fertilization, and other factors, the total biomass productivity can approach 100 T/ha/yr. One unresolved issue is the trade-off between accumulation of toxic elements and productivity [104]. In practice, a maximum harvest biomass yield of 10–20 T/ha/yr is likely, particularly for plants that accumulate metals.

These values for the productivity of biomass and the metal content of soil would limit the annual capacity for removal of metals to approximately 10–400 kg/ha/yr, depending on pollutant, species of plant, climate, and other factors. For a target soil depth of 30 cm (4000 T/ha), this capacity amounts to an annual reduction of 2.5–100 mg/kg of soil contaminants. This rate of removal of contamination is often acceptable, allowing total remediation of a site over a period of a few years to several decades [102].

13.12.3.2 Cost

The practical objective of phytoremediation is to achieve major reductions in the cost of cleanup of hazardous sites. Salt and others [90] note the cost-effectiveness of phytoremediation with an example: Using phytoremediation to clean up one acre of sandy loam soil to a depth of 50 cm typically will cost \$60,000–\$100,000, compared with a cost of at least \$400,000 for excavation and disposal storage without treatment [90]. One objective of field tests is to use commercially available agricultural equipment and supplies for phytoremediation to reduce costs. Therefore, in addition to their remediation qualities, the agronomic characteristics of plants must be evaluated.

The processing and ultimate disposal of the biomass generated is likely to be a major percentage of overall costs, particularly when highly toxic metals and radionuclides are present at a site. Analysis of the costs of phytoremediation must include the entire cycle of the process, from the growing and harvesting of the plants to the final processing and disposal of the biomass. It is difficult to predict costs of phytoremediation, compared with overall cleanup costs at a site. Phytoremediation may also be used as a follow-up technique after areas with high concentrations of pollutants have been mitigated or in conjunction with other remediation technologies, making cost analysis more difficult.

13.12.3.3 Future Directions

Because metal hyperaccumulators generally produce small quantities of biomass, they are unsuited agronomically for phytoremediation. Nevertheless, such plants are a valuable store of genetic and physiologic material and data [87]. To provide effective cleanup of contaminated soils, it is essential to find, breed, or engineer plants that absorb, translocate, and tolerate levels of metals in the range of 0.1–1.0%. It is also necessary to develop a methodology for selecting plants that are native to the area.

Three grasses are commercially available for the stabilization of lead, copper, and zinc wastes [90]. An integrated approach that involves basic and applied research, along with consideration of safety, legal, and policy issues, will be necessary to establish phytoremediation as a practicable cleanup technology [87].

According to a DOE report, three broad areas of research and development can be identified for the *in situ* treatment of soil contaminated with metals [102]:

1. *Mechanisms of uptake, transport, and accumulation:* Research is needed to develop better understanding of the use of physiological, biochemical, and genetic processes in plants. Research on the uptake and transport mechanisms is providing improved knowledge about the adaptability of those systems and how they might be used in phytoremediation.
2. *Genetic evaluation of hyperaccumulators:* Research is being conducted to collect plants growing in soils that contain high levels of metals and screen them for specific traits useful in phytoremediation. Plants that tolerate and colonize environments polluted with metals

are a valuable resource, both as candidates for use in phytoremediation and as sources of genes for classical plant breeding and molecular genetic engineering.

3. *Field evaluation and validation:* Research is being conducted to employ early and frequent field testing to accelerate implementation of phytoremediation technologies and to provide data to research programs. Standardization of field-test protocols and subsequent application of test results to real problems are also needed.

Research in these areas is expected to grow because many of the current engineering technologies for cleaning the surface soil of metals are costly and physically disruptive. Phytoremediation, when fully developed, could result in significant cost savings and in the restoration of numerous sites by a relatively noninvasive, solar-driven, *in situ* method that, in some forms, can be aesthetically pleasing [87].

13.12.4 SUMMARY OF PHYTOREMEDIATION TECHNOLOGY

Phytoremediation is in the early stage of development and is being field tested at various sites in the United States and overseas for its effectiveness in capturing or stabilizing metals, including radioactive wastes. Limited cost and performance data are currently available. Phytoremediation has the potential to develop into a practicable remediation option at sites where contaminants are near the surface, are relatively nonleachable, and pose little imminent threat to human health or the environment [87]. The efficiency of phytoremediation depends on the characteristics of the soil and the contaminants; these factors are summarized in the sections that follow.

13.12.4.1 Site Conditions

The effectiveness of phytoremediation is generally restricted to surface soils within the rooting zone. The most important limitation to phytoremediation is rooting depth, which can be 20, 50, or even 100 cm, depending on the plant and soil type. Therefore, one of the favorable site conditions for phytoremediation is contamination with metals that is located at the surface [102].

The type of soil, as well as the rooting structure of the plant relative to the location of contaminants, can have a strong influence on the uptake of any metal substance by the plant. Amendment of soils to change soil pH, nutrient compositions, or microbial activities must be selected in treatability studies to govern the efficiency of phytoremediation. Certain generalizations can be made about such cases; however, much work is needed in this area [87]. Since the amount of biomass that can be produced is one of the limiting factors affecting phytoremediation, optimal climatic conditions, with irrigation and fertilization of the site, should be considered for increased productivity of the best plants for the site [102].

13.12.4.2 Waste Characteristics

Sites that have low to moderate contamination with metals might be suitable for growing hyperaccumulating plants, although the most heavily contaminated soils do not allow plant growth without the addition of soil amendments. Unfortunately, one of the most difficult metal cations for plants to translocate is lead, which is present at numerous sites in need of remediation. Although a significant uptake of lead has not yet been demonstrated, one researcher is experimenting with soil amendments that make lead more available for uptake [90].

Capabilities to accumulate lead and other metals are dependent on the chemistry of the soil in which the plants are growing. Most metals, and lead in particular, occur in numerous forms in the soil, not all of which are equally available for uptake by plants [87,105]. Maximum removal of lead requires a balance between the nutritional requirements of plants for biomass production and the bioavailability of lead for uptake by plants. Maximizing the availability of lead requires low pH and low levels of available phosphate and sulfate. However, limiting the fertility of the soil in such a manner directly affects the health and vigor of plants [87].

13.13 USE OF TREATMENT TRAINS

Several of the metal remediation technologies discussed are often enhanced through the use of treatment trains. Treatment trains use two or more remedial options applied sequentially to contaminated soil and often increase the effectiveness while decreasing the cost of remediation. Processes involved in treatment trains include soil pretreatment, physical separation designed to decrease the amount of soil requiring treatment, additional treatment of process residuals or off-gases, and a variety of other physical and chemical techniques, which can greatly improve the performance of the remediation technology. Table 13.12 provides examples of treatment trains used to enhance each of the proved and commercialized metal remediation technologies [5].

TABLE 13.12
Typical Treatment Trains

	Containment	S/S	Vitrification	Soil Washing	Pyrometallurgical	Soil Flushing
Pretreatment						
Excavation	•	E, P	I, E	•	•	
Debris removal		E, P	E	•	•	
Oversize reduction		E, P	E	•	•	
Adjust pH	•	I, E, P				
Reduction [e.g., Cr(VI) to Cr(III)]	•	I, E				
Oxidation [e.g., As(III) to As (V)]	•	I, E				
Treatment to remove or destroy organics		I,				
Physical separation of rich and lean fractions		I, E, P	E	•	•	
Dewatering and drying for wet sludge	•	P	E		•	
Conversion of metals to less volatile forms [e.g., As ₂ O ₃ to Ca ₃ (AsO ₄) ₂]			E			
Addition of high-temperature reductants					•	
Pelletizing					•	
Flushing fluid delivery and extraction system						•
Containment barriers	•	I, E, P	I	•		•
Posttreatment/Residuals Management						
Disposal of treated solid residuals (preferably below the frost line and above the water table)		I, E, P	E		•	
Containment barriers		I, E, P	I, E			•
Off-gas treatment		I, E, P	I, E		•	
Reuse for on-site paving		P				
Metal recovery from extraction fluid by aqueous processing (ion exchange, electrowinning, etc.)				•		
Pyrometallurgical recovery of metal from sludge				•		
Processing and reuse of leaching solution				•	•	
S/S treatment of leached residual				•		

continued

TABLE 13.12 (continued)

	Containment	S/S	Vitrification	Soil washing	Pyrometallurgical	Soil flushing
Disposal of solid process residuals (preferably below the frostline and above the water table)				•		
Disposal of liquid process residuals				•		•
S/S treatment of slag or fly ash					•	
Reuse of slag/vitreous product as construction material			E	•		
Reuse of metal or metal compound					•	
Further processing of metal or metal compound					•	
Flushing liquid/groundwater treatment/ disposal						•

Source: U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

Note: Technology has been divided into the following categories: I = *in situ* process; E = *ex situ* process; P = polymer microencapsulation *ex situ*.

13.14 COST RANGES OF REMEDIAL TECHNOLOGIES

Estimated cost ranges for the basic operation of the technology are presented in Table 13.13. The reader is cautioned that the cost estimates generally do not include pretreatment, site preparation, regulatory compliance costs, costs for additional treatment of process residuals (e.g., stabilization of incinerator ash or disposal of metals concentrated by solvent extraction), or profit [5,106]. Since the

TABLE 13.13
Estimated Cost Ranges of Metals Remediation Technologies

Type of Remediation	Cost Range 2007 USD/T
Containment ^a	13–120
S/S	80–380
Vitrification	520–1140
Soil washing	80–320
Soil flushing ^b	80–215
Pyrometallurgical	330–730
Electrokinetics ^b	60–160
Phytoremediation ^c	30–50

Source: U.S. EPA. *Recent Developments for In Situ Treatment of Metal Contaminated Soils*. Contract # 68-W5-0055, U.S. Environmental Protection Agency, Washington, DC, March 1997; U.S. EPA. *Technology Alternatives for the Remediation of Soils Contaminated with AS, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Cincinnati, OH, August 1997.

^a Includes landfill caps and slurry walls. A slurry wall depth of 6 m is assumed.

^b Costs reported in USD/m³, assumed soil specific gravity of 1.6.

^c Costs reported per acre for a soil depth of 0.50 m.

actual cost of employing a remedial technology at a specific site may be significantly different from these estimates, data are best used for order-of-magnitude cost evaluations.

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14 Remediation of Metal Finishing Brownfield Sites

Nazih K. Shammass

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14.1 INTRODUCTION

14.1.1 BACKGROUND

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund [1] defines brownfields sites as “real property, the expansion, redevelopment, or reuse of which may be complicated by the presence or potential presence of a hazardous substance, pollutant, or contaminant.” According to the U.S. Environmental Protection Agency (U.S. EPA), brownfields sites are abandoned, idled, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination [2]. Concerns about liability, cost, and potential health risks associated with brownfields sites often prompt businesses to migrate to “greenfields” outside the city. Left behind are communities burdened with environmental contamination, declining property values, and increased unemployment.

U.S. EPA's Brownfields Economic Redevelopment Initiative was established to enable states, site planners, and other community stakeholders to work together in a timely manner to prevent, assess, safely cleanup, and sustainably reuse brownfields sites [3]. With the enactment of the Small Business Liability Relief and Brownfields Revitalization Act in 2002, U.S. EPA assistance was expanded to provide greater support for brownfields cleanup and reuse. Many states and local jurisdictions also help businesses and communities to adapt environmental cleanup programs to the special needs of brownfields sites.

Preparing brownfields sites for productive reuse requires integration of many elements—financial issues, community involvement, liability considerations, environmental assessment and cleanup, regulatory requirements, and more—as well as coordination among many groups of stakeholders [4]. The assessment and cleanup of a site must be carried out in a way that integrates all these factors into the overall redevelopment process. In addition, the cleanup strategy will vary from site to site. At some sites, cleanup will be completed before the properties are transferred to new owners. At other sites, cleanup may take place simultaneously with construction and redevelopment activities.

Regardless of when and how cleanups are accomplished, the challenge to any brownfields program is to clean up sites in accordance with redevelopment goals. Such goals may include cost-effectiveness, timeliness, avoidance of adverse effects to site structures and neighboring communities, and redevelopment of land in a way that benefits communities and local economies. Regulators and site managers are increasingly recognizing the value of implementing a more dynamic approach to streamline assessment and cleanup activities at brownfields sites. This approach, referred to as the Triad, is flexible and recognizes site-specific decisions and data needs [4].

The Triad approach focuses on management of decision uncertainty by incorporating (a) systematic project planning, (b) dynamic work planning strategies, and (c) use of real-time measurement technologies, including innovative technologies, to accelerate and improve the cleanup process. The Triad approach can reduce costs, improve decision certainty, expedite site closeout, and positively affect regulatory and community acceptance. This approach is well aligned with brownfields site priorities, which are affected by the economics of redevelopment, community involvement, and liability considerations.

Numerous technology options are available to assist those involved in brownfields cleanup. U.S. EPA's Office of Superfund Remediation and Technology Innovation (OSRTI) encourages use of smarter solutions for characterizing and cleaning up contaminated sites by advocating more effective, less costly technological approaches. Use of innovative technologies to characterize and clean up brownfields sites provides opportunities for stakeholders to reduce cleanup costs and accelerate cleanup schedules. Often, innovative approaches are also more acceptable to communities.

The cornerstone of U.S. EPA's Brownfields Initiative is the Pilot Program. Under this program, U.S. EPA is funding more than 200 brownfields assessment pilot projects in states, cities, towns, counties, and tribes across the country [2]. The pilots, each funded at up to USD 200,000 over 2 years, are bringing together community groups, investors, lenders, developers, and other affected parties to address the issues associated with assessing and cleaning up contaminated brownfields sites and returning them to appropriate, productive use. U.S. EPA's regional brownfields coordinators can provide communities with technical assistance such as targeted brownfields assessments. In addition to the hundreds of brownfields sites being addressed by these pilots, over 40 states have established brownfields or voluntary cleanup programs (VCPs) to encourage municipalities and private sector organizations to assess, clean up, and redevelop brownfields sites.

14.1.2 METALS AND METALLOIDS

Metals are one of the three groups of elements distinguished by their ionization and bonding properties, along with metalloids and nonmetals. Metals have certain characteristic physical properties: they are usually shiny, have a high density, are ductile and malleable, usually have a high melting point, are usually hard, and conduct electricity and heat well. Metalloids have properties that are

TABLE 14.1
Typical Metals and Metalloids at Brownfields Sites

Metals and Metalloids			
Aluminum	Calcium	Mercury	
Antimony	Chromium	Molybdenum	
Arsenic	Cobalt	Nickel	Tin
Barium	Copper	Potassium	Titanium
Beryllium	Iron	Selenium	Vanadium
Bismuth	Lead	Silver	Zinc
Boron	Magnesium	Sodium	Zirconium
Cadmium	Manganese	Thallium	

Source: U.S. EPA. *Road Map to Understanding Innovative Technology Options for Brownfields Investigation and Cleanup*, 4th edition, EPA 542-B-05-001, U.S. Environmental Protection Agency, Washington, DC, September 2005.

intermediate between those of metals and nonmetals. There is no unique way of distinguishing a metalloid from a true metal, but the most common way is that metalloids are usually semiconductors rather than conductors [4].

Locations where metals and metalloids may be found include artillery and small arms impact areas, battery disposal areas, burn pits, chemical disposal areas, contaminated marine sediments, disposal wells and leach fields, electroplating and metal finishing shops, firefighting training areas, landfills and burial pits, leaking storage tanks, radioactive and mixed waste disposal areas, oxidation ponds and lagoons, paint stripping and spray booth areas, sand blasting areas, surface impoundments, and vehicle maintenance areas. Typical metals and metalloids encountered at many sites include those listed in Table 14.1.

14.1.3 PURPOSE

U.S. EPA has developed a set of technical guides to assist communities, states, municipalities, and the private sector to more effectively address brownfields sites. Each guide in this series contains information on a different type of brownfields site (classified according to former industrial use). In addition, a supplementary guide contains information on cost-estimating tools and resources for brownfields sites [4–6].

The overview of the technical process involved in assessing and cleaning up brownfields sites can assist planners in making decisions at various stages of the project. An understanding of land use and industrial processes conducted in the past at a site can help the planner to conceptualize the site and identify likely areas of contamination that may require cleanup. Numerous resources are suggested to facilitate characterization of the site and consideration of cleanup technologies [2–6].

Specifically, the objective of this chapter is to provide decision-makers with

1. An understanding of common industrial processes at metal finishing facilities and the relationship between such processes and potential releases of contaminants to the environment.
2. Information on the types of contaminants likely to be present at a metal finishing site.
3. A discussion of site assessment (also known as site characterization), screening and cleanup levels, and cleanup technologies that can be used to assess and clean up the types of contaminants likely to be present at metal finishing sites.
4. A conceptual framework for identifying potential contaminants at the site, pathways by which contaminants may migrate off site, and environmental and human health concerns.

5. Information on developing an appropriate cleanup plan for metal finishing sites where contamination levels must be reduced to allow a site's reuse.
6. A discussion of pertinent issues and factors should be considered when developing a site assessment and cleanup plan and selecting appropriate technologies for brownfields, given time and budget constraints.

14.2 INDUSTRIAL PROCESSES AND CONTAMINANTS AT METAL FINISHING SITES

Understanding the industrial processes used during a metal finishing facility's active life and the types of contaminants that may be present provides important information to guide planners in the assessment, cleanup, and restoration of the site to an acceptable condition for sale or reuse. This section provides a general overview of the processes, chemicals, and contaminants used or found at metal finishing sites. Specific metal finishing brownfields sites may have had a different combination of these processes, chemicals, and contaminants. Therefore, this information can be used only to develop a framework of likely past activities. Planners should obtain facility-specific information on industrial processes at their site whenever possible. Site-specific information is also important to obtain because the site may have been used for other industrial purposes at other times in the past.

This section describes waste-generating surface preparation operations; metal finishing operations and the types of waste streams and specific contaminants associated with each process; auxiliary areas at metal finishing sites that may produce contaminants and nonprocess-related contamination problems associated with metal finishing sites. [Figure 14.1](#) presents typical metal finishing processes and land areas, along with the types of waste streams associated with each area [7]. [Table 14.2](#) lists the specific contaminants associated with each waste stream [2].

14.2.1 SURFACE PREPARATION OPERATIONS

Metal finishing processes are typically housed within one structure. The surface of metal products generally requires preparation (i.e., cleaning) prior to applying a finish. An initial set of degreasing tanks ([A] in [Figure 14.1](#)) are used to remove oils, grease, and other foreign matter from the surface of the metal so that a coating can be applied. Metal finishing facilities may use solvents or emulsion solutions (i.e., solvents dispersed in an aqueous medium with the aid of an emulsifying agent) in the degreasing tanks to clean and prepare the surfaces of metal parts. Wastewaters generated from cleaning operations are primarily rinse waters, which are usually combined with other metal finishing wastewaters and treated on-site by conventional chemical precipitation. These wastewaters may contain solvents, as listed in [Table 14.2](#). Solid wastes such as wastewater treatment sludges, still bottoms, and cleaning tank residues may also be generated.

14.2.2 METAL FINISHING OPERATIONS

Metal finishing operations are typically performed in a series of tanks (baths) followed by rinsing cycles. Acid or alkaline baths "pickle" the surface of the steel to improve the adherence of the coating. After the pickling baths, the metal products are moved to plating tanks, where the final coat is applied. Wastes generated during finishing operations derive from the solvents and cleansers applied to the surface and the metal-ion-bearing aqueous solutions used in acid/alkaline rinsing and bathing operations. Common metal finishing operations include anodizing, chemical conversion coating, electroplating, electroless plating, and painting. Common waste streams include metals and acids in the wastewater; metals in sludges and solid waste; and solvents from painting operations, as listed in [Table 14.2](#). If these wastes were managed or disposed of on-site, it is possible that pollutants were released into the environment. Even at facilities where wastes were not stored

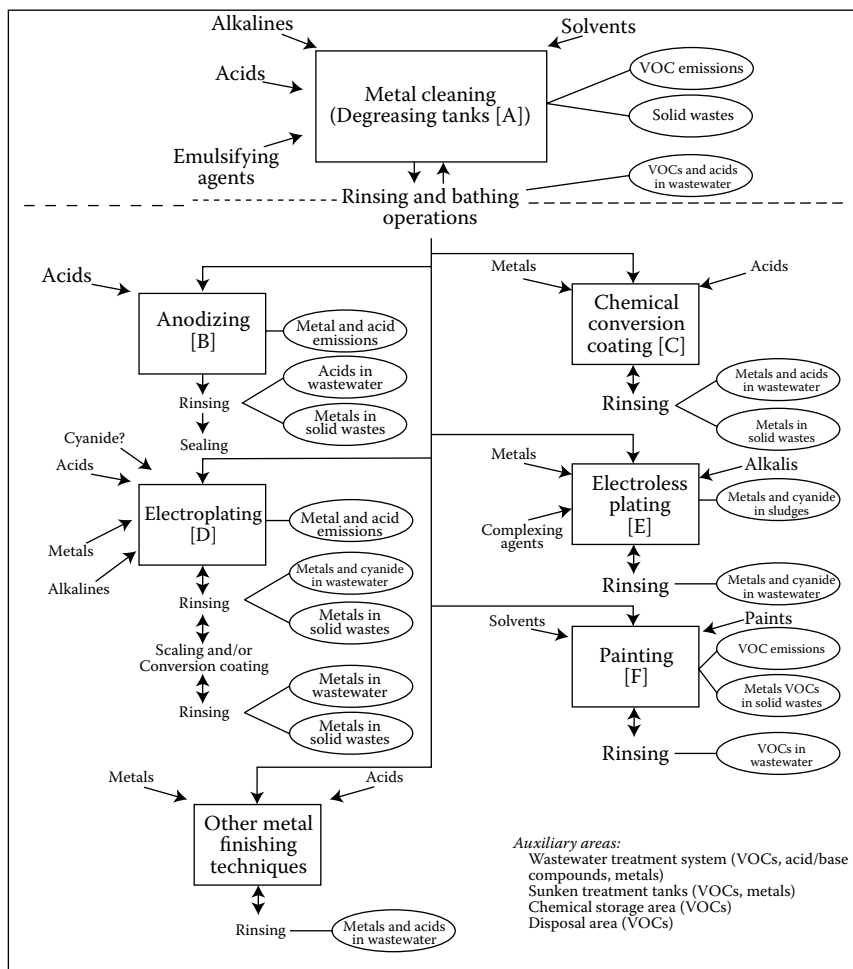


FIGURE 14.1 Typical metal finishing facility. (Adapted from U.S. EPA. *Brownfields and Land Revitalization Tools and Technical Information*. U.S. Environmental Protection Agency, Washington, DC, 2007. Available at: <http://www.epa.gov/brownfields/toolsandtech.htm>.)

TABLE 14.2
Common Contaminants at Metal Finishing Sites

Contaminant Group	Contaminant Name
VOCs	Acetone, benzene, isopropyl alcohol, 2-dichlorobenzene, 4-trimethylbenzene, dichloromethane, ethyl benzene, freon 113, methanol, methyl isobutyl ketone, methyl ethyl ketone, phenol, tetrachloroethylene, toluene, trichloroethylene, xylene (mixed isomers)
Metals/inorganics	Aluminum, antimony, arsenic, asbestos (friable), barium, cadmium, chromium, cobalt, copper, lead, cyanide, manganese, mercury, nickel, silver, zinc
Acids	Hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid

Source: U.S. EPA. *Technical Approaches to Characterizing and Cleaning Up Metal Finishing Sites under the Brownfields Initiative*. EPA/625/R-98/006, U.S. Environmental Protection Agency, Cincinnati, OH, March 1999.

Note: VOCs, Volatile organic compounds.

on-site, releases may have occurred during the handling and use of chemicals. Metal finishing operations are described below [2].

14.2.2.1 Anodizing Operations

Anodizing is an electrolytic process that uses acids from the combined electrolytic solution/acid bath tank to convert the metal surface into an insoluble oxide coating ([B] in Figure 14.1). After anodizing, metal parts are typically rinsed and then sealed. Anodizing operations produce contaminated wastewaters and solid wastes.

14.2.2.2 Chemical Conversion Coating

Chemical conversion coating ([C] in Figure 14.1) includes the following processes:

Chromating: Chromate conversion coatings are produced on various metals by chemical or electrochemical treatment. Acid solutions react with the metal surface to form a layer of a complex mixture of the constituent compounds, including chromium and the base metal.

Phosphating: Phosphate conversion coating involves the immersion of steel-, iron-, or zinc-plated steel into a dilute solution of phosphate salts, phosphoric acid, and other reagents to condition the surfaces for further processing.

Metal coloring: Metal coloring involves chemically converting the metal surface into an oxide or similar metallic compound to produce a decorative finish.

Passivating: Passivating is the process of forming a protective film on metals by immersing them in an acid solution (usually nitric acid or nitric acid with sodium dichromate).

Pollutants associated with chemical conversion processes enter the wastestream through rinsing and batch dumping of process baths. Wastewaters containing chromium are usually pretreated; this process generates a sludge that is sent off-site for metals reclamation and/or disposal.

14.2.2.3 Electroplating

Electroplating is the production of a surface coating of one metal upon another by electrodeposition ([D] in Figure 14.1). In electroplating, metal ions (in acid, alkaline, or neutral solutions) are reduced on the cathodic surfaces of the work pieces being plated. Electroplating operations produce contaminated wastewaters and solid wastes. Contaminated wastewaters result from work piece rinsing and process cleanup waters. Rinse waters from electroplating are usually combined with other metal finishing wastewaters and treated on-site by conventional chemical precipitation, which results in wastewater treatment sludges. Other wastes generated from electroplating include spent process solutions and quench baths that may be discarded periodically when the concentrations of contaminants inhibit their proper functions.

14.2.2.4 Electroless and Immersion Plating

Electroless plating involves chemically depositing a metal coating onto a plastic object by immersing the object in a plating solution ([E] in Figure 14.1). Immersion plating produces a thin metal deposit, commonly zinc or silver, by chemical displacement. Both produce contaminated wastewater and solid wastes. Facilities generally treat spent plating solutions and rinse waters chemically to precipitate the toxic metals; however, some plating solutions can be difficult to treat because of the presence of chelates. Most waste sludges resulting from electroless and immersion plating contain significant concentrations of toxic metals.

14.2.2.5 Painting

Painting is the application of predominantly organic coatings for protective and/or decorative purposes ([F] in Figure 14.1). Paint is applied in various forms, including dry powder, solvent diluted formulations, and waterborne formulations, most commonly via spray painting and electrodeposition. Painting operations may result in solvent-containing waste and the direct release of solvents, paint sludge wastes, and paint-bearing wastewaters. Paint cleanup operations may also contribute to

the release of chlorinated solvents. Discharge from water curtain booths generates the most wastewater. On-site wastewater treatment processes generate a sludge that is taken off-site for disposal. Other sources of wastes include emission control devices (e.g., paint booth collection systems, ventilation filters) and discarded paints. Sandblasting may be performed to remove paint and to clean metal surfaces for painting or resurfacing; this practice may be of particular concern if the paint being removed contains lead.

14.2.2.6 Other Metal Finishing Techniques

Polishing, hot dip coating, and etching are other processes used to finish metal. Wastewaters are often generated during these processes. For example, after polishing operations, area cleaning and washdown can produce metal-bearing wastewaters. Hot dip coating techniques, such as galvanizing, use water for rinses following precleaning and for quenching after coating. Hot dip coatings also generate a solid waste, oxide dross that is periodically skimmed off the heated tank. Etching solutions are composed of strong acids or bases, which may result in etching solution wastes that contain metals and acids.

14.2.3 AUXILIARY ACTIVITY AREAS AND POTENTIAL CONTAMINANTS

14.2.3.1 Wastewater Treatment

Many of the operations involved in metal finishing produce wastewaters, which usually are combined and treated on-site, often by conventional chemical precipitation. Even though the facility would have been required to meet state wastewater discharge standards before releasing wastes, spills of process wastewater may have occurred in the area. At abandoned sites, any remaining wastewater left in tanks or floor drains could contain solvents, metals, and acids, such as those listed in [Table 14.2](#). In addition, it is possible that wastewater sludges, which can contain metals, were left at the site in baths or tanks.

14.2.3.2 Sunken Wastewater Treatment Tank

Some metal finishing facilities have wastewater treatment tanks sunk into the concrete slab to rest on the underlying soils. This is done by design to aid facility operators in accessing the tanks. If these tanks develop leaks, the lost material, which may contain volatile organic compounds (VOCs) and metals, may be released directly to the soils beneath the building.

14.2.3.3 Chemical Storage Area

At most metal finishing sites, an area for storing chemicals used in the various operations was designated. Bulk containers stored in these areas may have leaked or spilled, resulting in discharges to floor drains or cracks in the floor. VOCs such as those listed in [Table 14.2](#) may be found in such areas. Acids and alkaline reagents may also be found in this area.

14.2.3.4 Disposal Area

Materials, both liquid and solid, from process baths may have been disposed of at a designated area at the site. Such areas may be identified by stained soils or a lack of vegetation. These areas may contain VOCs, such as those listed in [Table 14.2](#).

14.2.3.5 Other Considerations

Not all releases are related to the industrial processes described above. Some releases result from the associated services required to maintain the industrial processes. For example, electroplating facilities are large consumers of electricity, which requires a number of transformers. At older facilities, these transformers may have been disposed of in unmarked areas of the facility, which

makes it difficult to know where leaks of polychlorinated biphenyl (PCB)-laden oils used as coolants may have occurred. Similarly, large machinery used to move metal pieces requires periodic maintenance. In the past, chemicals used for maintenance operations, such as solvents, oils, and grease, may have been flushed down drain and sumps after use. Stormwater runoff from paved areas such as parking lots may contain petroleum hydrocarbons and oils, which can contaminate areas located downgradient. When conducting initial site evaluations, planners should expand their investigations to include these types of activities.

In addition, metal finishing facilities may have been located in older buildings that contain lead paint and asbestos insulation and tiling. Any structure built before 1970 should be assessed for the presence of these materials. They can cause significant problems during demolition or renovation of the structures for reuse. Special handling and disposal requirements under state and federal laws can significantly increase the cost of construction.

14.3 SITE ASSESSMENT

The site investigation phase focuses on confirming whether any contamination exists at a site, locating any contamination, and characterizing the nature and extent of that contamination [8]. It is essential that an appropriately detailed study of the site be performed to identify the cause, nature, and extent of contamination and the possible threats to the environment or to any people living or working nearby. For brownfields sites, the results of such a study can be used in determining goals for cleanup, quantifying risks, determining acceptable and unacceptable risks, and developing effective cleanup plans that minimize delays or costs in the redevelopment and reuse of property. To ensure that sufficient information is obtained to support future decisions, the proposed cleanup measures and the proposed end use of the site should be considered when identifying data needs during the site investigation [4].

The elements of a site assessment are designed to help planners build a conceptual framework of the facility, which will aid site characterization efforts [9]. The conceptual framework should identify [2]:

1. Potential contaminants that remain in and around the facility
2. Pathways along which contaminants may move
3. Potential risks to the environment and human health that exist along the migration pathways.

This section highlights the key role that state environmental agencies usually play in brownfields projects. The types of information that planners should attempt to collect to characterize the site in a Phase I site assessment (i.e., the facility's history) are discussed. Information is presented about where to find and how to use this information to determine whether or not contamination is likely. Additionally, this section provides information to assist planners in conducting a Phase II site assessment, including sampling the site and determining the magnitude of contamination. Other considerations in assessing iron and steel sites are also discussed, and general sampling costs are included. The linking of the decision to be taken to the collected data and technologies is illustrated in [Figure 14.2](#).

14.3.1 THE CENTRAL ROLE OF THE STATE AGENCIES

A brownfields redevelopment project involves partnerships among site planners (whether private or public sector), state and local officials, and the local community. State environmental agencies often are key decision-makers and a primary source of information for Brownfields projects. Brownfields sites are generally cleaned up under state programs, particularly state voluntary cleanup or Brownfields programs; thus, planners will need to work closely with state program managers to

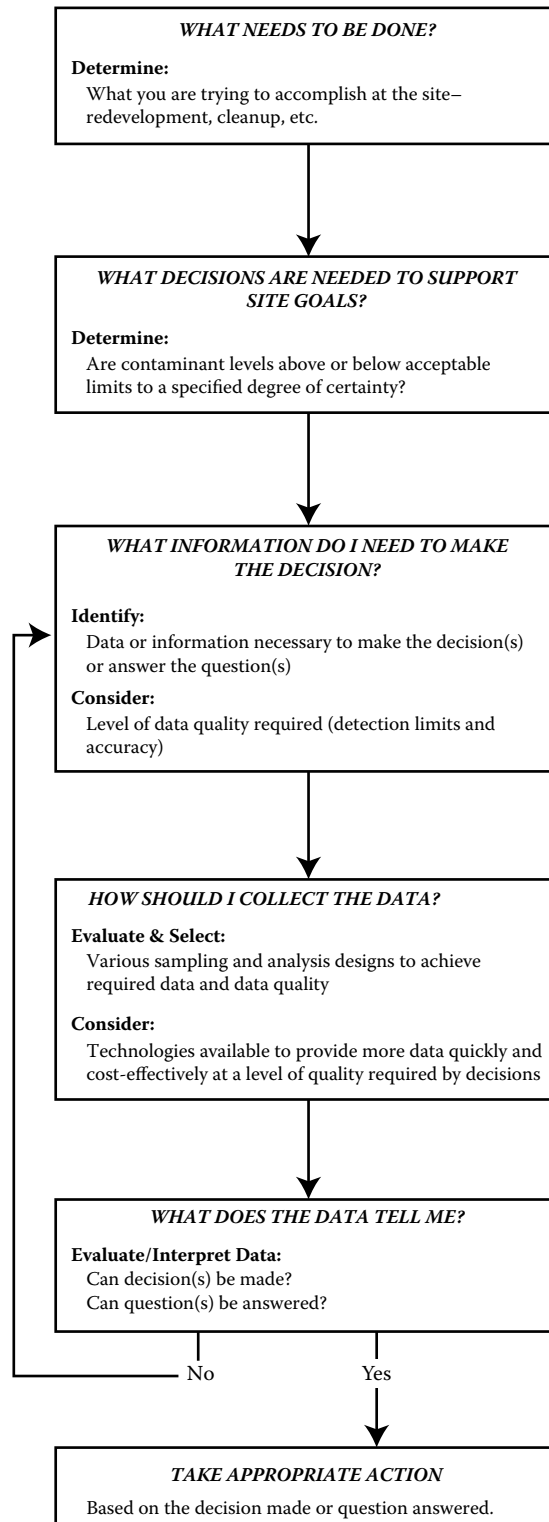


FIGURE 14.2 Linking the decision, data, and technology. (Adapted from U.S. EPA. *Road Map to Understanding Innovative Technology Options for Brownfields Investigation and Cleanup*, 4th edition, EPA 542-B-05-001, U.S. Environmental Protection Agency, Washington, DC, September 2005.)

determine their particular state's requirements for brownfields development. Planners may also need to meet additional federal requirements. Key state functions include [2]:

1. Overseeing brownfields site assessment and cleanup processes, including the management of VCPs
2. Providing guidance on contaminant screening levels
3. Serving as a source of site information, as well as legal and technical guidance.

14.3.1.1 State VCPs

State VCPs are designed to streamline brownfields redevelopment, reduce transaction costs, and provide state liability protection for past contamination. Planners should be aware of the fact that state cleanup requirements vary significantly and should contact the state brownfield manager; brownfields managers from state agencies will be able to identify their state requirements for planners and will clarify how their state requirements relate to federal requirements.

14.3.1.2 Levels of Contaminant Screening and Cleanup

Identifying the level of site contamination and determining the risk, if any, associated with that contamination level is a crucial step in determining whether cleanup is needed. Some state environmental agencies, as well as federal and regional U.S. EPA offices, have developed screening levels for certain contaminants, which are incorporated into some brownfields programs. Screening levels represent breakpoints in risk-based concentrations of chemicals in soil, air, or water. If contaminant concentrations are below the screening level, no action is required; above the level, further investigation is needed.

In addition to screening levels, U.S. EPA regional offices and some states have developed cleanup standards; if contaminant concentrations are above cleanup standards, cleanup must be pursued. The section on "Performing a Phase II Site Assessment" in this chapter provides more information on screening levels and the section on "Site Cleanup" provides more information on cleanup standards.

14.3.2 PERFORMING A PHASE I SITE ASSESSMENT: OBTAINING FACILITY BACKGROUND INFORMATION FROM EXISTING DATA

Planners should compile a history of the iron and steel manufacturing facility to identify likely site contaminants and their probable locations. Financial institutions typically require a Phase I site assessment prior to lending money to potential property buyers to protect the institution's role as a mortgage holder [10]. In addition, parties involved in the transfer, foreclosure, leasing, or marketing of properties recommend some form of site evaluation. The site history should include:

1. A review of readily available records (e.g., former site use, building plans, and records of any prior contamination events).
2. A site visit to observe the areas used for various industrial processes and the condition of the property.
3. Interviews with knowledgeable people (e.g., site owners, operators, and occupants; neighbors; local government officials).
4. A report that includes an assessment of the likelihood that contaminants are present at the site.

The Phase I site assessment should be conducted by an environmental professional, and may take 3–4 weeks to complete. Site evaluations are required in part as a response to concerns over environmental liabilities associated with property ownership. A property owner needs to perform "due diligence," that is fully inquire into the previous ownership and uses of a property to demonstrate that all reasonable efforts to find site contamination have been made. Because brownfields sites often contain low levels of contamination and pose low risks, due diligence through a

Phase I site assessment will help to answer key questions about the levels of contamination. Several federal and state programs exist to minimize owner liability at brownfields sites and facilitate cleanup and redevelopment; planners should contact the state environmental or regional U.S. EPA office for further formation.

Information on how to review records, conduct site visits and interviews, and develop a report during a Phase I site assessment is provided below.

14.3.2.1 Facility Records

Facility records are often the best source of information on former site activities. If past owners are not initially known, a local records office should have deed books that contain ownership history. Generally, records pertaining specifically to the site in question are adequate for review purposes. In some cases, however, records of adjacent properties may also need to be reviewed to assess the possibility of contaminants migrating from or to the site, based on geologic or hydrogeologic conditions. If the brownfields property resides in a low-lying area, in close proximity to other industrial facilities or formerly industrialized sites, or downgradient from current or former industrialized sites, an investigation of adjacent properties is warranted.

14.3.2.2 Other Sources of Recorded Information

Planners may need to use other sources in addition to facility records to develop a complete history. American Society for Testing and Materials (ASTM) Standard 1527 identifies standard sources such as historical aerial photographs, fire insurance maps, property tax files, recorded land title records, topographic maps, local street directories, building department records, zoning/land use records, and newspaper archives [10].

Some metal finishing site managers may have worked with state environmental regulators; these offices may be key sources of information. Federal (e.g., U.S. EPA) records may also be useful. The types of information provided by regulators may include facility maps that identify activities and disposal areas, lists of stored pollutants, and the types and levels of pollutants released. State offices and other sources where planners can search for site-specific information are presented below:

1. The state offices responsible for industrial waste management and hazardous waste should have a record of any emergency removal actions at the site (e.g., the removal of leaking drums that posed an “imminent threat” to local residents); any Resource Conservation and Recovery Act (RCRA) [11] permits issued at the site; notices of violations issued; and any environmental investigations.
2. The state office responsible for discharges of wastewater to water bodies under the National Pollutant Discharge Elimination System (NPDES) [12] program will have a record of any permits issued for discharges into surface water at or near the site. The local publicly owned treatment works (POTWs) will have records for permits issued for indirect discharges into sewers (e.g., floor drain discharges to a sanitary sewer).
3. The state office responsible for underground storage tanks (USTs) may also have records of tanks located at the site, as well as records of any past releases.
4. The state office responsible for air emissions may be able to provide information on air pollutants associated with particular types of on-site contamination.
5. U.S. EPA’s Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) [13] of potentially contaminated sites should have a record of any previously reported contamination at or near the site.
6. U.S. EPA Regional Offices can provide records of sites that have hazardous substances. Information is available from the Federal National Priorities List (NPL) and lists of treatment, storage, and disposal (TSD) facilities subject to corrective action under RCRA. RCRA non-TSD facilities, RCRA generators, and Emergency Response Notification System (ERNS) information on contaminated or potentially contaminated sites can help to determine

whether neighboring facilities are recorded as having released hazardous substances into the immediate environment.

7. State and local records may indicate any permit violations or significant contaminant releases from or near the site.
8. Residents and former employees may be able to provide useful information on waste management practices, but these reports should be substantiated.
9. Local fire departments may have responded to emergency events at the facility. Fire departments or city halls may have fire insurance maps or other historical maps or data that indicate the location of hazardous waste storage areas at the site.
10. Local waste haulers may have records of the facility's disposal of hazardous or other waste materials.
11. Utility records.
12. Local building permits.

14.3.2.3 Identifying Migration Pathways and Potentially Exposed Populations

Off-site migration of contaminants may pose a risk to human health and the environment; planners should gather as much readily available information on the physical characteristics of the site as possible. Migration pathways, that is, soil, groundwater, and air, will depend on site-specific characteristics such as geology and the physical characteristics of the individual contaminants (e.g., mobility). Information on the physical characteristics of the general area can play an important role in identifying potential migration pathways and focusing environmental sampling activities, if needed. Planners should collect three types of information to obtain a better understanding of migration pathways, including topographic, soil and subsurface, and groundwater data, as described below [14–17].

14.3.3 GATHERING TOPOGRAPHIC INFORMATION

In this preliminary investigation, topographic information will be helpful in determining whether the site may be subject to contamination by adjoining properties or may be the source of contamination of other properties. Topographic information will help planners identify low-lying areas of the facility where rain and snowmelt (and any contaminants in them) may collect and contribute both water and contaminants to the underlying aquifer or surface runoff to nearby areas. The U.S. Geological Survey (USGS) of the Department of the Interior has topographic maps for nearly every part of the country.

14.3.4 GATHERING SOIL AND SUBSURFACE INFORMATION

Planners should know about the types of soils at the site from the ground surface extending down to the water table because soil characteristics play a large role in how contaminants move in the environment. For example, clay soils limit downward movement of pollutants into underlying groundwater but facilitate surface runoff. Sandy soils, on the other hand, can promote rapid infiltration into the water table while inhibiting surface runoff. Soil information can be obtained through a number of sources [2]:

1. Local planning agencies should have soil maps to support land use planning activities. These maps provide a general description of the soil types present within a county (or sometimes a smaller administrative unit, such as a township).
2. The Natural Resource Conservation Service and Co-operative Extension Service offices of the U.S. Department of Agriculture (USDA) are also likely to have soil maps.
3. Well-water companies are likely to be familiar with local subsurface conditions, and local water districts and state water divisions may have well-logging information.
4. Local health departments may be familiar with subsurface conditions because of their interest in septic drain fields.

5. Local construction contractors are likely to be familiar with subsurface conditions from their work with foundations.

Soil characteristics can vary widely within a relatively small area, and it is common to find that the top layer of soil in urban areas is composed of fill materials, not native soils. While local soil maps and other general soil information can be used for screening purposes such as in a Phase I assessment, site-specific information will be needed in the event that cleanup is necessary.

14.3.5 GATHERING GROUNDWATER INFORMATION

Planners should obtain general groundwater information about the site area, including:

1. State classifications of underlying aquifers
2. Depth to the groundwater tables
3. Groundwater flow direction and rate.

This information can be obtained by contacting state environmental agencies or from several local sources, including water authorities, well drilling companies, health departments, and Agricultural Extension and Natural Resource Conservation Service offices.

14.3.5.1 Identifying Potential Environmental and Human Health Concerns

Identifying possible environmental and human health risks early in the process can influence decisions regarding the viability of a site for cleanup and the choice of cleanup methods used. A visual inspection of the area will usually suffice to identify on-site or nearby wetlands and water bodies that may be particularly sensitive to releases of contaminants during characterization or cleanup activities. Planners should also review available information (e.g., from state and local environmental agencies) to ascertain the proximity of residential dwellings, nearby industrial/commercial activities, and wetlands/water bodies, and to identify people, animals, or plants that might receive migrating contamination; any particularly sensitive populations in the area (e.g., children; endangered species); and whether any major contamination events have occurred previously in the area (e.g., drinking water problems; groundwater contamination).

For environmental information, planners can contact the U.S. Army Corps of Engineers, state environmental agencies, local planning and conservation authorities, the USGS, and the USDA Natural Resource Conservation Service. State and local agencies and organizations can usually provide information on local fauna and the habitats of any sensitive and/or endangered species.

For human health information, planners can contact:

1. *State and local health assessment organizations:* Organizations such as health departments should have data on the quality of local well water used as a drinking water source, as well as any human health risk studies that have been conducted. In addition, these groups may have other relevant information, such as how certain types of contaminants (e.g., volatile organics, such as benzene and phenols) might pose a health risk (e.g., dermal exposure to volatile organics during site characterization); information on exposures to particular contaminants and potential associated health risks can also be found in health profile documents developed by the Agency for Toxic Substances and Disease Registry (ATSDR). In addition, ATSDR may have conducted a health consultation or health assessment in the area if an environmental contamination event that may have posed a health risk occurred in the past; such an event and assessment should have been identified in the Phase I records review of prior contamination incidents at the site if any occurred.
2. *Local water and health departments:* During the site visit (described below), when visually inspecting the area around the facility, planners should identify any residential dwellings

or commercial activities near the facility and evaluate whether people there may come into contact with contamination along one of the migration pathways. Where groundwater contamination may pose a problem, planners should identify any nearby waterways or aquifers that may be impacted by groundwater discharge of contaminated water, including any drinking water wells that may be downgradient of the site, such as a municipal well field. Local water departments will have a count of well connections to the public water supply. Planners should also pay particular attention to information on private wells in the area downgradient of the facility, since, depending on their location, they may be vulnerable to contaminants migrating off-site even when the public municipal drinking water supply is not vulnerable. Local health departments often have information on the locations of private wells.

In addition to groundwater sources and migration pathways, surface water sources and pathways should be evaluated since groundwater and surface waters can interface at some (or several) point(s) in the region. Contaminants in groundwater can eventually migrate to surface waters, and contaminants in surface waters can migrate to groundwater.

14.3.5.2 Community Involvement

It is important that brownfields decision-makers encourage acceptance of redevelopment plans and cleanup alternatives by involving members of the community early in the decision-making process through community meetings, newsletters, or other outreach activities. For an individual site, the community should be informed about how the use of a proposed technology might affect redevelopment plans or the adjacent neighborhood [4]. For example, the planting of trees for the use of phytoremediation may create aesthetic or visual improvements; on the other hand, the use of phytoremediation may bring about issues related to site security or long-term maintenance that could affect access to the site.

Community-based organizations represent a wide range of issues, from environmental concerns to housing issues to economic development. These groups can often be helpful in educating planners and others in the community about local brownfields sites, which can contribute to successful brownfields site assessment and cleanup activities. In addition, most state VCPs require that local communities be adequately informed about brownfields cleanup activities. Planners can contact the local Chamber of Commerce, local philanthropic organizations, local service organizations, and neighborhood committees for community input. State and local environmental groups may be able to supply relevant information and identify other appropriate community organizations. Local community involvement in brownfields projects is a key component in the success of such projects [2].

U.S. EPA can assist members of the brownfields community by directing its members to appropriate resources and providing opportunities to network and participate in the sharing of information. A number of Internet sites, databases, newsletters, and reports provide opportunities for brownfields stakeholders to network with other stakeholders to identify information about cleanup and technology options. U.S. EPA's Brownfields and Land Revitalization Technology Support Center is a valuable resource for brownfields decision-makers.

14.3.5.3 Conducting a Site Visit

In addition to collecting and reviewing available records, planners need to conduct a site visit to visually and physically observe the uses and conditions of the property, including both outdoor areas and the interior of any structure or property. Current and past uses involving the use, treatment, storage, disposal, or generation of hazardous substances or petroleum products should be noted. Current or past uses of abutting properties that can be observed readily while conducting the site visit also should be noted. In addition, readily observable geologic, hydrologic, and topographic conditions should be identified, including any possibility of hazardous substances migrating on- or off-site.

Roads, water supplies, and wastewater systems should be identified, as well as any storage tanks, whether above or below ground. If any hazardous substances or petroleum products are found, their

type, quantity, and storage conditions should be noted. Any odors, pools of liquids, drums or other containers, and equipment likely to contain PCBs should be noted. Additionally, indoors, heating and cooling systems should be noted, as well as any stains, corrosion, drains, or sumps. Outdoors, any pits, ponds, lagoons, stained soil or pavement, stressed vegetation, solid waste, wastewater, and wells should be noted [10].

14.3.5.4 Conducting Interviews

In addition to reviewing available records and visiting the site, conducting interviews with the site owner and/or site manager, site occupants, and local officials is highly recommended to obtain information about the prior and/or current uses and conditions of the property, and to inquire about any useful documents that exist regarding the property. Such documents include environmental audit reports, environmental permits, registrations for storage tanks, material safety data sheets, community right-to-know plans, safety plans, government agency notices or correspondence, hazardous-waste-generator reports or notices, geotechnical studies, or any proceedings involving the property [10]. Interviews with at least one staff person from the following local government agencies are recommended: the fire department, health agency, and the agency with authority for hazardous waste disposal or other environmental matters. Interviews can be conducted in person, by telephone, or in writing.

ASTM standard 1528 [18] provides a questionnaire that may be appropriate for use in interviews for certain sites. ASTM suggests that this questionnaire be posed to the current property owner, any major occupant of the property (or at least 10% of the occupants of the property if no major occupant exists), or “any occupant likely to be using, treating, generating, storing, or disposing of hazardous substances or petroleum products on or from the property.” A user’s guide accompanies the ASTM questionnaire to assist the investigator in conducting interviews, as well as researching records and making site visits.

14.3.5.5 Developing a Report

Toward the end of the Phase I assessment, planners should develop a report that includes all of the important information obtained during record reviews, the site visit, and interviews. Documentation, such as references and important exhibits, should be included, as well as the credentials of the environmental professional that conducted the Phase I environmental site assessment. The report should include all information regarding the presence or likely presence of hazardous substances or petroleum products on the property and any conditions that indicate an existing, past, or potential release of such substances into property structures or into the ground, groundwater, or surface water of the property [10]. The report should include the environmental professional’s opinion of the impact of the presence or likely presence of any contaminants, and a findings and conclusion section that either indicates that the Phase I environmental site assessment revealed no evidence of contaminants in connection with the property, or discusses what evidence of contamination was found.

Additional sections of the report might include a recommendations section (e.g., for a Phase II site assessment, if appropriate); and sections on the presence or absence of asbestos, lead paint, lead in drinking water, radon, and wetlands. Some states or financial institutions may require information on these substances.

If the Phase I site assessment adequately informs state and local officials, planners, community representatives, and other stakeholders that no contamination exists at the site, or that contamination is so minimal that it does not pose a health or environmental risk, then those involved may decide that adequate site assessment has been accomplished and the process of redevelopment may proceed. In some cases where evidence of contamination exists, stakeholders may decide that enough information is available from the Phase I site assessment to characterize the site and determine an appropriate approach for site cleanup of the contamination. In other cases, stakeholders may decide that additional site assessment is warranted, and a Phase II site assessment would be conducted.

14.3.6 THE TRIAD APPROACH: STREAMLINING SITE INVESTIGATIONS AND CLEANUP DECISIONS

The modernization of the collection, analysis, interpretation, and management of data to support decisions about hazardous waste sites rests on U.S. EPA's three-pronged or "Triad" approach [19–21]. The introduction of new technologies in a dynamic framework allows project managers to meet clearly defined objectives. Such an approach incorporates the elements described below [4,19–21].

Systematic planning is a common-sense approach to assuring that the level of detail in project planning matches the intended use of the data being collected. Once cleanup goals have been defined, systematic planning is undertaken to chart a course for the project that is resource effective, as well as technically sound and defensible to reach these project-critical goals. A team of multidisciplinary, experienced technical staff works to translate the project's goals into realistic technical objectives. The Conceptual Site Model (CSM) is the planning tool that organizes the information that already is known about the site; the CSM helps the team identify the additional information that must be obtained. The systematic planning process ties project goals to individual activities necessary to reach these goals by identifying data gaps in the CSM. The team then uses the CSM to direct the gathering of needed information, allowing the CSM to evolve and mature as work progresses at the site.

A *dynamic working strategy* approach relies on real-time data to reach decision points. The logic for decision-making is identified and responsibilities, authority, and lines of communication are established. Dynamic work strategy implementation relies on and is driven by critical project decisions needed to reach closure. It uses a decision-tree and real-time uncertainty management practices to reach critical decision points in as few mobilizations as possible. Success of a dynamic approach depends on the presence of experienced staff in the field empowered to make decisions based on the decision logic and their capability to deal with new data and any unexpected issues, as they arise. Field staff maintains close communication with regulators or others overseeing the project during implementation of dynamic work plans.

The use of on-site analytical tools, rapid sampling platforms, and on-site interpretation and management of data makes dynamic work strategies possible. Such *real-time measurement tools* are among the key streamlined site investigation tools because they provide the data that are used for on-site decision-making. The tools are a broad category of analytical methods and equipment that can be applied at the sample collection site. They include methods that can be used outdoors with hand-held, portable equipment, as well as more rigorous methods that require the controlled environments of a mobile laboratory (transportable). During the planning process, the team identifies the type, rigor, and quantity of data needed to answer the questions raised by the CSM. Those decisions then guide the design sampling modifications and the selection of analytical tools.

The Triad approach enables project managers to minimize uncertainty while expediting site cleanup and reducing project costs. For example, U.S. EPA collaborated with the Town of Greenwich, Connecticut, to implement the Triad approach to characterize a former power plant site scheduled for redevelopment as a waterfront park. The Triad approach yielded an estimated cost savings of 50–60% when compared with a traditional approach involving two mobilizations and comprehensive analytical methods at a fixed laboratory. The City of Trenton, New Jersey, began implementing the Triad approach in 2001 as part of its program to redevelop a large number of abandoned industrial sites. Overall, the Triad approach eliminated costs associated with follow-on investigation activities while accelerating the redevelopment schedule and reducing decision uncertainty. Additional details about these and other examples are available in the U.S. EPA's Technology News and Trends newsletter [22].

14.3.7 PERFORMING A PHASE II SITE ASSESSMENT: SAMPLING THE SITE

A Phase II site assessment [23] typically involves taking soil, water, and air samples to identify the types, quantity, and extent of contamination in these various environmental media. The types of data used in a Phase II site assessment can vary from existing site data (if adequate), to limited

sampling of the site, to more extensive contaminant-specific or site-specific sampling data. Planners should use knowledge of past facility operations whenever possible to focus the site evaluation on those process areas where pollutants were stored, handled, used, or disposed. These will be the areas where potential contamination will be most readily identified. Generally, to minimize costs, a Phase II site assessment will begin with limited sampling (assuming readily available data do not exist that adequately characterize the type and extent of contamination on the site) and will proceed to more comprehensive sampling if needed (e.g., if the initial sampling could not identify the geographical limits of contamination).

This section explains the importance of setting Data Quality Objectives (DQOs) and provides brief guidance for doing so; describes screening levels to which sampling results can be compared; and provides an overview of environmental sampling and data analysis, including sampling methods and ways to increase data certainty.

14.3.7.1 Setting DQOs

U.S. EPA has developed a guidance document that describes key principles and best practices for brownfields site assessment quality assurance and quality control based on program experience [24–26].

U.S. EPA has adopted the DQOs Process [26] as a framework for making decisions. The DQO Process is a common-sense, systematic planning tool based on the scientific method. Using a systematic planning approach, such as the DQO Process, ensures that the data collected to support defensible site decision-making will be of sufficient quality and quantity, as well as be generated through the most cost-effective means possible. DQOs, themselves, are statements that unambiguously communicate the following:

1. The study objective
2. The most appropriate type of data to collect
3. The most appropriate conditions under which to collect the data
4. The amount of uncertainty that will be tolerated when making decisions.

It is important to understand the concept of uncertainty and its relationship to site decision-making [27–29]. Regulatory agencies, and the public they represent, want to be as confident as possible about the safety of reusing brownfields sites. Public acceptance of site decisions may depend on the site manager's being able to scientifically document the adequacy of site decisions. During negotiations with stakeholders, effective communication about the trade-offs between project costs and confidence in the site decision can help set the stage for a project's successful completion. When the limits on uncertainty (e.g., only a 5%, 10%, or 20% chance of a particular decision error is permitted) are clearly defined in the project, subsequent activities can be planned so that data collection efforts will be able to support those confidence goals in a resource-effective manner. On the one hand, a manager would like to reduce the chance of making a decision error as much as possible, but on the other hand, reducing the chance of making that decision error requires collecting more data, which is, in itself, a costly process.

Striking a balance between these two competing goals—more scientific certainty versus less cost—requires careful thought and planning, as well as the application of professional expertise [27–29].

The following steps are involved in systematic planning:

1. Agree on intended land reuse: All parties should agree early in the process on the intended reuse for the property because the type of use may strongly influence the choice of assessment and cleanup approaches. For example, if the area is to be a park, removal of all contamination will most likely be needed. If the land will be used for a shopping center, with most of the land covered by buildings and parking lots, it may be appropriate to reduce, rather than totally remove, contaminants to specified levels (e.g., state cleanup levels; see [Section 14.4](#) later in this chapter).

2. Clarify the objective of the site assessment: What is the overall decision(s) that must be made for the site? Parties should agree on the purpose of the assessment. Is the objective to confirm that no contamination is present? Or is the goal to identify the type, level, and distribution of contamination above the levels, which are specified, based on the intended land use. These are two fundamentally different goals that suggest different strategies. The costs associated with each approach will also vary.

As noted above, parties should also agree on the total amount of uncertainty allowable in the overall decision(s). Conducting a risk assessment involves identifying the levels of uncertainty associated with characterization and cleanup decisions. A risk assessment involves identifying potential contaminants and analyzing the pathways through which people, other species of concern, or the environment can become exposed to those contaminants. Such an assessment can help identify the risks associated with varying the levels of acceptable uncertainty in the site decision and can provide decision-makers with greater confidence about their choice of land use decisions and the objective of the site assessment. If cleanup is required, a risk assessment can also help determine how clean the site needs to be, based on expected reuse (e.g., residential or industrial), to safeguard people from exposure to contaminants.

3. Define the appropriate type(s) of data that will be needed to make an informed decision at the desired confidence level: Parties should agree on the type of data to be collected by defining a preliminary list of suspected analytes, media, and analyte-specific action levels (screening levels). Define how the data will be used to make site decisions. For example, data values for a particular analyte may or may not be averaged across the site for the purposes of reaching a decision to proceed with work. Are there maximum values, which a contaminant(s) cannot exceed? If found, will concentrations of contaminants above a certain action level (hotspots) be characterized and treated separately? These discussions should also address the types of analyses to be performed at different stages of the project. Planners and regulators can reach an agreement to focus initial characterization efforts in those areas where the preliminary information indicates that potential sources of contamination may be located. It may be appropriate to analyze for a broad class of contaminants by less expensive screening methods in the early stages of the project in order to limit the number of samples needing analysis by higher quality, more expensive methods later. Different types of data may be used at different stages of the project to support interim decisions that efficiently direct the course of the project as it moves forward.
4. Determine the most appropriate conditions under which to collect the data: Parties should agree on the timing of sampling activities, since weather conditions can influence how representative the samples are of actual conditions.
5. Identify appropriate contingency plans/actions: Certain aspects of the project may not develop as planned. Early recognition of this possibility can be a useful part of the DQO Process. For example, planners, regulators, and other stakeholders can acknowledge that screening-level sampling may lead to the discovery of other contaminants on the site than were originally anticipated. During the DQO process, stakeholders may specify appropriate contingency actions to be taken in the event that contamination is found. Identifying contingency actions early in the project can help ensure that the project will proceed even in light of new developments. The use of a dynamic workplan combined with the use of rapid turnaround field analytical methods can enable the project to move forward with a minimum of time delay and wasted effort.
6. Develop a sampling and analysis plan that can meet the goals and permissible uncertainties described in the proceeding steps: The overall uncertainty in a site decision is a function of several factors: the number of samples across the site (the density of sample coverage), the heterogeneity of analytes from sample to sample (spatial variability of contaminant concentrations), and the accuracy of the analytical method(s). Studies have

demonstrated that analytical variability tends to contribute much less to the uncertainty of site decisions than does sample variability due to matrix heterogeneity. Therefore, spending money to increase the sample density across the site will usually (for most contaminants) make a larger contribution to confidence in the site decision, and thus be more cost-effective, than will spending money to achieve the highest data quality possible, but a lower sampling density.

Examples of important consideration for developing a sampling and analysis plan include:

- Determine the sampling location placement that can provide an estimate of the matrix heterogeneity and thus address the desired certainty. Is locating hotspots of a certain size important? Can composite sampling be used to increase coverage of the site (and decrease overall uncertainty due to sample heterogeneity) while lowering analytical costs?
 - Evaluate the available pool of analytical technologies/methods (both field methods and laboratory methods, which might be implemented in either a fixed or mobile laboratory) for those methods that can address the desired action levels (the analytical methods quantification limit should be well below the action level). Account for possible or expected matrix interferences when considering appropriate methods. Can field analytical methods produce data that will meet all of the desired goals when sampling uncertainty is also taken into account? Evaluate whether a combination of screening and definitive methods may produce a more cost-effective means to generate data. Can economy of scale be used? For example, the expense of a mobile laboratory is seldom cost-effective for a single small site, but might be cost-effective if several sites can be characterized sequentially by a single mobile laboratory.
 - When the sampling procedures, sample preparation, and analytical methods have been selected, design a quality control protocol for each procedure and method that ensures that the data generated will be of known, defensible quality.
7. Through a number of iterations, refine the sampling and analysis plan to one that can most cost-effectively address the decision-making needs of the site planner.
 8. Review agreements often: As more information becomes available, some decisions that were based on earlier, limited information should be reviewed to see if they are still valid. If they are not, the parties can again use the DQO framework to revise and refine site assessment and cleanup goals and activities.

The data needed to support decision-making for brownfields sites generally are not complicated and are less extensive than those required for more heavily contaminated, higher-risk sites (e.g., Superfund sites). But data uncertainty may still be a concern at brownfields sites because knowledge of past activities at a site may be less than comprehensive, resulting in limited site characterization. Establishing DQOs can help address the issue of data uncertainty in such cases. Examples of DQOs include verifying the presence of soil contaminants and assessing whether contaminant concentrations exceed screening levels.

14.3.7.2 Screening Levels

In the initial stages of a Phase II site assessment an appropriate set of screening levels for contaminants in soil, water, and/or air should be established. Screening levels are risk-based benchmarks that represent concentrations of chemicals in environmental media that do not pose an unacceptable risk. Sample analyses of soils, water, and air at the facility can be compared with these benchmarks. If on-site contaminant levels exceed the screening levels, further investigation will be needed to determine if and to what extent cleanup is appropriate.

Some states have developed generic screening levels (e.g., for industrial and residential use). These levels may not account for site-specific factors that affect the concentration or migration of

contaminants. Alternatively, screening levels can be developed using site-specific factors. While site-specific screening levels can more effectively incorporate elements unique to the site, developing site-specific standards is a time- and resource-intensive process. Planners should contact their state environmental offices and/or U.S. EPA regional offices for assistance in using screening levels and in developing site-specific screening levels.

Risk-based screening levels are based on calculations/models that determine the likelihood that exposure of a particular organism or plant to a particular level of a contaminant would result in a certain adverse effect. Risk-based screening levels have been developed for tap water, ambient air, fish, and soil. Some states or U.S. EPA regions also use regional background levels (or ranges) of contaminants in soil and maximum contaminant levels (MCLs) in water established under the Safe Drinking Water Act [30] as screening levels for some chemicals. In addition, some states and/or U.S. EPA regional offices have developed equations for converting soil screening levels to comparative levels for the analysis of air and groundwater.

When a contaminant concentration exceeds a screening level, further site assessment (such as sampling the site at strategic locations and/or performing more detailed analysis) is needed to determine that: (a) the concentration of the contaminant is relatively low and/or the extent of contamination is small and does not warrant cleanup for that particular chemical, or (b) the concentration or extent of contamination is high, and that site cleanup is needed.

Using state cleanup standards for an initial brownfields assessment may be beneficial if no industrial screening levels are available or if the site may be used for residential purposes. U.S. EPA's soil screening guidance is a tool developed by U.S. EPA to help standardize and accelerate the evaluation and cleanup of contaminated soils at sites on the NPL where future residential land use is anticipated. This guidance may be useful at corrective action or VCP sites where site conditions are similar. However, use of this guidance for sites where residential land use assumptions do not apply could result in overly conservative screening levels.

14.3.7.3 Environmental Sampling and Data Analysis

Environmental sampling and data analysis are integral parts of a Phase II site assessment process. Many different technologies are available to perform these activities, as discussed below.

14.3.7.4 Levels of Sampling and Analysis

There are two levels of sampling and analysis: screening and contaminant specific. Planners are likely to use both at different stages of the site assessment.

Screening: Screening sampling and analysis use relatively low-cost technologies to take a limited number of samples at the most likely points of contamination and analyze them for a limited number of parameters. Screening analyses often test only for broad classes of contaminants, such as total petroleum hydrocarbons (TPHs), rather than for specific contaminants, such as benzene or toluene. Screening is used to narrow the range of areas of potential contamination and reduce the number of samples requiring further, more costly, analysis. Screening is generally performed on-site, with a small percentage of samples (e.g., generally 10%) submitted to a state-approved laboratory for a full organic and inorganic screening analysis to validate or clarify the results obtained.

Some geophysical methods are used in site assessments because they are noninvasive (i.e., do not disturb environmental media as sampling does). Geophysical methods are commonly used to detect underground objects that might exist at a site, such as USTs, dry wells, and drums. The two most common and cost-effective technologies used in geophysical surveys are ground-penetrating radar and electromagnetics [31].

Contaminant specific: For a more in-depth understanding of contamination at a site (e.g., when screening data are not detailed enough), it may be necessary to analyze samples for specific contaminants. With contaminant-specific sampling and analysis, the number of parameters analyzed is much greater than that for screening-level sampling, and analysis includes more accurate, higher-cost field, and laboratory methods. Such analyses may take several weeks.

Computerization, microfabrication, and biotechnology have permitted the recent development of an analytical equipment that can be generated in the field, on-site in a mobile laboratory and off-site in a laboratory. The same kind of equipment might be used in two or more locations.

14.3.8 INCREASING THE CERTAINTY OF SAMPLING RESULTS

One approach to reducing the level of uncertainty associated with site data is to implement a statistical sampling plan. Statistical sampling plans use statistical principles to determine the number of samples needed to accurately represent the contamination present. With the statistical sampling method, samples are usually analyzed with highly accurate laboratory or field technologies, which increase costs and take additional time. Using this approach, planners can negotiate with regulators and determine in advance specific measures of allowable uncertainty (e.g., an 80% level of confidence with a 25% allowable error).

Another approach to increasing the certainty of sampling results is to use lower-cost technologies with higher detection limits to collect a greater number of samples. This approach would provide a more comprehensive picture of contamination at the site, but with less detail regarding the specific contamination. Such an approach would not be recommended to identify the extent of contamination by a specific contaminant, such as benzene, but may be an excellent approach for defining the extent of contamination by total organic compounds with a strong degree of certainty. Planners will find that there is a trade-off between scope and detail. Performing a limited number of detailed analyses provides good detail but less certainty about overall contamination, while performing a larger number of general analyses provides less detail but improves the understanding and certainty of the scope of contamination.

14.3.9 SITE ASSESSMENT TECHNOLOGIES

This section discusses the differences between using field and laboratory technologies and provides an overview of applicable site assessment technologies [32,33]. In recent years, several innovative technologies that have been field tested and applied to hazardous waste problems have emerged. In many cases, innovative technologies may cost less than conventional techniques and can successfully provide the needed data. Operating conditions may affect the cost and effectiveness of individual technologies.

14.3.9.1 Field versus Laboratory Analysis

The principal advantages of performing field sampling and field analysis are that results are immediately available and more samples can be taken during the same sampling event; also, sampling locations can be adjusted immediately to clarify the first round of sampling results if warranted. This approach may reduce costs associated with conducting additional sampling events after receipt of laboratory analysis. Field assessment methods have improved significantly over recent years; however, while many field technologies may be comparable to laboratory technologies, some field technologies may not detect contamination at levels as low as laboratory methods, and may not be contaminant specific. To validate the field results or to gain more information on specific contaminants, a small percentage of the samples can be sent for laboratory analysis. The choice of sampling and analytical procedures should be based on DQOs established earlier in the process, which determine the quality (e.g., precision, level of detection) of the data needed to adequately evaluate site conditions and identify appropriate cleanup technologies.

14.3.9.2 Sample Collection and Analysis Technologies

Tables 14.3 and 14.4 list sample collection technologies for oil in subsurface and groundwater, which may be appropriate for metal finishing brownfields sites. Technology selection depends on the medium being sampled and the type of analysis required, based on DQOs. Soil samples are

TABLE 14.3
Soil and Subsurface Sampling Tools

Technique/Instrumentation	Media		Relative Cost per Sample	Sample Quality
	Soil	Groundwater		
Drilling Methods				
Cable	X	X	Mid-range expensive	Soil properties will most likely be altered
Casing advancement	X	X	Most expensive	Soil properties will likely be altered
Direct air rotary with rotary hammer	X	X	Mid-range expensive	Soil properties will most likely be altered
Direct mud rotary	X	X	Mid-range expensive	Soil properties may be altered
Directional drilling	X	X	Most expensive	Soil properties may be altered
Hollow-stem auger	X	X	Mid-range expensive	Soil properties may be altered
Jetting methods	X	X	Least expensive	Soil properties may be altered
Rotary diamond drilling	X	X	Most expensive	Soil properties may be altered
Rotating core	X		Mid-range expensive	Soil properties may be altered
Solid flight and bucket augers	X	X	Mid-range expensive	Soil properties will likely be altered
Sonic drilling	X	X	Most expensive	Soil properties will most likely not be altered
Split and solid barrel	X		Least expensive	Soil properties may be altered
Thin-wall open tube	X		Mid-range expensive	Soil properties will most likely not be altered
Thin-wall piston/specialized thin wall	X		Mid-range expensive	Soil properties will most likely not be altered
Direct Push Methods				
Cone penetrometer	X	X	Mid-range expensive	Soil properties may be altered
Driven wells		X	Mid-range expensive	Soil properties may be altered
Hand-Held Methods				
Augers	X	X	Least expensive	Soil properties may be altered
Rotating core	X		Mid-range expensive	Soil properties may be altered
Scoop, spoons, and shovels	X		Least expensive	Soil properties may be altered
Split and solid barrel	X		Least expensive	Soil properties may be altered
Thin-wall open tube	X		Mid-range expensive	Soil properties will most likely not be altered
Thin-wall piston/specialized thin wall	X		Mid-range expensive	Soil properties will most likely not be altered
Tubes	X		Least expensive	Soil properties will most likely not be altered

Source: U.S. EPA. *Technical Approaches to Characterizing and Cleaning Up Metal Finishing Sites under the Brownfields Initiative*. EPA/625/R-98/006, U.S. Environmental Protection Agency, Cincinnati, OH, March 1999.

generally collected using spoons, scoops, and shovels. The selection of a subsurface sample collection technology depends on the subsurface conditions (e.g., consolidated materials, bedrock), the required sampling depth and level of analysis, and the extent of sampling anticipated. For example, if subsequent sampling efforts are likely, then installing semipermanent well casings with a well drilling rig may be appropriate. If limited sampling is expected, direct push methods, such as cone

TABLE 14.4
Groundwater Sampling Tools

Technique/Instrumentation	Contaminants	Relative Cost per Sample	Sample Quality
Portable Grab Samplers			
Bailers	Metals, VOCs	Least expensive	Liquid properties may be altered
Pneumatic depth-specific samplers	Metals, VOCs	Mid-range expensive	Liquid properties will most likely not be altered
Portable <i>In Situ</i> Groundwater Samplers/Sensors			
Cone penetrometer samplers	Metals, VOCs	Least expensive	Liquid properties will most likely not be altered
Direct drive samplers	Metals, VOCs	Least expensive	Liquid properties will most likely not be altered
Hydropunch	Metals, VOCs	Mid-range expensive	Liquid properties will most likely not be altered
Fixed <i>Situ</i> Samplers			
Multilevel capsule samplers	Metals, VOCs	Mid-range expensive	Liquid properties will most likely not be altered
Multiple-port casings	Metals, VOCs	Least expensive	Liquid properties will most likely not be altered
Passive multilayer samplers	VOCs	Least expensive	Liquid properties will most likely not be altered

Source: U.S. EPA. *Technical Approaches to Characterizing and Cleaning Up Metal Finishing Sites under the Brownfields Initiative*. EPA/625/R-98/006, U.S. Environmental Protection Agency, Cincinnati, OH, March 1999.

Note: VOCs, Volatile organic compounds.

penetrometers, may be more cost-effective. The types of contaminants will also play a key role in the selection of sampling methods, devices, containers, and preservation techniques.

Table 14.5 lists analytical technologies that may be appropriate for assessing metal finishing sites, the types of contamination they can measure, applicable environmental media, and the relative cost of each. The final two columns of the table contain the applicability (e.g., field and/or laboratory) of analytical methods and the technology's ability to generate quantitative versus qualitative results. Less expensive technologies that have rapid turnaround times and produce only qualitative results generally should be sufficient for many brownfields sites.

14.3.10 ADDITIONAL CONSIDERATIONS FOR ASSESSING METAL FINISHING SITES

When assessing a metal finishing brownfields site, planners should focus on the most likely areas of contamination. Although the specific locations vary from site to site, this section provides some general guidelines.

14.3.10.1 Where to Sample

Most metal finishing facilities perform all operations indoors. Consequently, most site assessment activities should focus on contamination inside and underneath the facility. Outdoor assessment activities should evaluate points where drain pipes may have carried contaminated wastewater or spilled materials.

The typical metal finishing facility is comprised of one or more large, warehouse-type buildings that contain the bath tanks, chemical storage areas, and wastewater treatment system. The floors are

TABLE 14.5
Sample Analysis Technologies

Technique/ Instrumentation	Analytes	Soil	Media Groundwater	Gas	Relative Cost per Analysis	Application	Produces Quantitative Data
Laser-induced breakdown spectrometry	Metals	X			Least expensive	Usually used in field	Additional effort required
Titrimetry kits	Metals	X	X		Least expensive	Usually used in laboratory	Additional effort required
Particle-induced x-ray emissions	Metals	X	X		Mid-range expensive	Usually used in laboratory	Additional effort required
Atomic adsorption spectrometry	Metals	X*	X	X	Most expensive	Usually used in laboratory	Yes
Inductively coupled plasma-atomic emission spectroscopy	Metals	X	X	X	Most expensive	Usually used in laboratory	Yes
Field bioassessment	Metals	X	X		Most expensive	Usually used in field	No
X-ray fluorescence	Metals	X	X	X	Least expensive	Laboratory and field	Yes (limited)
Chemical calorimetric kits	VOCs	X	X		Least expensive	Can be used in field, usually used in laboratory	Additional effort required
Flame ionization detector (hand- held)	VOCs	X	X	X	Least expensive	Immediate, can be used in field	No
Explosimeter	VOCs	X	X*	X	Least expensive	Immediate, can be used in field	No
Photo ionization detector (hand- held)	VOCs	X	X	X	Least expensive	Immediate, can be used in field	No
Catalytic surface oxidation	VOCs	X*	X	X	Least expensive	Usually used in laboratory	No
Near IR reflectance/ trans spectroscopy	VOCs	X			Mid-range expensive	Usually used in laboratory	Additional effort required
Ion mobility spectrometer	VOCs	X*	X	X	Mid-range expensive	Usually used in laboratory	Yes
Raman spectroscopy/ SERS	VOCs	X	X	X*	Mid-range expensive	Usually used in laboratory	Additional effort required
Infrared spectroscopy	VOCs	X	X	X	Mid-range expensive	Usually used in laboratory	Additional effort required
Scattering/ absorption lidar	VOCs	X*	X	X	Mid-range expensive	Usually used in laboratory	Additional effort required

continued

TABLE 14.5 (continued)

Technique/ Instrumentation	Analytes	Soil	Media Groundwater	Gas	Relative Cost per Analysis	Application	Produces Quantitative Data
FTIR spectroscopy	VOCs	X	X	X	Mid-range expensive	Laboratory and field	Additional effort required
Synchronous luminescence/ fluorescence	VOCs	X	X		Mid-range expensive	Usually used in laboratory, can be used in field	Additional effort required
Gas chroma- tography (GC) (can be used with numerous detectors)	VOCs	X*	X	X	Mid-range expensive	Usually used in laboratory, can be used in field	Yes
UV-visible spectrophotometry	VOCs	X	X	X	Mid-range expensive	Usually used in laboratory	Additional effort required
UV fluorescence	VOCs	X	X	X	Mid-range expensive	Usually used in laboratory	Additional effort required
Ion trap	VOCs	X	X*	X	Most expensive	Laboratory and field	Yes
Other chemical reaction-based test papers	VOCs, metals	X	X		Least expensive	Usually used in field	Yes
Immunoassay and calorimetric kits	VOCs, metals	X	X		Least expensive	Usually used in laboratory, can be used in field	Additional effort required

Source: U.S. EPA. *Technical Approaches to Characterizing and Cleaning Up Metal Finishing Sites under the Brownfields Initiative*. EPA/625/R-98/006, U.S. Environmental Protection Agency, Cincinnati, OH, March 1999.

Notes: X* indicates that there must be extraction of the sample to gas or liquid phase; VOCs, volatile organic compounds.

likely to be a continuous concrete slab containing several drains leading to a central storm drain or sewer access. In older facilities, the feed lines from bath to wastewater tanks are underneath the floor slab. In newer facilities, the bath tanks and/or the wastewater tanks will likely be partially submerged in the floor slab and positioned directly on the ground.

A visual inspection of the site should identify the most likely points of potential contaminant releases. These include the areas surrounding:

1. Floor drains in chemical storage and process bath areas
2. Sludges left in process bath and wastewater treatment tanks
3. Pipes underneath the floor slab
4. Tanks set through the floor slab
5. Cracks in the floor or stains in low spots in the floor.

Solvents can be highly mobile on release, and can seep into and through the concrete flooring, which is porous. The inspection of the facility floor should look not only for cracks through

which solvents could migrate, but also for stained areas where spilled solvents may have pooled. Wipe samples should be taken along the walls of the facility, as solvent vapors may have penetrated wall materials.

Since metal finishing operations are typically conducted inside the facility, outside points of potential release are likely to be limited to:

1. Points of discharge from effluent pipes
2. Waterways, canals, and ditches at points of pipe discharge
3. Areas where process bath materials may have been dumped.

While discharge points may be visually obvious, areas of dumping may be less apparent. Often these areas are marked by stained soils and a lack of vegetation. Low-lying areas should also be investigated, as they make natural dumping areas and contaminants may drain to these points.

14.3.10.2 How Many Samples to Collect

Samples should be taken in and around the areas of potential release mentioned above [34]. Planners should expect that two to three samples will be required in each area, depending on DQOs. A cost-effective approach is to perform screening analyses using field methods on all samples and then to submit one sample to a laboratory for analysis by an accepted U.S. EPA method. Although the screening analyses can be conducted for broad contaminant groups, such as total organics, a contaminant-specific analysis should be conducted as a full screen for organic and inorganic contaminants and to validate the screening analyses. Contaminant-specific analyses may be conducted either in the field using appropriate technologies and protocols or in a laboratory.

14.3.10.3 What Types of Analysis to Perform

The selection of analytical procedures will be based on the DQOs established. Generally, the following analyses may be appropriate at metal finishing sites:

1. Residuals taken from drain sumps in storage areas should be screened for total organics and acids. Screening analyses for these contaminants can be performed inexpensively using a photo ionization detector (PID) or flame ionization detector (FID) for total organics.
2. Residuals taken from drains in the process and wastewater treatment areas should be screened for a similar range of organic contaminants, but additional analyses should be performed to screen for the presence of inorganic contaminants, such as the metals used in the metal finishing process. Immunoassays are an inexpensive field technology that can be used to perform the screening analyses for organic contaminants and mercury. X-ray fluorescence (XRF) is another innovative technology that can be used to perform either field or laboratory analyses.
3. Soil gas should be collected at points underneath the floor slab, particularly near any tanks that are set through the floor slab, to detect the presence of solvents and other organic contaminants. These samples can be analyzed with the PID/FID technology described above. Corings of the floor slab may need to be taken and sent to a laboratory to determine whether contaminants have penetrated floor slabs.
4. Wipe samples taken from walls should be analyzed for organic compounds. These analyses can be performed using the same technologies that are used to analyze residual samples.
5. Soils and sediments at points of pipe discharge should be screened for both organic and inorganic contaminants using the PID/FID technology. XRF can be used for field or laboratory analyses.
6. Water samples collected in swales, canals, and ditches should be screened for organics. Inorganic contamination can sometimes be detected in water samples, but conditions do not always allow it.

In addition, as discussed earlier, many older structures contain lead paint and asbestos insulation and tiling. Numerous kits are readily available to test for lead paint. Experienced professionals may be able to visually identify asbestos insulation, but specialized equipment may be needed to confirm the presence of asbestos in other areas. Core or wipe samples can be analyzed for asbestos using polarized light microscopy (PLM). Local and state laws regarding lead and asbestos should be consulted to determine how they may affect the selection of DQOs, sampling, and analysis.

14.3.11 GENERAL SAMPLING COSTS

Site assessment costs vary widely, depending on the nature and extent of the contamination and the size of the sampling area. The sample collection costs discussed below are based on an assumed labor rate of USD 40/h plus USD 12 per sample for shipping and handling. All costs have been updated to 2007 USD using USACE Yearly Average Cost Index for Utilities [35].

14.3.11.1 Soil Collection Costs

Surface soil samples can be collected with tools as simple as a stainless-steel spoon, shovel, or hand auger. Samples can be collected using hand tools in soft soil for as low as USD 12 per sample (assuming that a field technician can collect 10 samples/h). When soils are hard, or deeper samples are required, a hammer-driven split spoon sampler or a direct push rig is needed. Using a drill rig equipped with a split spoon sampler or a direct push rig typically costs more than \$700/d for rig operation [36], with the cost per sample exceeding USD 35 (assuming that a field technician can collect 2 samples/h). Labor costs generally increase when heavy machinery is needed.

14.3.11.2 Groundwater Sampling Costs

Groundwater samples can be extracted through conventional drilling of a permanent monitoring well or using the direct push methods listed in [Table 14.3](#). The conventional, hollow stem auger-drilled monitoring well is more widely accepted but generally takes more time than direct push methods. Typical quality assurance protocols for the conventional monitoring well require the well to be drilled, developed, and allowed to achieve equilibrium for 24–48h. After the development period, a groundwater sample is extracted. With the direct push sampling method, a probe is either hydraulically pressed or vibrated into the ground, and groundwater percolates into a sampling container attached to the probe. The direct push method costs are contingent upon the hardness of the subsurface, depth to the water table, and permeability of the aquifer. Costs for both conventional and direct push techniques are generally more than USD 47 per sample (assuming that a field technician can collect 1 sample/h); well installation costs must be added to that number.

14.3.11.3 Surface Water and Sediment Sampling Costs

Surface water and sediment sampling costs depend on the location and depth of the required samples. Obtaining surface water and sediment samples can cost as little as USD 35 per sample (assuming that a field technician can collect 2 samples/h). Sampling sediment in deep water or sampling a deep level of surface water, however, requires the use of larger equipment, which drives up the cost. Also, if surface water presents a hazard during sampling and protective measures are required, costs will increase greatly.

14.3.11.4 Sample Analysis Costs

Costs for analyzing samples in any medium can range from as little as USD 32 per sample for a relatively simple test (e.g., an immunoassay test for metals) to greater than USD 470 per sample for a more extensive analysis (e.g., for semivolatiles) and up to USD 1400 per sample for dioxins [32]. Major

factors that affect the cost of sample analysis include the type of analytical technology used, the level of expertise needed to interpret the results, and the number of samples to be analyzed. Planners should make sure that laboratories that have been certified by state programs are used.

For information on costs for brownfields cleanup, the reader is referred to U.S. EPA document [37], guide [38], and remediation cost compendium [39].

14.4 SITE CLEANUP

The purpose of this section is to guide planners in the selection of appropriate cleanup technologies. The principal factors that will influence the selection of a cleanup technology include [2]:

1. Types of contamination present;
2. Cleanup and reuse goals;
3. Length of time required to reach cleanup goals;
4. Post-treatment care needed;
5. Budget.

The selection of appropriate cleanup technologies often involves a trade-off between time and cost. The U.S. EPA document on cost-estimating tools and resources [37] provides information on cost factors and developing cost estimates. In general, the more intensive the cleanup approach, the more quickly the contamination will be mitigated and the more costly the effort. In the case of brownfields cleanup, this can be a major point of concern, considering the planner's desire to return the facility to the point of reuse as quickly as possible. Thus, the planner may wish to explore a number of options and weigh carefully the costs and benefits of each. One effective method of comparison is the cleanup plan, as discussed below. Planners should involve stakeholders in the community in the development of the cleanup plan.

The intended future use of a brownfields site will drive the level of cleanup needed to make the site safe for redevelopment and reuse. Brownfields sites are by definition not Superfund NPL sites; that is, brownfields sites usually have lower levels of contamination present and therefore generally require less extensive cleanup efforts than Superfund NPL sites. Nevertheless, all potential pathways of exposure, based on the intended reuse of the site, must be addressed in the site assessment and cleanup; if no pathways of exposure exist, less cleanup (or possibly none) may be required.

Some regional U.S. EPA and state offices have developed cleanup standards for different chemicals, which may serve as guidelines or legal requirements for cleanups. It is important to understand that screening levels are different from cleanup levels. Screening levels indicate whether further site investigation is warranted for a particular contaminant. Cleanup levels indicate whether cleanup action is needed and how extensive it needs to be. Planners should check with their state environmental office for guidance and/or requirements for cleanup standards.

This section contains information on developing a cleanup plan, various alternatives for addressing contamination at the site (i.e., institutional controls and containment and cleanup technologies), using different technologies for cleaning up metal finishing sites, and postconstruction issues that planners need to consider when considering alternatives.

14.4.1 DEVELOPING A CLEANUP

If the results of the site evaluation indicate the presence of contamination above acceptable levels, planners will need to have a cleanup plan developed by a professional environmental engineer that describes the approach that will be used to contain and possibly cleanup the contamination present at the site. In developing this plan, planners and their engineers should consider a range of possible options, with the intent of identifying the most cost-effective approaches for

cleaning up the site, given time and cost concerns. The cleanup plan can include the following elements [2,4,40,41]:

1. A clear delineation of environmental concerns at the site. Areas should be discussed separately if the cleanup approach for an area is different from that for other areas of the site. Clear documentation of existing conditions at the site and a summarized assessment of the nature and scope of contamination should be included.
2. A recommended cleanup approach for each environmental concern that takes into account expected land reuse plans and the adequacy of the technology selected.
3. A cost estimate that reflects both expected capital and operating/maintenance costs.
4. Postconstruction maintenance requirements for the recommended approach.
5. A discussion of the assumptions made to support the recommended cleanup approach, as well as the limitations of the approach.

Planners can use the framework developed during the initial site evaluation and the controls and technologies described below to compare the effectiveness of the least costly approaches for meeting the required cleanup goals established in the DQOs. These goals should be established at levels that are consistent with the expected reuse plans. A final cleanup plan may include a combination of actions, such as institutional controls, containment technologies, and cleanup technologies, as discussed below.

14.4.1.1 Institutional Controls

Institutional controls may play an important role in returning a metal finishing brownfields site to a marketable condition. Institutional controls are mechanisms that control the current and future use of, and access to, a site. They are established, in the case of brownfields, to protect people from possible contamination. Institutional controls can range from a security fence prohibiting access to a certain portion of the site to deed restrictions imposed on the future use of the site. If the overall cleanup approach does not include the complete cleanup of the facility (i.e., the complete removal or destruction of on-site contamination), a deed restriction will likely be required that clearly states that hazardous waste is being left in place within the site boundaries. Many state brownfields programs include institutional controls.

14.4.1.2 Containment Technologies

Containment technologies, in many instances, will be the likely cleanup approach for landfilled waste and wastewater lagoons (after contaminated wastewaters have been removed) at metal finishing facilities. The purpose of containment is to reduce the potential for off-site migration of contaminants and, possible subsequent exposure. Containment technologies include engineered barriers such as caps [42] for contaminated soils, slurry walls [43], and hydraulic containment. Often, soils contaminated with metals can be solidified [44,45] by mixing them with cement-like materials, and the resulting stabilized material can be stored on-site in a landfill. Like institutional controls, containment technologies do not remove or destroy contamination, but mitigate potential risk by limiting access to it.

If contamination is found underneath the floor slab at metal finishing facilities, leaving the contaminated materials in place and repairing any damage to the floor slab may be justified. The likelihood that such an approach will be acceptable to regulators will depend on whether potential risk can be mitigated and managed effectively over the long term. In determining whether containment is feasible, planners should consider [2,4]:

1. *Depth to groundwater:* Planners should be prepared to prove to regulators that groundwater levels will not rise, due to seasonal conditions, and come into contact with contaminated soils.

2. *Soil types*: If contaminants are left in place, the native soils should not be highly porous, as are sandy or gravelly soils, which enable contaminants to migrate easily. Clay and fine silty soils provide a much better barrier.
3. *Surface water control*: Planners should be prepared to prove to regulators that rainwater and snowmelt cannot infiltrate under the floor slab and flush the contaminants downward.
4. *Volatilization of organic contaminants*: Regulators are likely to require that air monitors be placed inside the building to monitor the level of organics that may be escaping upward through the floor and drains.

14.4.1.3 Types of Cleanup Technologies

Cleanup may be required to remove or destroy on-site contamination if regulators are unwilling to accept the level of contamination present or if the types of contamination are not conducive to the use of institutional controls or containment technologies. Cleanup technologies fall broadly into two categories—*ex situ* and *in situ*—as described below.

1. *Ex situ*: An *ex situ* technology treats contaminated materials after they have been removed and transported to another location. After treatment, if the remaining materials, or residuals, meet cleanup goals, they can be returned to the site. If the residuals do not yet meet cleanup goals, they can be subjected to further treatment, contained on-site, or moved to another location for storage or further treatment. A cost-effective approach to cleaning up a metal finishing brownfields site may be the partial treatment of contaminated soils or groundwater, followed by containment, storage, or further treatment off-site [2]. For example, it is common practice for operating metal finishing facilities to treat wastewaters to an intermediate level and then send the treated water to the local POTW.
2. *In situ*: The use of *in situ* technologies has increased dramatically in recent years. *In situ* technologies treat contamination in place and are often innovative technologies. Examples of *in situ* technologies include bioremediation [46], soil flushing [47], oxygen releasing compounds [48], air sparging [49], and treatment walls [50]. In some cases, *in situ* technologies are feasible, cost-effective choices for the types of contamination that are likely at metal finishing sites. Planners, however, do need to be aware that cleanup with *in situ* technologies is likely to take longer than with *ex situ* technologies.

Maintenance requirements associated with *in situ* technologies depend on the technology used and vary widely in both effort and cost. For example, containment technologies such as caps and liners will require regular maintenance, such as maintaining the vegetative cover and performing periodic inspections to ensure the long-term integrity of the cover system. Groundwater treatment systems will require varying levels of post-cleanup care. If an *ex situ* system is in use at the site, it will require regular operations support and periodic maintenance to ensure that the system is operating as designed.

14.4.2 KEYS TO TECHNOLOGY SELECTION AND ACCEPTANCE

Innovative technologies and technology approaches offer many advantages in the cleanup of brownfields sites [51–56]. Stakeholders in such sites, however, must first accept the technology. Brownfields decision-makers should consider the following elements to increase the likelihood that the technology will be accepted, thereby facilitating the cleanup of the site [4]:

1. Focus on the decisions that support site goals: The Triad approach systematic planning is an important element of all cleanup activities. Clear and specific planning to meet explicit decision objectives is essential in managing the process of cleaning up contaminated sites: site assessment, site investigation, site monitoring, and remedy selection. With good planning,

brownfields decision-makers can establish the cleanup goals for the site, identify the decisions necessary to achieve those goals, and develop and implement a strategy for addressing the decision needs. Technology decisions are made in the context of the requirements for such decisions. All cleanup activities are driven by the project goals. An explicit statement of the decisions to be made and the way in which the planned approach supports the decisions should be included in the work plan.

2. **Build consensus:** Investing time, before the site work begins, in developing decisions that are acceptable to all decision-makers will foster more efficient site activities and make successful cleanup more likely. Conversely, allowing work to begin at a site before a common understanding and acceptance of the decisions have been established increases the likelihood that the cleanup process will be inefficient, resulting in delays and inefficient use of time and money. Further, decision-makers must understand that there is uncertainty in all scientific and technical decisions. Clearly defining and accepting uncertainty thresholds before making decisions about the site remedy will build consensus. Decisions also should be made in the context of applicable regulatory requirements, political considerations, budget available for the project, and time constraints.
3. **Understand the technology:** A thorough knowledge of a technology's capabilities and limitations is necessary to secure its acceptance. All technologies are subject to limitations in performance. Planning for the strengths and weaknesses of a technology maximizes understanding of its benefits and its acceptance. "Technology approvers," typically regulators, community groups, and financial service providers are likely to be more receptive of a new approach if the proposer provides a clear explanation of the rationale for its use and demonstrates confidence in its applicability to specific site conditions and needs. This latter point underscores the importance of carefully selecting an experienced, multidimensional team of professionals who have the expertise necessary to plan, present, and implement the chosen approach.
4. **Allow flexibility:** Streamlining site activities, whether site assessment, site investigation, removal, treatment, or monitoring, requires a flexible approach. Site-specific conditions, including various physical conditions, contamination issues, stakeholder needs, uses of the site, and supporting decisions, require that all decision-makers understand the need for flexibility. Although presumptive remedies, standard methods, applications at other sites, and program guidance can serve as the basis for designing a site-specific cleanup plan and can help decision-makers avoid "starting from scratch" at each site, decision-makers should be wary of depending too heavily on "boilerplate language" and prescriptive methodologies, as well as standard operating procedures and "accepted" methods. While such tools provide excellent starting points, they lack the flexibility to meet site-specific goals. To ensure an efficient and effective cleanup, the actual technology approach, whether established or innovative, must focus on decisions specific to the site.
5. **Narrow the list of potential technologies that are most appropriate for addressing the contamination identified at the site and that are compatible with the specific conditions of the site and the proposed reuse of the property:**
 - Network with other brownfields stakeholders and environmental professionals to learn about their experiences and to tap their expertise.
 - Determine whether sufficient data are available to support identification and evaluation of cleanup alternatives.
 - Evaluate the options against a number of factors, including toxicity levels, exposure pathways, associated risks, future land use, and economic considerations.
 - Analyze the applicability of a particular technology to the contamination identified at a site.
 - Determine the effects of various technology alternatives on redevelopment objectives.

6. Continue to work with appropriate regulatory agencies to ensure that regulatory requirements are addressed properly:
 - Consult with the appropriate federal, state, local, and tribal regulatory agencies to include them in the decision-making process as early as possible
 - Contact the U.S. EPA regional brownfields coordinator to identify and determine the availability of U.S. EPA support programs.
7. Integrate cleanup alternatives with reuse alternatives to identify potential constraints on reuse and time schedules and to assess cost and risk factors.
8. To provide a measure of certainty and stability to the project, investigate environmental insurance policies, such as protection against cost overruns, undiscovered contamination, and third-party litigation, and integrate their cost into the project financial package.
9. Select an acceptable remedy that not only achieves cleanup goals and addresses the risk of contamination, but also best meets the objectives for redevelopment and reuse of the property and is compatible with the needs of the community.
10. Communicate information about the proposed cleanup option to brownfields stakeholders, including the affected community.

14.4.3 SUMMARY OF TECHNOLOGIES FOR TREATING METALS/METALLOIDS AT BROWNFIELD SITES

Chemical treatment: Chemical treatment, also known as chemical reduction/oxidation (redox) [48], typically involves redox reactions that chemically convert hazardous contaminants into compounds that are nonhazardous, less toxic, 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 reactant is reduced (gains electrons). The oxidizing agents used for the treatment of hazardous contaminants in soil include ozone, hydrogen peroxide, hypochlorites, potassium permanganate, Fenton's reagent (hydrogen peroxide and iron), chlorine, and chlorine dioxide. This method may be applied *in situ* or *ex situ* to soils, sludges, sediments, and other solids and may also be applied to groundwater *in situ* or *ex situ* chemical treatment using pump and treat technology. Chemical treatment may also include use of ultraviolet (UV) light in a process known as UV oxidation.

Electrokinetics: Electrokinetics is based on the theory that a low-density current will mobilize contaminants in the form of charged species [57]. A current passed between electrodes is intended to cause aqueous media, ions, and particulates to move through soil, waste, and water. Contaminants arriving at the electrodes can be removed by means of electroplating or electrodeposition, precipitation or coprecipitation, adsorption, complexing with ion exchange resins, or pumping of water (or other fluid) near the electrodes.

Flushing: For flushing, a solution of water, surfactants, or cosolvents is applied to soil or injected into the subsurface to treat contaminated soil or groundwater [47]. When soil is being treated, injection is often designed to raise the water table into the contaminated soil zone. Injected water and treatment agents are recovered together with flushed contaminants.

Permeable reactive barriers: Permeable reactive barriers, also known as passive treatment walls, are installed across the flow path of a contaminated groundwater plume, allowing the water portion of the plume to flow through the wall [50]. These barriers allow passage of water while prohibiting movement of contaminants by means of treatment agents within the wall such as zero-valent metals (usually zero-valent iron), chelators, sorbents, compost, and microbes. The contaminants are either degraded or retained in a concentrated form by the barrier material, which may need to be replaced periodically.

Physical separation: Physical separation processes use physical properties to separate contaminated and uncontaminated media or to separate different types of media [58–60]. For example, different-sized sieves and screens can be used to separate contaminated soil from

relatively uncontaminated debris. Another application of physical separation is dewatering of sediments or sludge.

Phytoremediation: Phytoremediation is a process in which plants are used to remove, transfer, stabilize, or destroy contaminants in soil, sediment, or groundwater. The mechanisms of phytoremediation include enhanced rhizosphere biodegradation (which takes place in soil or groundwater immediately around plant roots), phytoextraction (also known as phytoaccumulation, the uptake of contaminants by plant roots and the translocation and 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 roots and soil). The term phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants (including the rhizosphere) and that aid in the cleanup of contaminated substances [61–64]. Phytoremediation may be applied *in situ* or *ex situ* to soils, sludges, sediments, other solids, or groundwater.

Environment Canada [64] studied the effectiveness of phytoremediation in the Quebec's climate using herbaceous plants (Indian mustard and fescue) and shrubs (willow) to absorb heavy metals (lead, copper, and zinc). They reported that metal concentration levels in the leaves reached 1500–2300 mg/kg that resulted in total extraction of between 2 and 13 kg of metal per ha, per growth period.

Pump and treat: Pump and treat involves extraction of groundwater from an aquifer and treatment of the water above the ground. The extraction step is usually conducted by pumping groundwater from a well or trench [65]. The treatment step can involve a variety of technologies such as adsorption, air stripping, bioremediation, chemical treatment, filtration, ion exchange, metal precipitation, and membrane filtration [58–60].

Soil washing: For soil washing, contaminants sorbed onto fine soil particles are separated from bulk soil in a water-based system based on particle size [66]. The wash water may be augmented with a basic leaching agent, surfactant, or chelating agent or by adjustment of pH to help remove contaminants. 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 by means of gravity settling [58].

Solidification/stabilization: Solidification/stabilization (S/S) reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means [44,45]. The S/S process physically binds or encloses contaminants within a stabilized mass. S/S can be performed both *ex situ* and *in situ*. *Ex situ* S/S requires excavation of the material to be treated, and the treated material must be disposed of. *In situ* S/S involves use of auger or caisson systems and injector head systems to add binders to contaminated soil or waste without excavation, and the treated material is left in place [67,68].

Solvent extraction: Solvent extraction involves use of an organic solvent as an extractant to separate 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 [69].

Vitrification: Vitrification involves use of an electric current to melt contaminated soil at elevated temperatures (1600–2000°C or 2900–3650°F). Upon cooling, the vitrification product is a chemically stable, leach-resistant, glass and crystalline material similar to obsidian or basalt rock. The high-temperature component of the process destroys or removes organic materials. Radionuclides and heavy metals are retained within the vitrified product. Vitrification may be conducted *in situ* or *ex situ* [70].

14.4.4 CLEANUP TECHNOLOGIES OPTIONS FOR METAL FINISHING SITES

Table 14.6 presents the technologies that may be appropriate for use at metal finishing sites. In addition to more conventional technologies, a number of innovative technology options are listed. Many possible cleanup approaches use institutional controls and one or a combination of the technologies described in Table 14.6. Whatever cleanup approach is ultimately chosen, planners should explore a number of cost-effective options.

TABLE 14.6
Cleanup Technologies for Metal Finishing Brownfields Sites Sample Analysis Technologies

Applicable Technology	Description	Examples of Applicable Land/ Process Areas	Contaminants Treated by This Technology	Limitations
Containment Technologies				
Sheet piling	Steel or iron sheets are driven into the ground to form a subsurface barrier Low-cost containment method Used primarily for shallow aquifers	Metal cleaning, rinsing and bathing operations, chemical storage, wastewater treatment	Not contaminant specific	Not effective in the absence of a continuous aquitard Can leak at the intersection of the sheets and the aquitard or through pile wall joints
Grout curtain	Grout curtains are injected into subsurface soils and bedrock Forms an impermeable barrier in the subsurface	Metal cleaning, rinsing and bathing operations, chemical storage, wastewater treatment	Not contaminant specific	Difficult to ensure a complete curtain without gaps through which the plume can escape; however, new techniques have improved continuity of curtain
Slurry walls	Consist of a vertically excavated slurry-filled trench The slurry hydraulically shores the trench to prevent collapse and forms a filtercake to reduce groundwater flow Often used where the waste mass is too large for treatment and where soluble and mobile constituents pose an imminent threat to a source of drinking water Often constructed of a soil, bentonite, and water mixture	Metal cleaning, rinsing and bathing operations, chemical storage, wastewater treatment	Not contaminant specific	Contains contaminants only within a specified area Soil-bentonite backfills are not able to withstand attack by strong acids, bases, salt solutions, and some organic chemicals Potential for the slurry walls to degrade or deteriorate over time
Capping	Used to cover buried waste materials to prevent migration Made of a relatively impermeable material that will minimize rainwater infiltration Waste materials can be left in place Requires periodic inspections and routine monitoring Contaminant migration must be monitored periodically	Anodizing, solid wastes from anodizing, electroplating, electroplating wastewaters and solid wastes, finishing wastewaters, chemical conversion coating wastewaters and solid wastes, electroless plating, electroless plating wastewaters, solid wastes from painting, wastewater treatment system, sunken treatment tank	Metals	Costs associated with routine sampling and analysis may be high Long-term maintenance may be required to ensure impermeability May have to be replaced after 20–30 years of operation May not be effective if ground water table is high

continued

TABLE 14.6 (continued)

Applicable Technology	Description	Examples of Applicable Land/ Process Areas	Contaminants Treated by This Technology	Limitations
Ex Situ Technologies				
Excavation/offsite disposal	Removes contaminated material to an EPA-approved landfill	Wastes from painting, wastewater treatment system, sunken treatment tanks, chemical storage, disposal	Not contaminant specific	Generation of fugitive emissions may be a problem during operations The distance from the contaminated site to the nearest disposal facility will affect cost Depth and composition of the media requiring excavation must be considered Transportation of the soil through populated areas may affect community acceptability Disposal options for certain waste (e.g., mixed waste or transuranic waste) may be limited. There is currently only one licensed disposal facility for radioactive and mixed waste in the United States
Chemical oxidation/reduction	Reduction/oxidation (redox) reactions 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 The oxidizing agents commonly used are ozone, hydrogen peroxide, hypochlorite, chlorine, and chlorine dioxide	Wastes from anodizing, electroplating, finishing, chemical conversion coating, electroless plating, painting, rinsing operations, wastewater treatment system, sunken treatment tank	Metals Cyanide	Not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required Oil and grease in the media should be minimized to optimize process efficiency
UV oxidation	Destruction process that oxidizes constituents in wastewater by the addition of strong oxidizers and irradiation with UV light Practically any organic contaminant that is reactive with the hydroxyl radical can potentially be treated	Wastes from metal cleaning, painting, rinsing operations, wastewater treatment system, sunken treatment tank, chemical storage area, disposal area	VOCs	The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference) Metal ions in the wastewater may limit effectiveness VOCs may volatilize before oxidation can occur

	The oxidation reactions are achieved through the synergistic action of UV light in combination with ozone or hydrogen peroxide Can be configured in batch or continuous flow models, depending on the throughput rate under consideration			Off-gas may require treatment Costs may be higher than competing technologies because of energy needs Handling and storage of oxidizers require special safety precautions
Precipitation	Involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate Precipitates can be removed from the treated water by physical methods such as clarification or filtration Often used as a pretreatment for other treatment technologies where the presence of metals would interfere with the treatment processes Primary method for treating metal-laden industrial wastewater	Wastes from anodizing, electroplating, finishing, chemical conversion coating, electroless plating, painting, rinsing operations, wastewater treatment system, sunken treatment tank	Metals	Contamination source is not removed The presence of multiple metal species may lead to removal difficulties Discharge standard may necessitate further treatment of effluent Metal hydroxide sludges must pass TCLP criteria prior to land disposal Treated water will often require pH adjustment
Liquid-phase carbon adsorption	Groundwater is pumped through a series of vessels containing activated carbon, to which dissolved contaminants adsorb Effective for polishing water discharges from other remedial technologies to attain regulatory compliance Can be quickly installed High contaminant-removal efficiencies	Wastes from metal cleaning, painting, rinsing operations, wastewater treatment system, sunken treatment tank, chemical storage area, disposal area	VOCs	The presence of multiple contaminants can affect process performance Metals can foul the system Costs are high if used as the primary treatment on waste streams with high contaminant concentration levels Type and pore size of the carbon and operating temperature will impact process performance Transport and disposal of spent carbon can be expensive Water-soluble compounds and small molecules are not adsorbed well
Air stripping	Contaminants are partitioned from groundwater by greatly increasing the surface area of the contaminated water exposed to air Aeration methods include packed towers, diffused aeration, tray aeration, and spray aeration Can be operated continuously or in a batch mode, where the air stripper is intermittently fed from a collection tank	Wastes from metal cleaning, painting, rinsing operations, wastewater treatment system, sunken treatment tank, chemical storage area, disposal area	VOCs	Potential for inorganic (iron greater than 5 ppm, hardness greater than 800 ppm) or biological fouling of the equipment, requiring pretreatment of groundwater or periodic column cleaning Consideration should be given to the Henry's law constant of the VOCs in the water stream and the type and amount of packing used in the tower

continued

TABLE 14.6 (continued)

Applicable Technology	Description	Examples of Applicable Land/ Process Areas	Contaminants Treated by This Technology	Limitations
	The batch mode ensures consistent air stripper performance and greater efficiency than continuously operated units because mixing in the storage tank eliminates any inconsistencies in feed water composition			Compounds with low volatility at ambient temperature may require preheating of the groundwater Off-gases may require treatment based on mass emission rate and state and federal air pollution laws
	<i>In Situ Technologies</i>			
Natural attenuation	Natural subsurface processes such as dilution, volatilization, biodegradation, adsorption, and chemical reactions with subsurface media can reduce contaminant concentrations to acceptable levels Consideration of this option requires modeling and evaluation of contaminant degradation rates and pathways Sampling and analyses must be conducted throughout the process to confirm that degradation is proceeding at sufficient rates to meet cleanup objectives	Metal cleaning, metal cleaning wastewaters, painting, painting wastewaters and solid wastes, wastewater treatment system, sunken treatment tank, chemical storage area, and disposal area	VOCs	Intermediate degradation products may be more mobile and more toxic than original contaminants Contaminants may migrate before they degrade The site may have to be fenced and may not be available for reuse until hazard levels are reduced Source areas may require removal for natural attenuation to be effective Modeling contaminant degradation rates, and sampling and analysis to confirm modeled predictions extremely expensive
Soil vapor extraction	A vacuum is applied to the soil to induce controlled air flow and remove contaminants from the unsaturated (vadose) zone of the soil The gas leaving the soil may be treated to recover or destroy the contaminants The continuous air flow promotes <i>in situ</i> biodegradation of low-volatility organic compounds that may be present	Metal cleaning, metal cleaning wastewaters, painting, painting wastewaters and solid wastes, wastewater treatment system, sunken treatment tank, chemical storage area, disposal area	VOCs	Tight or extremely moist content (>50%) has a reduced permeability to air, requiring higher vacuums Large screened intervals are required in extraction wells for soil with highly variable permeabilities Air emissions may require treatment to eliminate possible harm to the public or environment Off-gas treatment residual liquids and spent activated carbon may require treatment or disposal Not effective in the saturated zone

Soil flushing	Extraction of contaminants from the soil with water or other aqueous solutions Accomplished by passing the extraction fluid through in-place soils using injection or infiltration processes Extraction fluids must be recovered with extraction wells from the underlying aquifer and recycled when possible	Anodizing, solid wastes from anodizing, electroplating, electroplating wastewaters and solid wastes, finishing wastewaters, chemical conversion coating wastewaters and solid wastes, electroless plating, electroless plating wastewaters, solid wastes from painting, wastewater treatment system, sunken treatment tank	Metals	Low-permeability soils are difficult to treat Surfactants can adhere to soil and reduce effective soil porosity Reactions of flushing fluids with soil can reduce contaminant mobility Potential of washing the contaminant beyond the capture zone and the introduction of surfactants to the subsurface
Air sparging	<i>In situ</i> technology in which air is injected under pressure below the water table to increase groundwater oxygen concentrations and enhance the rate of biological degradation of contaminants by naturally occurring microbes Increases the mixing in the saturated zone, which increases the contact between groundwater and soil Air bubbles traverse horizontally and vertically through the soil column, creating an underground stripper that volatilizes contaminants Air bubbles travel to a soil vapor extraction system Air sparging is effective for facilitating extraction of deep contamination, contamination in low-permeability soils, and contamination in the saturated zone	Metal cleaning, metal cleaning wastewaters, painting, painting wastewaters and solid wastes, wastewater treatment system, sunken treatment tank, chemical storage area, disposal area	VOCs	Depth of contaminants and specific site geology must be considered Air flow through the saturated zone may not be uniform A permeability differential such as a clay layer above the air injection zone can reduce the effectiveness Vapors may rise through the vadose zone and be released into the atmosphere Increased pressure in the vadose zone can build up vapors in basements, which are generally low-pressure areas
Passive treatment walls	A permeable reaction wall is installed inground, across the flow path of a contaminant plume, allowing the water portion of the plume to passively move through the wall Allows the passage of water while prohibiting the movement of contaminants by employing agents such as iron, chelators (ligands selected for their specificity for a given metal), sorbents, microbes, and others	Appropriately selected location for the wall	VOCs Metals	The system requires control of pH levels When pH levels within the passive treatment wall rise, it reduces the reaction rate and can inhibit the effectiveness of the wall Depth and width of the plume For large-scale plumes, installation cost may be high Cost of treatment medium (iron) Biological activity may reduce the permeability of the wall

continued

TABLE 14.6 (continued)

Applicable Technology	Description	Examples of Applicable Land/ Process Areas	Contaminants Treated by This Technology	Limitations
Biodegradation	Contaminants are typically completely degraded by the treatment wall			Walls may lose their reactive capacity, requiring replacement of the reactive medium
	Indigenous or introduced microorganisms degrade organic contaminants found in soil and groundwater	Metal cleaning, metal cleaning wastewaters, painting, painting wastewaters and solid wastes,	VOCs	Cleanup goals may not be attained if the soil matrix prevents sufficient mixing
	Used successfully to remediate soils, sludges, and groundwater	wastewater treatment system, sunken treatment tank, chemical storage area, disposal area		Circulation of water-based solutions through the soil may increase contaminant mobility and necessitate treatment of underlying groundwater
	Especially effective for remediating low-level residual contamination in conjunction with source removal			Injection wells may clog and prevent adequate flow rates
				Preferential flow paths may result in nonuniform distribution of injected fluids
				Should not be used for clay, highly layered, or heterogeneous subsurface environments
				High concentrations of heavy metals, highly chlorinated organics, long-chain hydrocarbons, or inorganic salts are likely to be toxic to microorganisms
				Low temperatures slow bioremediation
				Chlorinated solvents may not degrade fully under certain subsurface conditions

Source: U.S. EPA. *Technical Approaches to Characterizing and Cleaning Up Metal Finishing Sites under the Brownfields Initiative*. EPA/625/R-98/006, U.S. Environmental Protection Agency, Cincinnati, OH, March 1999.

Cleanup at metal finishing facilities will most likely entail removing a complex mix of contaminants, primarily organic solvents and metals. The cleanup will usually require more than one technology, or treatment train, because single technologies tend not to address both metal and organic contaminants. S/S can address metal contamination by limiting mobility (solubility) and thereby limit risk. Approaches at metal finishing sites depend on local conditions. At larger metal finishing sites, one approach may be to excavate and stabilize the contaminated material with either on-site or off-site disposal or treatment of material. Access to contaminated soils may be limited at smaller sites requiring excavation and off-site treatment or disposal. The stabilized material can be placed on-site or sent to an U.S. EPA-approved landfill.

14.4.5 POSTCONSTRUCTION CARE

Many of the cleanup technologies that leave contamination on-site, either in containment systems or because of the long periods required to reach cleanup goals, will require long-term maintenance and possibly operation. If waste is left on-site, regulators will likely require long-term monitoring of applicable media (i.e., soil, water, and/or air) to ensure that the cleanup approach selected is continuing to function as planned (e.g., residual contamination, if any, remains at acceptable levels and is not migrating). If long-term monitoring is required (e.g., by the state), periodic sampling, analysis, and reporting requirements will also be involved. Planners should be aware of these requirements and provide for them in cleanup budgets. Postconstruction sampling, analysis, and reporting costs in their cleanup budgets can be a significant problem as these costs can be substantial.

14.5 CONCLUSION

Brownfields redevelopment contributes to the revitalization of communities across the U.S. Reuse of these abandoned, contaminated sites spurs economic growth, builds community pride, protects public health, and helps maintain our nation's "greenfields," often at a relatively low cost. This chapter provides brownfields planners with the technical methods that can be used to achieve successful site assessment and cleanup, which are the two key components in the brownfields redevelopment process.

While the general guidance provided in this chapter will be applicable to many brownfields projects, it is important to recognize the heterogeneous nature of brownfields work. That is, no two brownfields sites will be identical, and planners will need to base site assessment and cleanup activities on the conditions at their particular site. Some of the conditions that may vary by site include the type of contaminants present, the geographic location and extent of contamination, the availability of site records, hydrogeological conditions, and state and local regulatory requirements. Based on these factors, as well as financial resources and desired timeframes, planners will find different assessment and cleanup approaches appropriate.

Consultation with state and local environmental officials and community leaders, as well as careful planning early in the project, will assist planners in developing the most appropriate site assessment and cleanup approaches. Planners should also determine early on if they are likely to require the assistance of environmental engineers. A site assessment strategy should be agreeable to all stakeholders and should address:

1. The type and extent of contamination, if any, present at the site
2. The types of data needed to adequately assess the site
3. Appropriate sampling and analytical methods for characterizing contamination
4. An acceptable level of data uncertainty.

When used appropriately, the site assessment methods described in this chapter will help to ensure that a good strategy is developed and implemented effectively.

Once the site has been assessed and stakeholders agree that cleanup is needed, planners will need to consider cleanup options. Many different types of cleanup technologies are available. The guidance provided in this chapter on selecting appropriate methods directs planners to base cleanup initiatives on site- and project-specific conditions. The type and extent of cleanup will depend in large part on the type and level of contamination present, reuse goals, and the budget available. Certain cleanup technologies are used on-site, while others require off-site treatment. Also, in certain circumstances, containment of contamination on-site and the use of institutional controls may be important components of the cleanup effort. Finally, planners will need to include budgetary provisions and plans for postcleanup and postconstruction care if it is required at the brownfields site. By developing a technically sound site assessment and cleanup approach that is based on site-specific conditions and addresses the concerns of all project stakeholders, planners can achieve brownfields redevelopment and reuse goals effectively and safely.

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15 Control, Management, and Treatment of Metal Emissions from Motor Vehicles

*Rajasekhar Balasubramanian, Jun He, and
Lawrence K. Wang*

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15.1 INTRODUCTION

Metals comprise a complex group of elements with a broad range of toxicity, including effects on genes, nervous and immune systems, and the induction of cancer. Some metals (e.g., lead) are toxic at very low levels, whereas others (e.g., manganese) are essential to living systems at low concentrations, but may be toxic at higher concentrations. Metals may exist in several valence states that differ in toxicity and may be associated with organic matter and inorganic materials that can affect their toxicity. The presence of metals in the environment has received a great deal of attention in recent years. Their accumulation in the environment is of concern because of their persistence. Among metals, transition metals are particularly of concern because they are considered to be toxic.

Industrial facilities, waste incinerating plants, and fossil fuel burning are considered the main sources of anthropogenic heavy metal emissions in industrialized areas and countries. Air in industrial and metropolitan areas is more heavily contaminated with heavy metals than air in rural areas [1]. Consequently, emissions from industry and other point sources were of most acute concern. However, these emissions have decreased compared with their previous levels due to effective control measures taken in developed countries. There has been a shift in heavy metal emission sources over the last few decades [2].

Several studies of metal flows in the anthroposphere point to the traffic sector as a major contributor of diffuse metal emissions [2–5]. Especially close to roads, motor vehicle traffic is the largest emission source. Metals such as As, Cd, Co, Ni, Pb, Sb, V, Zn, and the platinum group elements (PGEs) Pt, Pd, and Rh can be characterized as being road-specific heavy metals. They are mainly derived from combustion residues and losses from fuels and engine and transmission oils, abrasion from tires, brake linings, exhaust catalysts, and road pavement, and corrosion of galvanized protection barriers [6]. Catalysts are used in catalytic converters to eliminate more than 95% of the harmful nitrogen oxide, hydrocarbon, and carbon monoxide emissions in automobile exhausts.

Exhaust catalysts are also the main emission source of PGEs and cerium (Ce) in the vicinity of roads [7–9]. Mechanical stress on the catalyst material, that is, through temperature cycles, vibrations, and abrasion, can lead to the release of small amounts of platinum metals to the atmosphere, leading to increased environmental platinum concentrations [9–15]. These elements are rare in natural environments. Their natural concentrations in the earth's crust are about 0.4–5 µg/kg [16]. Owing to PGE emissions, the use of exhaust catalysts has been debated since their introduction in the United States and Germany in 1975 and in 1986 [9]. PGEs are also used in other car parts such as in the electrodes of the long-life spark plug. Adhesives containing Pt catalyst traces are used in tires, providing another potential source of PGEs. Additional sources of emissions are fuel and electronics. Hoppstock and Michulitz [17] found average Pt concentrations of 3 (0.9 ng/L in normal unleaded gasoline), 5.2 (1.9 ng/L in super unleaded gasoline), and 1.4 (0.7 ng/L in super plus unleaded gasoline).

Particles of road traffic source have received great attention by environmental protection agencies because they may cause several adverse health effects on urban populations. To date, the International Agency for Research on Cancer (IARC) has classified engine exhaust emission elements as probable carcinogens [18]. Many studies have been conducted to investigate the mechanisms associated with pulmonary carcinogenicity caused by vehicle emissions. However, it should be noted that the vehicle emissions contain various metal contents attached onto fine granular matters in the engine exhaust. Owing to their fine particle sizes, they can penetrate into the deep respiratory tract and cause respiratory diseases. It has been indicated that the deposition of metals (especially Fe) on the lower airway will firstly generate hydroxyl radicals (in aqueous buffered solutions, in the presence of hydrogen peroxide), then trigger the production of oxygen-free radicals, and finally cause both acute and chronic lung injuries [19]. Therefore, it is expected that apart from the organic contents and particulate matter, the investigation of metal contents from the road traffic is important for assessing health effects associated with on-road mobile sources.

On-road mobile metal emission sources usually include exhaust fumes, brake lining, tires, etc. Metal emissions from exhaust fumes are derived from fossil fuels and the aging processes of engines and catalysts. Combustion of leaded gasoline was the major source of Pb until about a decade ago. The use of Pb as an antiknocking additive in gasoline was phased out in many countries due to its toxicity. However, there are still some emissions of Cd, Cr, Cu, Ni, Pb, and V from fossil fuels [20–22]. As a result of the asbestos ban, producers of brake linings were forced to substitute materials during the 1980s. The friction material in vehicle brake linings nowadays consists of a wide range of compounds with, for instance, fibers of steel, glass, and plastic serving as reinforcements. In addition, some compounds are used for their heat-conducting properties (brass chips) and good filling properties (antimony compounds) [2]. The metals of concern for emissions from brake linings are Cd, Cr, Cu, Ni, Pb, Sb, and Zn [2,23]. The effects of this material substitution have been shown in some studies as increased copper levels close to roads [24]. Wear from vehicle tires is

another major metal source, especially for Zn, and tires as well have traceable amounts of several other metals such as Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, and Pb [24–27].

15.2 VEHICLE EMISSION

15.2.1 LEADED GASOLINE POLLUTION

Among the different contemporary sources of lead pollution, traffic-induced emissions from the combustion of leaded gasoline are of particular concern, as they constitute most of the total lead emissions into the atmosphere in congested urban areas where no phase-out activities have been adopted [28]. It has been reported that 90% of all lead emissions in the United States have been from the combustion of gasoline containing lead alkyl additives [29]. However, most western industrialized nations have reduced or eliminated lead additives in gasoline due to increasing evidence of the harmful effects of lead on human health [30,31]. Figure 15.1 shows the historical consumption of lead in gasoline in the United States as an example and the highest usage during the 1970s could be observed [29,30].

Pacyna and Pacyna [32] provided expert estimates of European atmospheric lead emissions for the reference years of 1955, 1965, 1975, 1985, 1990, and 1995, and projection estimates for the year 2010 [32]. Atmospheric lead emissions by source category are given in Table 15.1 [33], in which the projection for the year 2010 was estimated and the evolution over four decades exhibits a sharp rise leading up to the mid-1970s as well and shows that the major source had been always road traffic.

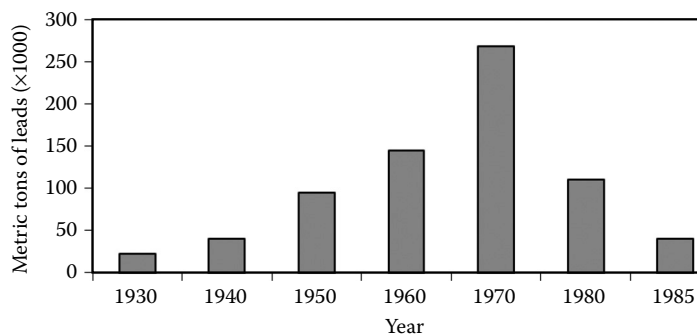


FIGURE 15.1 Historical consumption of lead in gasoline in the United States.

TABLE 15.1

Lead Emission (Ton) by Source Category in Each Year of Estimate

Year Source Category	1955	1965	1975	1985	1990	1995	2010
Total emission	62,531.7	110,587.9	159,233.0	81,581.0	58,130.0	28,390.2	12,608.0
Road transport	30,953.2	68,675.1	119,265.5	62,083.1	41,911.7	19,504.1	7,590.0
Nonferrous metal manufacturing	12,631.4	16,809.4	20,381.8	10,442.4	8,254.5	3,350.0	2,168.6
Stationary fuel combustion	5,440.3	6,524.7	6,847.0	3,508.0	3,545.9	2,697.1	1,311.2
Iron and steel production	7,003.6	10,395.3	7,643.2	3,915.9	3,139.0	2,242.8	1,159.9
Waste disposal	125.1	331.8	955.4	489.5	232.5	255.5	100.9
Come at production	750.4	1,437.6	1,592.3	815.8	0.0	0.0	0.0
Other sources	5,627.9	6,414.1	636.9	326.3	1,046.3	340.7	277.4

15.2.2 OTHER METAL-CONTAINING ANTIKNOCK AGENTS

Gasoline additives are used to increase gasoline's octane rating or act as corrosion inhibitors or lubricators, thus allowing the use of higher compression ratios for greater efficiency and power; however, some carry heavy environmental risks. Those metal-containing additives mainly refer to antiknock agents such as tetraethyl lead (TEL), methylcyclopentadienyl manganese tricarbonyl (MMT), ferrocene, iron pentacarbonyl, and so on.

TEL, an organometallic compound with the formula $(\text{CH}_3\text{CH}_2)_4\text{Pb}$, has been a common antiknock additive in gasoline, the lead pollution from which is discussed as above. TEL usage was largely discontinued because of the toxicity of lead and its deleterious effects on catalytic converters, but is still used as an additive in aviation fuel for piston engine-powered aircraft.

MMT, an organometallic compound with the formula $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, was marketed initially in 1958 as a supplement to the gasoline additive TEL to increase the fuel's octane rating and was later used in unleaded gasoline. Although banned as a gasoline additive in the United States from 1977 to 1995, MMT has been used in Canadian gasoline since 1976 and was recently introduced in Australia.

Originally, the combustion products of MMT were thought to be manganese (Mn) oxide, mainly tetraoxide or hausmannite [34]. Recent car exhaust studies provided qualitative data on the chemical composition of particles collected from a tailpipe and found that the Mn particles emitted are mostly Mn phosphate, Mn sulfate, and a small amount of Mn oxides [35,36]. It has been suggested that the combustion of the organomanganese compound MMT may be a significant source of contamination by inorganic Mn in urban areas, and it was reported that the contribution of Mn from MMT source relative to total Mn emissions was 28% (334 tons of Mn from MMT in 1999 in all the Canadian provinces versus 1,225 tons total emissions) in 1999 [37].

Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) and iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) are iron-based organometallic compounds, both of which were once used as antiknock agents in the fuel for gasoline engines and could reduce soot formation inside engines, relatively safer than TEL. However, these two compounds have not been used widely due to their emissions from engines and their toxic nature [38,39].

15.2.3 CATALYTIC CONVERTER

The phase out of leaded gasoline was also accelerated by the introduction of a catalytic converter into the exhaust emission control, because the lead content can cause catalyst poisoning. A catalytic converter is a device used to reduce the toxicity of emissions from an internal combustion engine. It was first widely introduced in series production automobiles in the U.S. market for the 1975 model year to comply with tightening Environmental Protection Agency (EPA) regulations on auto-exhaust, and even now is still most commonly used in motor vehicle exhaust systems. The catalyst itself is most often a precious metal. Platinum is the most active catalyst and is widely used. However, it is not suitable for all applications because of unwanted additional reactions and/or cost. Palladium and rhodium are two other precious metals that are used. Platinum and rhodium are used as a reduction catalyst, whereas platinum and palladium are used as an oxidization catalyst. Nickel and copper are also used, although each has its own limitations. Nickel is not legal for use in the European Union (due to reaction with carbon monoxide) [40]. While copper can be used, its use is illegal in North America due to the formation of dioxin [41]. However, the catalytic converter is also a serious potential source of heavy metals due to the aging of catalysts by thermal effects, which could be emitted with other exhaust components [42].

15.2.4 DIESEL ENGINE EMISSION

Diesel engines use compression ignition, based on the diesel cycle, a process by which fuel is injected after the air is compressed in the combustion chamber causing the fuel to ignite. Diesel

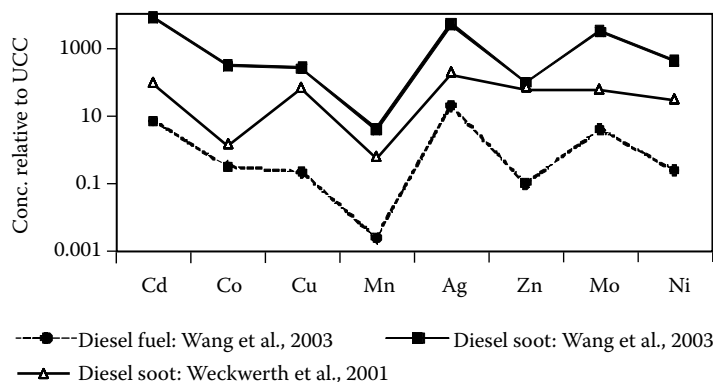


FIGURE 15.2 UCC normalized metal distribution patterns for the diesel soot and diesel fuel.

vehicles can produce black soot [or more specifically diesel particulate matter (DPM)] from their exhaust, which consists of unburned carbon compounds together with those impurities of heavy metals bound within those particulate matters as well. On the other hand, the composition of heavy metals from diesel vehicle emissions is strongly affected by the vehicle's operating conditions such as driving conditions, driving speed, and so on [43]. To illustrate the metal content emissions from diesel vehicles, two reference emission profiles normalized by upper continental crust (UCC) are presented in Figure 15.2.

The analyses of diesel soot from engine exhausts indicate top abundance of Zn and Cd contents in both studies with 100–10,000 times concentration relative to UCC (Figure 15.2); similar enrichments have also been found for Co, Cu, Mn, Ag, Mo, and Ni [23,43]. Technically, the refining process can separate all metals below the ppm level from diesel and mineral oils [23]. Therefore, these metals found in both diesel soot and diesel fuel are likely to have been added later as most of these elements (e.g., Zn, Mo, and Cu) are known to be used as additives.

15.2.5 BRAKE LININGS AND TIRES

The material used for braking linings is a complex mixture of various substances including reinforcement fibers of glass, steel, and plastic; “friction modifiers”; fillers in the form of antimony compounds and brass chips; and iron fillings and steel wool as heat-conducting materials [44]. The materials used in brake linings are of environmental relevance as a greater part of the material is dispersed directly into the environment when used [45]. It has clearly been shown that brake linings are a major source of metal emissions such as cadmium, copper, lead, and zinc in urban areas [3,46]. Furthermore, it has been shown that large amounts of antimony might be emitted from brake linings, as antimony (Sb_2S_3) is used by some manufacturers as a filler and lubricant in brake linings [42]. Similarly, studies have reported that tires have been a great source of heavy metals such as zinc, cadmium, and so on [25,47]. Researchers in Sweden compared metal emissions from brake linings and tires with other metal emission sources in Stockholm during 1995 and from 1998 to 2005 [45]. As Stockholm represents a rather average city in most respects, the results from this study may be relevant for many other urban areas. Some of the metal emission results are shown in Tables 15.2 and 15.3.

As can be seen from Table 15.1, during this period, copper and zinc emissions from brake linings remained relatively unchanged at high levels that make them a major source of these metals; brake linings were also a source of another toxic metal, antimony; by contrast, lead and cadmium emissions from brake linings decreased by one-tenth during this period. The study found that metal emissions from tire tread rubber declined between 1995 and 2005, as manufacturers reduced metal

TABLE 15.2

Calculated Total Metal Emissions from Road Traffic from Brake Linings in Stockholm (kg/year) for 1998 and 2005

	2005					1998				
	Cd	Cu	Pb	Sb	Zn	Cd	Cu	Pb	Sb	Zn
Private cars	0.052	2400	24	360	710	—	3731	549	—	771
Trucks	0.005	1200	4.8	350	180	—	68	3.9	—	68
Buses	0.007	210	6.5	0.33	110	—	76	3.2	—	56
Total	0.064	3800	35	710	1000	—	3900	560	—	900

TABLE 15.3

Calculated Metal Emissions (Cd, Cr, Cu, Ni, Pb, Sb, and Zn) from Tire Tread Rubber in Stockholm (kg/year) for 2005

	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Private cars	0.31	0.62	2.8	1.2	3.1	0.42	3400
Trucks	0.031	0.062	0.28	0.12	0.31	0.042	340
Buses	0.11	0.17	1.2	0.31	0.88	0.13	970
Total	0.45	0.85	4.3	1.6	4.3	0.60	4700

concentrations in tire treads [45]. Tires, however, remained one of the largest sources of zinc and an important source of cadmium as other studies mentioned above (Table 15.3).

15.3 MANAGEMENT, CONTROL, AND TREATMENT

Control of exhaust emissions especially for metals or heavy metals from internal combustion engines has followed two routes: (1) fuels could be modified in terms of reduction of metal contents such as less metallic additives added, or (2) could be replaced by alternative fuels with less metal content as well without compromising the engine performance; the pollutants could be minimized from the combustion chamber by installing some particulate metal trap systems.

15.3.1 LEADED GASOLINE PHASE-OUT

Lead has been blended with gasoline, primarily to boost octane levels since the early 1920s. Gradually, the toxicity of lead started to be known and studies showed that exposure to high concentrations of lead, particularly in young children, can result in damage to the central nervous system, renal organ, and may be associated with high blood pressure in adults. Human exposure to lead typically occurs via inhalation of air and ingestion of lead in food, soil, water, or dust. Consequently, to get the lead out of gasoline seemed to be essential for the sake of environmental protection and human health.

The phase-out period varies between countries. The U.S. EPA (United States Environmental Protection Agency) began working to reduce lead emissions soon after its inception, issuing the first reduction standards in 1973, which called for a gradual phase-down of lead to one-tenth of a gram per gallon by 1986. The average lead content in gasoline in 1973 was 2–3 g per gallon or about 200,000 tons of lead per year. In 1975, passenger cars and light trucks were manufactured with a more elaborate emission control system that included a catalytic converter that required lead-free

fuel. In 1995, leaded fuel accounted for only 0.6% of total gasoline sales and less than 2,000 tons of lead per year. Effective from January 1, 1996, the Clean Air Act banned the sale of the small amount of leaded fuel that was still available in some parts of the country for use in on-road vehicles. All of these efforts on removing lead from regular use resulted in an over 70% decline in blood-lead levels in Americans between 1978 and 1990 [48]. Other developed nations have followed the United States. The European countries such as Germany, France, and the United Kingdom began phase-out policy of leaded gasoline since the early 1980s, since when the concentrations in leaves and human blood have steadily declined [33]. However, as the industrial nations legislate lead's demise, the world's lead makers have been pushing to expand new markets, primarily in the developing countries. The complete phase-out (100% unleaded) all over the world still has a very long way to go.

Lead (or TEL) in gasoline enhances engine performance since it has the property of increasing the octane rating/number in gasoline, which makes the fuel resist knocking better [49]; lead also serves as a lubricant for the exhaust valves (valve seats). The introduction of catalytic converters was a turning point, and forced refineries to develop substitutes for lead additives during the 1980s. Catalytic converters are used to reduce emissions of hydrocarbons, carbon monoxide, and nitrogen oxides, not to solve the lead discharge. Since lead in gasoline destroys the catalytic converters, the introduction of catalytic converters called for the use of unleaded gasoline. Another side effect of the lead additives was to protect the valve seats from erosion. Many classic cars' engines have to make modifications to use lead-free gasoline due to the gradual unavailability of leaded gasoline.

When lead is reduced, or removed from a gasoline pool, the octane increment formerly provided by lead must be replaced by a combination of (i) increasing the proportion of high octane blendstocks in the pool and (ii) increasing the octane of at least some blendstocks. More specifically, to avoid using lead, the technical options for replacing octane provided by lead include

- Increasing the octane of reformat by increasing reformer severity within the limits of sustainable operations. In some cases, to achieve the necessary increase in reformer severity will call for revamping and modernizing the reformer.
- Increasing the production of high octane blendstocks (reformat, fluid catalytic cracking (FCC) gasoline, alkylate, isomerate, or oxygenate) in the refinery. It is known that oxygenate blending adds oxygen to the fuel in oxygen-bearing compounds such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and ethanol, and thus reduces the amount of carbon monoxide and unburned fuel in the exhaust gas.
- Blending MTBE into the gasoline pool raised serious concerns. Although MTBE may be good for air quality, it has proven to be very bad for other parts of the environment, especially ground water. Over the past few years, monitoring has detected MTBE in lakes, streams, and ground water. If MTBE gets into a drinking water supply, it creates a bad smell and may pose health concerns. Because gasoline is so widely used, MTBE finds its way into almost every part of the environment. MTBE can get into water supplies from gasoline leaks, storage tanks, pipelines, and spills. It may also get into surface waters from boats and personal water craft. MTBE evaporates into the air, but it is believed that most MTBE in air breaks down to other components. However, when MTBE gets into ground water, it does not readily evaporate or break down. It dissolves in the ground water and can move through an aquifer in the form of a "plume." Consequently, MTBE use has been phased out due to issues with contamination of ground water. In some places it is already banned. Ethanol and to a lesser extent the ethanol-derived ETBE are common replacements.
- Reducing the volume of light naphtha in the gasoline pool is another technical option to consider.

These technical options may be applied in any combination that is technically feasible in the refinery.

15.3.2 NONNOBLE METAL CATALYST

It is known that the manufacturing of automotive catalytic converters requires precious metals of palladium, platinum, or rhodium, which could have significant environmental effects such as the accumulation in the ecosystem [50]. Consequently, novel formulations to operate pollution-dampening catalytic converters without the need of expensive and toxic noble metals are quite necessary. It has been found that nonnoble metal transition metal catalysts can replace platinum in the oxidation–reduction reaction. In addition, a nonnoble metal, perovskite type of catalyst could be used to achieve conversion of pollutants. Perovskites are one of the most fascinating groups of catalytic materials having densely packed cubic lattice of the general formula ABO_3 [51].

Perovskite-type nonnoble metal-based catalytic materials have been developed for their possible applications in diesel exhaust emission control [52]. These materials have been evaluated for their applications in regeneration of diesel particulate filter (DPF) and also as a diesel catalytic converter (DCC). Both the applications require low-temperature oxidation catalysis properties. Temperature-programmed desorption studies revealed the low-temperature oxygen desorption of perovskite catalyst, which may be useful for the oxidation of carbon/soot at lower temperatures. Laboratory evaluation results on activated carbon show the carbon oxidation activity of the catalyst in the temperature range 300–450°C [52]. However, this was achieved under the tight contact of carbon and catalyst. Catalyst-coated ceramic foams have been used to fabricate laboratory prototype of regenerative-type DPF. Although its evaluation on a vehicle shows significant reduction in smoke density, the regeneration temperature was still higher than desired [52]. The DCC shows 10–25% reduction in smoke density depending on engine conditions. The perovskite-type catalyst appears to follow a redox mechanism for soot oxidation through oxygen removal and replenishment, whereas hydrocarbons adsorbed on soot particles may also help in oxidation of the carbonaceous part.

15.3.3 ALTERNATIVE FUELS

Other than the unleaded gasoline, the use of alternative fuels is one of the important ways for eliminating or controlling the emission of metals from internal combustion engines. The main alternative fuels that merit consideration from the air pollution control standpoint include liquefied petroleum gas (LPG), liquefied natural gas (LNG), compressed natural gas (CNG), hydrogen, dimethyl ether (DME), dimethyl carbonate (DMC), and bio-fuels such as ethanol. The significance of some of the representative alternative fuels is discussed below.

LPG is a mixture of gases produced commercially from petroleum or natural gas, and stored under pressure to keep it in a liquid state. LPG is composed primarily of propane with some butane, propylene, butylene, and other hydrocarbons, unlike gasoline, which is a complex mixture of hydrocarbons. LPG's average octane value is 104, which is higher than gasoline's range of 84–97, and can produce significantly better vehicle performance than the lower octane gasoline. When prepared as fuel, unlike gasoline, LPG is used as a dry gas without fuel additives, which just burns with little air pollution and little solid residues such as soot and particulate matter with heavy metals [53]. Even though LPG has been considered less polluting than gasoline and diesel due to the fact that it contains less sulfur and emits less hydrocarbons, NO_x , particulate matter, and CO, it has been reported that LPG has a high emission potential of volatile heavy metals such as mercury (Hg) [54]. Estimated Hg emission rates derived from original fuel Hg contents, under idling and driving modes, are presented in [Table 15.4](#).

CNG is a fossil fuel substitute for gasoline, diesel, or propane fuel. CNG is made by compressing natural gas, which is mainly composed of 90% methane (CH_4) and small amounts of ethane and other hydrocarbons, to less than 1% of its volume at standard atmospheric pressure. Natural gas has an octane value of 130, which is considerably higher than gasoline with octane value between 84 and 97, providing very good engine performance characteristics.

The toxic emissions with CNG, without exception, are lower than that for any other hydrocarbon fuel. This environmental benefit is due to the fact that CNG is a single hydrocarbon, methane.

TABLE 15.4
Comparison of the Estimated Hg Emission Rates

Estimated Hg Emission Rate (µg/h)	Gasoline	Diesel	LPG
Fuel analysis	3.6	1.0	10.9
Idling mode	0.07–0.4	0.1–0.2	0.7–1.3
Driving mode	0.6–2.5	0.7–1.9	4.5–6.1

Source: Adapted from Won, J.H., Park, J.Y., and Lee, T.G. *Atmos. Environ.* 41, 7547–7552, 2007.

Soot emission from the hydrocarbon flame is an important subject of concern since it is related to air pollutants such as airborne particulate matter with metals [55]. The use of CNG in internal combustion engines permits operation with decreased NO_x with little solid residues, but it still has an emission potential of volatile heavy metals such as Hg, which is indicated in the CNG quality standards [56,57]. However, the measured data of mercury emission from CNG engine is not available yet.

Dimethyl ether (CH_3OCH_3), also called DME, is currently attracting worldwide attention because it is a clean fuel that can be synthesized from various materials such as natural gas, coal, biomass, and so on [58]. DME can be used as a fuel in diesel engines, gasoline engines (30% DEM/70% LPG), and gas turbines. It works particularly well in diesel engines due to its high cetane number, which is greater than 55 compared with diesel with cetane numbers 38–53. Only moderate modifications are needed to convert a diesel engine to run on DME. The simplicity of this short-carbon-chain compound leads, during combustion, to very low emissions of airborne particulate matter, NO_x , CO, and no SO_x , meeting even the most stringent emission regulations in Europe, United States, and Japan [59]. Low emission of airborne particulate matter can also reduce the emission of metals bound in particles.

Ethanol, a biofuel, is manufactured from the conversion of carbon-based feed stocks such as sugar cane, sugar beet, switch grass, corn, and barley. Ethanol fuel can be combined with gasoline at different percentages, or can be used in its pure form as 100%. As a matter of fact, not every vehicle can run on 100% ethanol, but most run on small percentages of ethanol blends. Ethanol has become more common, because it is currently being used as an oxygenated additive, which could help achieve the reduction of soot emissions to some extent without the use of a metal-containing additive [60]. Ethanol fuel is a sustainable energy resource that is intended to provide a more environmentally and economically friendly alternative to fossil fuels such as diesel and gasoline. However, there are many debates surrounding the environmental friendliness of ethanol, and the production viability.

15.3.4 ALTERNATIVE VEHICLES

15.3.4.1 Battery-Powered Electric Vehicles

Battery power was one of the three leading contenders (along with gasoline and steam) when automobiles were first introduced a hundred years ago. However, the high cost and limited performance of batteries relative to gasoline engines were major factors preventing their widespread use. Today, battery-powered electric vehicles (EVs) still have a relatively limited driving range and higher initial cost relative to conventional automotives. However, the major attraction is that no air pollutants such as toxic metal vapors are directly emitted and no tailpipe is used.

Batteries are used to power individual electric motors that are connected to the drive wheels of a car. During braking, the motors can function as generators that allow some of the car's kinetic energy to be recovered. At regular intervals, the depleted batteries must be recharged from an external power

source. From an environmental perspective, battery-powered vehicles fulfill their promise of “zero emissions” along the roads and highways where they are driven. However, battery-powered vehicles have indirect impacts because of their demand for electricity, the main sources of which are coal, gas, and nuclear power, causing significant environmental impacts. Other indirect environmental impacts of batteries arise from the production and recycling of battery materials such as lead. Life cycle studies indicate that lead emissions to the environment would increase substantially in the absence of new control measures if lead-acid batteries were widely used to power EVs [61]. Advanced batteries use nickel–cadmium, nickel–metal hydride, sodium–sulfur, or other materials. Many of these batteries may cause emissions of toxic metals.

15.3.4.2 Hybrid Vehicles

A hybrid vehicle is a modified vehicle that uses two or more distinct power sources (EV operation, internal combustion engine, etc.) to propel the vehicle. The hybrid vehicle typically achieves greater fuel economy and lower emissions than conventional internal combustion engine vehicles (ICEVs). Fewer metal emissions are primarily achieved by the following design:

1. Shutting down the gasoline or diesel engine during traffic stops or while coasting or other idle periods.
2. Using low rolling resistance tires. Hybrid cars use special tires that are more inflated than regular tires and stiffer, which reduces the drag by about half, improving fuel economy by relieving stress of the engine.
3. Relying on both the gasoline (or diesel engine) and the electric motors for peak power needs, resulting in a smaller gasoline or diesel engine sized more for average usage rather than peak power usage.

These features make a hybrid vehicle particularly efficient for city traffic where there are frequent stops, coasting, and idling periods. However, the overall cost of a hybrid vehicle is still higher than a comparable gasoline-powered vehicle.

15.3.4.3 Fuel Cells

EVs powered by fuel cells are another promising new concept for early twenty-first-century automobiles. A fuel cell can be thought of as a gas-powered battery in which a continuous flow of hydrogen and oxygen gases replaces the solid electrodes of a conventional car battery.

Hydrogen is the most abundant element on the planet and the cleanest burning fuel on the basis of carbon atoms per fuel molecule. It also has the potential for producing only water when reacting with oxygen. Carbon emissions and metal pollutants from a hydrogen engine are virtually nonexistent [62]. A hydrogen-powered hybrid EV (HEV) can reduce petroleum demands and emissions. The component configuration is illustrated in [Figure 15.3](#).

However, hydrogen fuel cells are costly to produce and are quite fragile at present. It is still under study to produce inexpensive fuel cells that are robust enough to survive the bumps and vibrations that all automobiles experience. In addition, many designs require rare substances such as platinum as catalyst, which can again become contaminated by impurities in the hydrogen supply.

15.3.5 PARTICULATE FILTERS

The exhaust emissions from vehicle engines are the most difficult to control, within which most of the heavy metals from fuels could be bound and emitted with particulates. Consequently, removal of the airborne particles before they are exhausted into the atmospheric environment is another important control method for heavy metals originating from vehicles. The use of the particulate filter on diesel-engine vehicles represents a new exhaust post-treatment technology that removes solid particles from the exhaust gases.

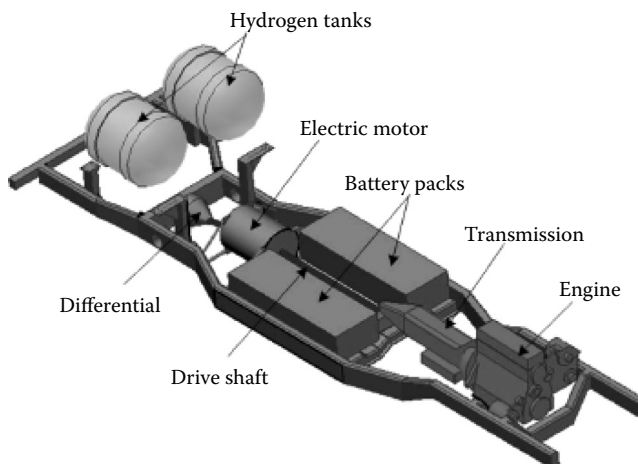


FIGURE 15.3 The component configuration of hydrogen-powered HEVs.

Particulate filters have been in use on on-road machines since the 1980s and in automobiles since 1996. Diesel engines during combustion of the fuel/air mix produce a variety of particles generally classified as DPM due to incomplete combustion. The metal composition of the particles varies widely depending on the engine type, age, and the emissions specification that the engine was designed to meet. Two-stroke diesel engines produce more DPM per horsepower output than do four-stroke diesel engines, as they burn the fuel/air mix less completely.

A DPF is a device designed to remove DPM or soot from the exhaust gas of a diesel engine. DPF is far more effective at reducing metal emissions associated with DPM than the diesel oxidation catalyst (DOC), which is able to oxidize compounds existing in the gas phase of the engine exhaust system. The latter device is not effective at reducing the solid soot particles in DPM by any appreciable amount. DPFs are quite efficient in reducing particulate matter emissions. For example, wall-flow DPFs usually remove 85% or more of the soot, and can at times (heavily loaded condition) attain soot removal efficiencies of close to 100% [63,64]. A diesel-powered vehicle equipped with a functioning filter will emit no visible smoke from its exhaust pipe.

Figure 15.4 shows one type of DPF that captures soot and larger sulfate particles in a series of ceramic honeycomb channels. Exhaust gases are directed into a cordierite or silicon carbide molded substrate with closed ends. Gas passes through the porous material, and the particulates are trapped and accumulate on the channel walls.

15.3.6 REDUCTION OF METALS IN BRAKE LININGS AND TIRES

It has been known that particles worn away from automobile brake linings and tires continue to be major sources of potentially toxic metal emissions in urban areas. New regulations and auto-industry efforts have to be undertaken to reduce the use of the metals in such automobile parts.

It has been reported that materials and components in vehicles produced after July 2003 should not contain lead, mercury, cadmium, or hexavalent chromium according to the directive of the European Parliament and Council [32]; brake linings were one of the components added in June 2002 to Appendix II of the directive as an exception to these restrictions, stating that the use of copper containing more than 0.5 wt% lead in brake linings is allowed for vehicle models approved before July 2003, but after that time, a concentration of up to 0.4 w% lead in copper in brake linings was permitted until July 2007. From Table 15.1, it can be seen that lead emissions from brake linings

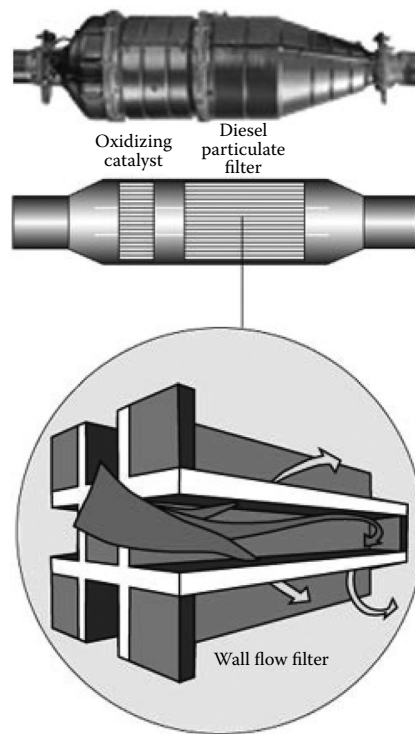


FIGURE 15.4 DPF with ceramic honeycomb channels.

really decreased by one-tenth during 1998–2005 in Stockholm, Sweden, as a result of implementation of this pro-active air pollution control strategy.

15.4 SUMMARY

The raised awareness of traffic as one of the major diffuse metal emission sources highlights the need for more effective technology developments to eliminate emissions of toxic metals. Many studies have reported elevated levels of metals in urban air and roadside soils, but as there are local, regional, and national differences in surrounding factors, total numbers of vehicles, and road construction, there are many different conditions to take into account before the full picture of the problem can be fully understood. New technological solutions and material substitutions change the metal emission rates, and “new” metals are entering this metal emission pathway. To assess present and future environmental or health risks, improved knowledge of traffic-related diffuse metal emissions is necessary.

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