CHAPTER 9.3

Treatment of Effluent Waste

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The *SME Mineral Processing Handbook* was published in 1985 (Weiss 1985). As predicted in that volume, the U.S. Environmental Protection Agency (EPA) has promulgated extensive additions and revisions to environmental regulations with respect to the mineral processing and extractive metallurgical industries; for example, Congress authorized the addition of the Hazardous and Solid Waste Amendments (EPA 1984) to the Resource Conservation and Recovery Act (EPA 2014c). These amendments directed the EPA to more aggressively manage some hazardous waste, and the RCRA restricted (banned) some hazardous waste from disposal without further stabilization. This initiated the land ban restrictions (LBR). Other environmental regulations have been formulated through the Clean Water Act (CWA) and its amendments, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, Superfund), and the Clean Air Act and its amendments that have significant consequences to the extractive metallurgical industries. The goal of this chapter is to supply a guide to the literature so that the user can evaluate and select appropriate technologies to treat effluent waste solutions and dispose of solid waste products in an environmentally safe manner.

The Society for Mining, Metallurgy & Exploration (SME) supports responsible environmental protection (Darling 2011):

> SME members recognize that there are environmental and social impacts that result from mining. Further, the industry strives to find innovative ways, based upon sound science and engineering principles, to explore the Earth, extract essential, critical and strategic minerals and to design and operate processing and manufacturing facilities that eliminate or minimize any adverse impacts. SME supports sustainable development principles that seek to return mined lands to useful and useable public and private lands for future generations. SME also recognizes the need for federal, state and local regulations to control and limit impacts of mining operations. There needs to be clear, concise and consistent interpretation and application of laws, regulations and guidance by the government that apply to the mining industry to assure environmental and economic justice for all citizens. In turn, the mining industry has a responsibility to participate in the public notice and comment process for new rules and then to comply with those rules and regulations that have been promulgated.

Hasen (2015) stated the following in an SME technical briefing:

> The mining, mineral processing and metallurgical industries support, and strictly follow, state and federal regulations to ensure protection of the environment and the health of industry workers.

This chapter focuses on the treatment of effluent wastewaters and solid waste, deemed in the literature as environmental hydrometallurgy. Doyle (2005) has characterized environmental hydrometallurgy as follows:

> *Environmentally compliant hydrometallurgy* refers to traditional hydrometallurgical processes (i.e., the production of metals and metal-bearing compounds using aqueous processing), but performed in such a way as to ensure little or no adverse impact on the environment…. *Hydrometallurgy for environmental compliance* covers hydrometallurgical processes used to assist in complying with waste discharge and management regulation, along with processes that lower the overall environmental impact of a particular process.

Both approaches are widely practiced in mineral and extractive metallurgical processing. Doyle makes an important point that hydrometallurgical unit operations are presently being used to treat waste solutions and/or waste solids to lower the impact of waste disposal by recycling treated solutions or solids to a process.

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DEFINITIONS OF MINING, BENEFICIATION, AND MINERAL PROCESSING WASTE

The EPA, through the RCRA, regulates hazardous waste under Subtitle C, and individual states regulate nonhazardous waste under Subtitle D. Congress required that RCRA exclude "solid waste from the extraction, beneficiation, and processing of ores and minerals from regulation as a hazardous waste" (Housman 1999). In 1980, Congress passed the Bevill Amendment, which amended the RCRA to exempt these wastes from regulation under Subtitle C. For this reason, these wastes are commonly designated as Bevill wastes. See Housman (1999) and Luther (2013) for detailed histories of the selection of "special" excluded waste from regulation as a hazardous waste. EPA's excluded special wastes are presented in Table 1 (EPA 2009), and excluded mining and mineral processing wastes are listed in Table 2 (EPA 2009).

The 20 mineral processing wastes (designated Bevill wastes) listed in Table 2 are excluded from the EPA hazardous waste listing. In 40 CFR Section 261.4(b), the EPA (2009) states the following:

> Solid waste from the extraction, beneficiation, and processing of ores and minerals (including coal, phosphate rock, and overburden from the mining of uranium ore), except as provided by Sec. 266.112 of this chapter for facilities that burn or process hazardous waste.
>
> (i) For purposes of Sec. 261.4(b)(7) beneficiation of ores and minerals is restricted to the following activities; crushing; grinding; washing; dissolution; crystallization; filtration; sorting; sizing; drying; sintering; pelletizing; briquetting; calcining to remove water and/or carbon dioxide; roasting, autoclaving, and/or chlorination in preparation for leaching (except where the roasting (and/or autoclaving and/or chlorination)/leaching sequence produces a final or intermediate product that does not undergo further beneficiation or processing); gravity concentration; magnetic separation; electrostatic separation; flotation; ion exchange; solvent extraction; electrowinning; precipitation; amalgamation; and heap, dump, vat, tank, and in situ leaching.
>
> (ii) For the purposes of Sec. 261.4(b)(7), solid waste from the processing of ores and minerals includes only the following wastes as generated:
>
> (iii) A residue derived from co-processing mineral processing secondary materials with normal beneficiation raw materials or with normal mineral processing raw materials remains excluded under paragraph (b) of this section if the owner or operator:
>
> (A) Processes at least 50 percent by weight normal beneficiation raw materials or normal mineral processing raw materials; and,
>
> (B) Legitimately reclaims the secondary mineral processing materials.

The Bevill exclusion exempts the 20 wastes listed in Table 2 from Subtitle C hazardous waste regulation; however, it does not provide protection from liability under other EPA regulations, including CERCLA and the CWA. Luther (2013) states that

> Exemption from Subtitle C does not mean the waste is unregulated. As noted above, the waste is subject to other state or federal regulatory requirements. Those "other" requirements would include any established by individual states, including requirements established under their solid waste management programs. Potentially applicable federal regulatory requirements include those established under the

Table 1 EPA exclusions for "special" waste

§261.4(b)(1) Household Hazardous Waste
§261.4(b)(2) Agricultural Waste
§261.4(b)(3) Mining Overburden
§261.4(b)(4) Fossil Fuel Combustion Waste (Bevill)
§261.4(b)(5) Oil, Gas, and Geothermal Wastes (Bentsen Amendment)
§261.4(b)(6) Trivalent Chromium Wastes
§261.4(b)(7) Mining and Mineral Processing Wastes (Bevill)
§261.4(b)(8) Cement Kiln Dust (Bevill)
§261.4(b)(9) Arsenically Treated Wood
§261.4(b)(10) Petroleum Contaminated Media and Debris from Underground Storage Tanks
§261.4(b)(11) Injected Groundwater
§261.4(b)(12) Spent Chlorofluorocarbon Refrigerants
§261.4(b)(13) Used Oil Filters
§261.4(b)(14) Used Oil Distillation Bottoms
§261.4(b)(15) Landfill Leachate or Gas Condensate Derived from Certain Listed Wastes

Source: EPA 2009
Note: Emphasis added by chapter author.

Table 2 EPA exclusions for mining and mineral processing wastes (Bevill)

(A) Slag from primary copper processing
(B) Slag from primary lead processing
(C) Red and brown muds from bauxite refining
(D) Phosphogypsum from phosphoric acid production
(E) Slag from elemental phosphorus production
(F) Gasifier ash from coal gasification
(G) Process wastewater from coal gasification
(H) Calcium sulfate wastewater treatment plant sludge from primary copper processing
(I) Slag tailings from primary copper processing
(J) Fluorogypsum from hydrofluoric acid production
(K) Process wastewater from hydrofluoric acid production
(L) Air pollution control dust/sludge from iron blast furnaces
(M) Iron blast furnace slag
(N) Treated residue from roasting/leaching of chrome ore
(O) Process wastewater from primary magnesium processing by the anhydrous process
(P) Process wastewater from phosphoric acid production
(Q) Basic oxygen furnace and open hearth furnace air pollution control dust/sludge from carbon steel production
(R) Basic oxygen furnace and open hearth furnace slag from carbon steel production
(S) Chloride process waste solids from titanium tetrachloride production
(T) Slag from primary zinc processing

Source: EPA 2009
Note: Emphasis added by chapter author.

> Clean Water Act (CWA) and Safe Drinking Water Act (SDWA). Commonly implemented by authorized states, both CWA and SDWA requirements apply to the management of some Bevill-Bentsen waste. For example, CWA requires that discharges of pollutants to surface waters (e.g., wastewater discharges to a river, bay, or ocean) must be authorized by a permit issued under the National Pollutant Discharge Elimination System (NPDES) program. Wastewater discharges to publicly owned treatment works (POTWs) are also subject to NPDES permitting requirements. Also, the SDWA regulates subsurface injection of fluids, including wastewater, pursuant to regulations established under the Underground Injection Control (UIC) program.

In general, the EPA views mining and beneficiation solids that are exempted from Subtitle C hazardous waste management to be those solids that have undergone physical changes but have not been transformed by chemical or temperature actions. The basic distinction between *beneficiation* and *mineral processing* wastes, as stated by Housman (1999), is as follows:

> Beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. Where heat or chemicals, such as acid, are applied in a beneficiation operation, it is generally to drive off impurities (e.g., water), dissolve mineral values in a solution as a means of separation (leaching), or retrieve dissolved values from a solution (e.g., crystallization or solvent extraction). A chemical change in the mineral value does not typically occur in beneficiation.
>
> Mineral Processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral into a more useful chemical form. This is often done by using heat or chemical reactions to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral-processing wastes are derived from melting and chemical changes.

NON-EXCLUDED MINERAL PROCESSING WASTE

All mineral processing solid wastes not listed in Table 2 are not excluded as hazardous waste; and treatment, handling, storage, and disposal of those wastes must abide by the RCRA regulations for hazardous waste. This is also true for some extractive metallurgical wastewater and waste solids. Hazardous solid waste is categorized as "listed" waste and "characteristic" waste.

Listed Waste

The EPA has determined that some wastes are hazardous, and they must be handled in compliance with the RCRA established hazardous waste regulations. These wastes are designated as listed wastes and are categorized as *F* (wastes from nonspecific sources; EPA 1981a), *K* (wastes from specific sources; EPA 1981b), and *P* and *U* (discarded commercial chemical products; EPA 1981c). Handling and disposal of these wastes must follow Subtitle C regulations with respect to treatment, storage, and disposal requirements (EPA 2014a). The EPA has specified best demonstrated available technologies (BDATs) for all the listed wastes, both wastewater and non-wastewater (solids). The BDAT documents support the selection of the appropriate treatment technology to minimize mobility or toxicity of the hazardous constituents, and the EPA has established standards that all listed and new hazardous waste must meet. These standards must be met for the designated solid waste or wastewater; however, alternative treatments can be used if the resulting toxicity characterization leach procedure (TCLP) tests confirm that the hazardous constituent is controlled to levels less than the designated standard. BDAT documentation reports for all listed wastes can be found using the National Service Center for Environmental Publications (EPA 2015a).

Characteristic Waste

If a waste is not a listed waste, it may still be deemed a hazardous characteristic waste. A waste is defined as a characteristic waste by evaluating whether it shows any or all of four characteristics:

1. Ignitability (D001; EPA 2012a)
2. Corrosivity (D002; EPA 2012b)
3. Reactivity (D003; EPA 2012c)
4. Toxicity (D004, EPA 2012d)

The toxicity characteristic designation for wastewaters and waste solids created in some of the mineral processing and extractive metallurgical industries is of special importance. Toxicity of a waste solid is determined by a single test protocol, the TCLP. If a wastewater exceeds the TCLP listed concentrations, then it is deemed a hazardous water without being subjected to the TCLP protocol and it must be treated. The TCLP method is designated as EPA Method 1311. The TCLP test protocol consist of exposing a waste solid material to a buffered glacial acetic acid leach procedure (EPA 1992). Eight characteristic elements, four pesticides, two herbicides, and 26 organic compounds must be evaluated by the TCLP test. The results of applying the TCLP test to a solid waste determine whether the waste must be designated as hazardous or not; if the solution concentration in the TCLP filtrate contains greater than 100 times the maximum concentration level (MCL, drinking water standard), then the waste is deemed hazardous. The "characteristic" regulatory concentrations for the eight elements are presented in Table 3. Some states require a different or additional test procedure and additional element analyses; for example, California requires the waste extraction test (WET) and designates the soluble threshold limit concentrations as its regulatory concentrations. California's "characteristic" regulatory concentrations are set for 17 elements, 10 pesticides, and 10 organic compounds. The regulatory levels for the elements are presented in Table 4

(DTSC 2015a). A comparison of the differences between the TCLP test and WET is presented in Table 5 (DTSC 2015b).

Land Disposal Restrictions

According to the EPA (1998, 2005)

> The primary goal of the Resource Conservation and Recovery Act (RCRA) Subtitle C program is to protect human health and the environment from the dangers associated with generation, transportation, treatment, storage, and disposal of hazardous waste. Disposal of hazardous waste on the land is a practice of particular concern to the RCRA program. Land disposal units, such as landfills and surface impoundments, must comply with stringent requirements for liners, leak detection systems, and groundwater monitoring. The land disposal restrictions (LDR) provide a second measure of protection from threats posed by hazardous waste disposal. The LDR program ensures that hazardous waste cannot be placed on the land until the waste meets specific treatment standards to reduce the mobility or toxicity of the hazardous constituents in the waste.

Table 3 TCLP regulatory levels

Metals	TCLP Regulatory Level, mg/L	EPA Hazardous Waste Designation
As	5.0	D004
Ba	100.0	D005
Cd	1.0	D006
Cr	5.0	D007
Pb	5.0	D008
Hg	0.2	D009
Se	1.0	D010
Ag	5.0	D011

Source: EPA 1992

Table 4 Soluble threshold limit concentrations

Metals	TCLP Regulatory Level, mg/L	California Regulatory Level, mg/L
As	5.0	5.0
Ba	100.0	100.0
Cd	1.0	1.0
Cr	5.0	5.0
Pb	5.0	5.0
Hg	0.2	0.2
Se	1.0	1.0
Ag	5.0	5.0
Be		0.075
Co		80
Cu		25
Mo		350
Ni		20
Tl		7.0
V		24
Zn		250

Adapted from DTSC 2015a

All solid waste, including mineral processing and extractive metallurgical wastes that are not excluded but fail the TCLP test, must be treated to further stabilize the waste before it can be placed in an EPA-permitted treatment, storage, and disposal facility (TSDF). The stabilized waste must then pass the TCLP test to standards established under the land disposal restrictions (LDR; commonly called LBR) universal treatment standards before the disposal of the waste is allowed. The present universal treatment standard requirements for elements are presented in Table 6 with a comparison to the TCLP toxicity characterization concentrations.

Treatment, Storage, and Disposal Facilities

A defined hazardous waste must be placed in an EPA- or state-permitted TSDF. The regulations for different activities are cited in Figure 1.

According to federal regulations, a TSDF must perform one or more of the following functions (EPA 2014a):

Table 5 Comparison of TCLP and WET methods

Toxicity Characterization Leach Procedure	Waste Extraction Test
Involves 20-fold dilution of the solid portion of the waste to extraction fluid	Involves 10-fold dilution of the solid portion of the waste to extraction fluid
Acetic acid extractant	Citric acid extractant
18 hours extraction	48 hours extraction
7 inorganic (less aggressive than WET)	19 inorganic (in general, more aggressive than TCLP)
23 organic (volatiles use a zero-headspace extractor)	18 organic (zero-headspace extractor not used)

Source: DTSC 2015b

Table 6 Universal treatment standards as specified in the LDR regulations

Element	Toxicity Characterization Level, mg/L	LBR Universal Treatment Standard	
		Wastewater, mg/L	Non-Wastewater in TCLP, mg/L
Antimony	—	1.9	1.15
Arsenic	5.0	1.4	5.0
Barium	100	1.2	21
Beryllium	—	0.82	1.22
Cadmium	1.0	0.69	0.11
Chromium	5.0	2.77	0.6
Lead	5.0	0.69	0.75
Mercury (from retort)	0.2	—	0.2
Mercury—all others	0.2	0.15	0.025
Nickel	—	3.98	11
Selenium	1.0	0.82	5.7
Silver	5.0	0.43	0.14
Thallium	—	1.4	0.2
Vanadium	—	4.3	1.6
Zinc	—	2.61	4.3

Source: EPA 1998, 2015b

Summary Chart

Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) Regulations
(Note: FDSys links are updated at the end of November; this version is 2014)

	Hazardous Waste Management/Permitting Activity	General Requirements	Permit Application Requirements	Closure/Post-Closure Requirements
1	General Facility Standards	264-B & 265-B	NA	NA
2	Preparedness and Prevention	264-C & 265-C	NA	NA
3	Contingency Plan and Emergency Procedures	264-D & 265-D	NA	NA
4	Manifest System, Recordkeeping and Reporting	264-E & 265-E	NA	NA
5	Releases from Solid Waste Management Units	264-F	NA	264.100
6	Groundwater Monitoring	265-F	NA	NA
7	Closure and Post-Closure	264-G & 265-G	NA	264-G & 265-G
8	Financial Assurance Requirements	264-H & 265-H	NA	NA
9	Use and Management of Containers	264-I & 265-I	270.15 & 270.27	264.178
10	Tank Systems	264-J & 265-J	270.16 & 270.27	264.197 & 265.197
11	Surface Impoundments	264-K & 265-K	270.17 & 270.27	264.228 & 265.228
12	Waste Piles	264-L & 265-L	270.18	264.258 & 265.258
13	Land Treatment	264-M & 265-M	270.20	264.280 & 265.280
14	Landfills	264-N & 265-N	270.21	264.310 & 265.310
15	Incinerators	264-O & 265-O & 63-EEE	270.19 & 270.62	264.351 & 265.351
16	Thermal Treatment	265-P	NA	265.381
17	Chemical, Physical, Biological Treatment	265-Q	NA	265.404
18	Underground Injection	265-R	NA	NA
19	Special Provisions for Cleanup	264-S	NA	NA
20	Drip Pads	264-W & 265-W	270.26	264.575 & 265.445
21	Miscellaneous Units	264-X	270.23	264.603
22	Air Emission Standards for Process Vents	264-AA & 265-AA	NA	NA
23	Air Emission Standards for Equipment Leaks	264-BB & 265-BB	NA	NA
24	Air Emission Standards for Tanks, Surface Impoundments and Containers	264-CC & 265-CC	NA	NA
25	Containment Buildings	264-DD & 265-DD	NA	264.1102 & 265.1102
26	Munitions and Explosives Storage	264-EE & 265-EE	NA	264.1202 & 265.1202
27	Solid Waste Management Units	264-F & 264-S	NA	264.101
28	Boilers/Industrial Furnaces	266-H & 63-EEE	270.66	NA
29	Land Disposal Restrictions	268	NA	NA
30	Hazardous Waste Permitting Program General Requirements	270	270	NA
31	Administrative Procedures Act Requirements for RCRA Permitting	124	124-B & 124-G	NA

Source: EPA 2014a

Figure 1 TSDF regulations by activity

> **Treatment**—Any method, technique, or process, including neutralization, designed to change the physical, chemical, or biological character or composition of any hazardous waste so as to neutralize such waste, or so as to recover energy or material resources from the waste, or so as to render such waste non-hazardous, or less hazardous; safer to transport, store, or dispose of; or amenable for recovery, amenable for storage, or reduced in volume.
>
> **Storage**—The holding of hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere.
>
> **Disposal**—The discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof may enter the environment or be emitted into the air or discharged into any waters, including ground waters.

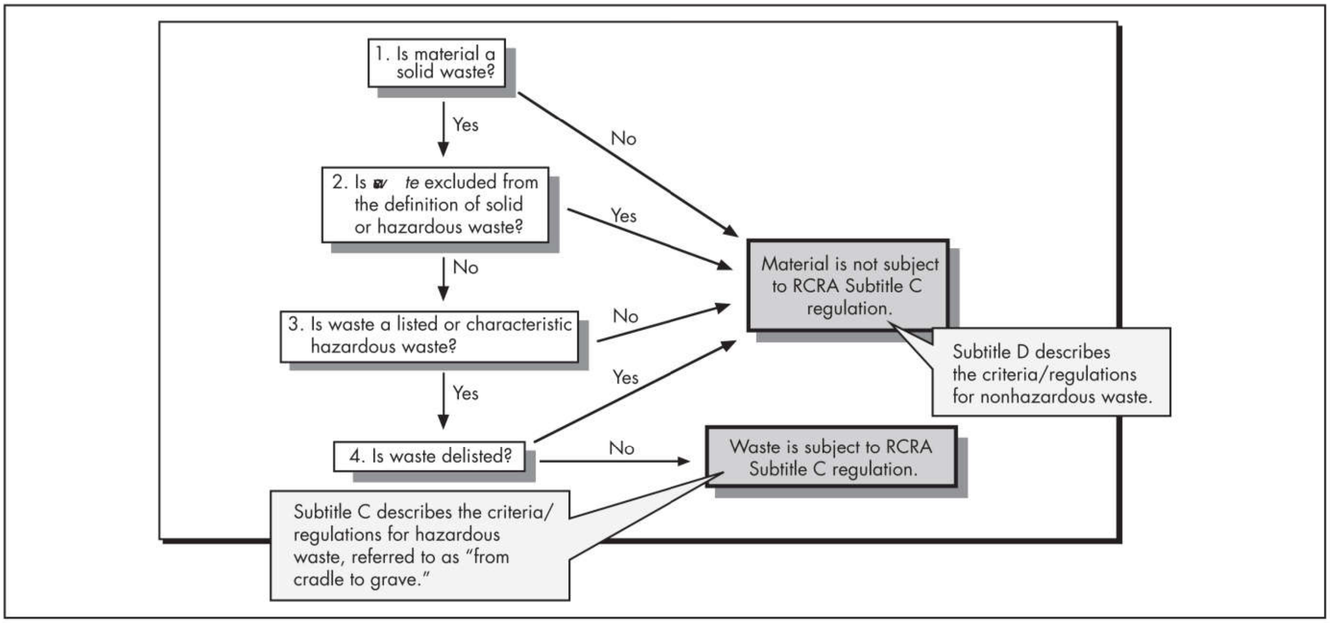
Care must be exercised in selecting a TSDF for disposing of a mineral processing or extractive metallurgical waste. It is important that a qualified TSDF is chosen because, according to RCRA, the "generator" of a waste is responsible for that waste from "cradle to grave." A company will share in the cost of cleanup if the hazardous waste is mismanaged, even if the TSDF facility is permitted to operate.

National Pollutant Discharge Elimination System

The CWA (1972, with many amendments thereafter) authorized the establishment of the National Pollutant Discharge Elimination System (NPDES) program (EPA 2015e). The NPDES requires permits for any water discharges into the waters of the United States, including publicly (or privately) owned (wastewater) treatment works. The permitting program is, with some exceptions, administered by authorized states. The states provide the permits, and monitor and enforce the regulations for the water discharges. The EPA has oversight on the states' programs and offers guideline regulations to the states; the states can accept the guidelines or set their own regulations, which may be more stringent than the federal requirements. Section 518(e) and (h) of the CWA authorizes the EPA to treat tribes in a manner similar to states for the purposes of administering certain CWA programs for tribal waters.

Determining Whether Solid Waste Is Hazardous

The process of determining if a mineral processing or extractive metallurgy solid waste is deemed hazardous can be very confusing, and competent environmental and legal assistance are required. A simplified schematic of the procedure is presented in Figure 2. It shows a series of decision steps. Step 1 asks, Is the waste a solid waste? (A *solid waste* is defined as any material that is discarded by being either abandoned, inherently waste-like, or recycled.) Is it a sludge from a wastewater treatment plant? If the answer is yes, then the waste



Source: EPA 1998

Figure 2 Waste treatment decision tree

consideration moves to step 2; if the answer is no, then the waste doses not need to be treated as an RCRA Subtitle C hazardous waste. Step 2 asks, Is the waste excluded from being required to follow hazardous waste protocols for handling and storage? If yes, then the waste does not have to follow hazardous protocols; if no, then the waste consideration moves to step 3. Step 3 asks, Is the waste a listed waste? If it is, it must follow the Subtitle C protocol; if it is a non-excluded waste, it must be evaluated to determine whether it is a characteristic waste, that is, whether the waste has one or more of the four characteristics (ignitability, corrosivity, reactivity, toxicity). Generally, mineral processing and extractive metallurgy wastes will need to be tested for toxicity. The determining test is the TCLP test. If the waste passes the TCLP test (where the hazardous constituent is less than 100 times the MCL limiting concentration), then it is deemed nonhazardous. If it fails the test, then the waste moves to step 4. Step 4 states, If the waste has been stabilized so that it passes the TCLP test, then it may be "delisted" and treated as a nonhazardous waste. If the waste is not delisted, then it must follow the Subtitle C regulation.

EFFLUENT SOLUTIONS

Mineral processing and extractive metallurgical operations create appreciable wastewater and waste solid products that have to be handled, treated for recycle, or treated for environmentally safe disposal. Complete coverage of all waste products is beyond the scope of this chapter. The topics covered here include acid mine drainage and hydrometallurgical effluent solutions, emphasizing arsenic, selenium, and metals.

Acid Mine Drainage

Acid mine drainage (AMD) or acid rock drainage (ARD) is often considered to be a major pollutant in countries that have historic or current mining activities. Its generation, mobility, and attenuation involve many complex processes that are based on combinations of physical, chemical, and biological interactions. Although AMD is an important topic for the mining, mineral processing, and extractive metallurgical industries, it is not the focus of this chapter. However, interested readers are referred to the following information sources.

Detailed discussions of ARD topics are presented by Verburg (2011) in the *SME Mining Engineering Handbook* (Darling 2011). The presented information is primarily based on the *Global Acid Rock Drainage Guide* (INAP 2014) and includes coverage of the following topics: formation of ARD and ARD management (characterization, prediction, prevention and mitigation, treatment, monitoring, and performance assessment). Nordstrom et al. (2015) discuss the hydrogeochemistry and microbiology of ARD:

> The extraction of mineral resources requires access through underground workings, or open pit operations, or through drillholes for solution mining. Additionally, mineral processing can generate large quantities of waste, including mill tailings, waste rock and refinery wastes, heap leach pads, and slag. Thus, through mining and mineral processing activities, large surface areas of sulfide minerals can be exposed to oxygen, water, and microbes, resulting in accelerated oxidation of sulfide and other minerals and the potential for the generation of low-quality drainage. The oxidation of sulfide minerals in mine wastes is accelerated by microbial catalysis of the oxidation of aqueous ferrous iron and sulfide. These reactions, particularly when combined with evaporation, can lead to extremely acidic drainage and very high concentrations of dissolved constituents. Although acid mine drainage is the most prevalent and damaging environmental concern associated with mining activities, generation of saline, basic and neutral drainage containing elevated concentrations of dissolved metals, non-metals, and metalloids has

> recently been recognized as a potential environmental concern. Acid neutralization reactions through the dissolution of carbonate, hydroxide, and silicate minerals and formation of secondary aluminum and ferric hydroxide phases can moderate the effects of acid generation and enhance the formation of secondary hydrated iron and aluminum minerals which may lessen the concentration of dissolved metals. Numerical models provide powerful tools for assessing impacts of these reactions on water quality.

Lapakko (2015) offers a preoperational assessment of mining operations:

> Environmental assessments are conducted prior to mineral development at proposed mining operations. Among the objectives of these assessments is prediction of solute release from mine wastes projected to be generated by the proposed mining and associated operations. This paper provides guidance to those engaged in these assessments and, in more detail, provides insights on solid-phase characterization and application of kinetic test results for predicting solute release from waste rock. The logic guiding the process is consistent with general model construction practices and recent publications. Baseline conditions at the proposed site are determined and a detailed operational plan is developed and imposed upon the site. Block modeling of the mine geology is conducted to identify the mineral assemblages present, their masses and compositional variations. This information is used to select samples, representative of waste rock to be generated, that will be analyzed and tested to describe characteristics influencing waste rock drainage quality. The characterization results are used to select samples for laboratory dissolution testing (kinetic tests). These tests provide empirical data on dissolution of the various mineral assemblages present as waste rock. The data generated are used, in conjunction with environmental conditions, the proposed method of mine waste storage, and scientific and technical principles, to estimate solute release rates for the operational scale waste rock Common concerns regarding waste rock are generation of acidic drainage and release of heavy metals and sulfate. Key solid phases in the assessments are those that dissolve to release acid and sulfate (iron sulfides, soluble iron sulfates, hydrated iron-sulfate minerals, minerals of the alunite–jarosite group), those that dissolve to neutralize acid (calcium and magnesium carbonates, silicate minerals), and those that release trace metals (trace metal sulfides, hydrated trace metal-sulfate minerals). Conventional mineralogic, petrographic, and geochemical analyses generally can be used to determine the quantities of these minerals present and to describe characteristics that influence their dissolution. A key solid-phase characteristic is the mineral surface area exposed for reaction, which is influenced by mode of occurrence (included, interstitial, and liberated) and the extent of mineral surface coating. Short-term dissolution tests can estimate the extent of hydrated sulfate minerals present. Longer term dissolution tests are necessary to describe the dependence of drainage pH and solute release rates on solid-phase variation. The extensive data compiled from baseline pre-development definition, the operational plan, solid-phase characterization, and dissolution testing are ultimately synthesized by means of a modeling exercise requiring considerable technical and scientific expertise. The predicted rates (model outputs) are expressed as probability distributions to allow assessment of risk. This exercise must be technically defensible and transparent so that regulators can confidently assess the results and evaluate the operational plan proposed. Technical and non-technical challenges involved in implementing such programs are identified to benefit management planning for both industry and government.

In addition, Parbhakar-Fox and Lottermoser (2015) provide a review of ARD prediction methods:

> Failure to accurately predict acid rock drainage (ARD) leads to long-term impacts on ecosystems and human health, in addition to substantial financial consequences and reputational damage to operators. Currently, a range of chemical static and kinetic tests are used to evaluate the acid producing nature of materials, from which risk assessments are prepared and waste classification schemes designed. However, these well-established tests and practices have inherent limitations, for example: (i) best-practice sampling is not pursued; (ii) risk assessments rely on limited static and kinetic test data, thus compromising the accuracy of resulting ARD block models; (iii) static tests are completed off-site and do not reflect actual field measurements; (iv) kinetic test data do not become available until later stages of mine development; (v) waste classification schemes generally categorise materials as only three types (i.e., PAF, NAF and UC) with other drainage forms (e.g., neutral metalliferous or saline) not considered; and (vi) conventional testing fails to consider that reactivity of waste is controlled by parameters other than chemistry (e.g., microbiology, type and occurrence of minerals, texture and hardness). Thus, accurate prediction is challenging because of the multifaceted processes leading to ARD. Hence, risk assessments need to consider mineralogical, textural and geometallurgical rock properties in addition to predictive geochemical test data. Instead, a new architecture of integrative, staged ARD testing should be pursued. Better ARD prediction must start with improving the definition of geoenvironmental models and waste units. Then, a range of low-cost and rapid tests for the screening of samples should be conducted on site prior to the performance of established tests and advanced analyses using state-of-the-art laboratories. Such an approach to ARD prediction would support more accurate and cost-effective waste management during operation, and ultimately less costly mine closure outcomes.

Included in the *SME Mining Engineering Handbook* is coverage of waste disposal and contamination management as related to mining, beneficiation, and mineral processing (Borden 2011). Topics covered include mineral waste, waste characterization and impact prediction, waste management strategy and facility environmental design, ongoing management and monitoring, nonmineral waste, hazardous materials and contamination control, contaminated water management, and contaminated site management. The discussion focuses on disposal of mining and beneficiation waste but does not cover wastewater and solid waste created during the hydrometallurgical processing of minerals to produce a metal product. Therefore, topics including in-plant processing unit operations are not covered, for example, heavily contaminated smelter blowdown wastewater and other unit operations applied to remove hazardous constituent as solid waste product. Recall from the discussion presented previously that EPA defines *mineral processing waste* differently than Borden does; that is, the EPA defines *mineral processing* as follows (Housman 1999):

> [Mineral] Processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral into a more useful chemical form. This is often done by using heat or chemical reactions to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral-processing wastes are derived from melting and chemical changes.

Other publications that address mining and beneficiation waste include Jamieson et al. (2015) who discuss the mineralogical characterization of mine waste:

> The application of mineralogical characterization to mine waste has the potential to improve risk assessment, guide appropriate mine planning for planned and active mines and optimize remediation design at closed or abandoned mines. Characterization of minerals, especially sulphide and carbonate phases, is particularly important for predicting the potential for acidic drainage and metal(loid) leaching. Another valuable outcome from mineralogical studies of mine waste is an understanding of the stability of reactive and metal(loid)-bearing minerals under various redox conditions. This paper reviews analytical methods that have been used to study mine waste mineralogy, including conventional methods such as X-ray diffraction and scanning electron microscopy, and advanced methods such as synchrotron-based microanalysis and automated mineralogy. We recommend direct collaboration between researchers and mining companies to choose the optimal mineralogical techniques to solve complex problems, to co-publish the results, and to ensure that mineralogical knowledge is used to inform mine waste management at all stages of the mining life cycle. A case study of arsenic-bearing gold mine tailings from Nova Scotia is presented to demonstrate the application of mineralogical techniques to improve human health risk assessment and the long-term management of historical mine wastes.

Kossoff et al. (2014) provide a review of mine tailings dams:

> On a global scale demand for the products of the extractive industries is ever increasing. Extraction of the targeted resource results in the concurrent production of a significant volume of waste material, including tailings, which are mixtures of crushed rock and processing fluids from mills, washeries or concentrators that remain after the extraction of economic metals, minerals, mineral fuels or coal. The volume of tailings is normally far in excess of the liberated resource, and the tailings often contain potentially hazardous contaminants. A priority for a reasonable and responsible mining organization must be to proactively isolate the tailings so as to forestall them from entering ground waters, rivers, lakes and the wind. There is ample evidence that, should such tailings enter these environments they may contaminate food chains and drinking water. Furthermore, the tailings undergo physical and chemical change after they have been deposited. The chemical changes are most often a function of exposure to atmospheric oxidation and tends to make previously, perhaps safely held contaminants mobile and available. If the tailings are stored under water, contact with the atmosphere is substantially reduced, thereby forestalling oxygen-mediated chemical change. It is therefore accepted practice for tailings to be stored in isolated impoundments under water and behind dams. However, these dams frequently fail, releasing enormous quantities of tailings into river catchments. These accidents pose a serious threat to animal and human health and are of concern for extractive industries and the wider community. It is therefore of importance to understand the nature of the material held within these dams, what best safety practice is for these structures and, should the worst happen, what adverse effects such accidents might have on the wider environment and how these might be mitigated. This paper reviews these factors, covering the characteristics, types and magnitudes, environmental impacts, and remediation of mine tailings dam failures.

The EPA's *Reference Guide to Treatment Technologies for Mining-Influenced Water* presents current information with respect to technology, constituents treated (metals, nitrate, arsenic, selenium), system operations, long-term maintenance, system limitations, costs, and effectiveness (EPA 2014b). An excerpt follows:

> This report provides an overview of select mining-influenced water (MIW) treatment technologies used or piloted as part of remediation efforts at mine sites. The report is intended to provide information on treatment technologies for MIW to federal, state and local regulators, site owners and operators,

consultants, and other stakeholders. The technologies described in this report are applicable to treatment of water from both coal and hard-rock mine operations. The report provides short descriptions of treatment technologies and presents information on the contaminants treated, pre-treatment requirements, long-term maintenance needs, performance and costs. Sample sites illustrate considerations associated with selecting a technology. Website links and sources for more information on each topic are also included.

MIW is defined as any water whose chemical composition has been affected by mining or mineral processing and includes acid rock drainage (ARD), neutral and alkaline waters, mineral processing waters and residual waters. MIW can contain metals, metalloids and other constituents in concentrations above regulatory standards. MIW affects over 10,000 miles of receiving waters in the United States, primarily by acidic drainage.

Hydrometallurgical Effluent Solutions

The EPA has established effluent limitation guideline standards for the treatment of industrial wastewater discharges to surface waters and municipal sewage treatment plants (EPA 2015c, 2015d). The guidelines are based on performance of present treatment and commonly used control technologies. The guidelines are included as a part of individual facility NPDES permits. The EPA has promulgated effluent guidelines and standards for the mineral, mining, and processing industries (40 CFR Part 436). The guidelines and regulations cover wastewater discharges from mine drainage, and mineral and extraction processing operations. Example effluent guidelines for smelter and refining operations are summarized in Table 7 (recommended global guidelines for all smelting and refining operations).

Table 7 Effluent levels for nickel, copper, lead, zinc, and aluminum smelting and refining

Pollutant	Smelting Type	Units	Guideline Value
Aluminum	Aluminum	mg/L	0.2
Arsenic	Copper, lead, and zinc	mg/L	0.05
Cadmium	Nickel, copper	mg/L	0.05
Chemical oxygen demand	All	mg/L	50
Copper	Copper	mg/L	0.1
Fluoride	Aluminum	mg/L	5
Hydrocarbons	Aluminum	mg/L	5
Lead	—	—	0.1
Mercury	All	mg/L	0.01
Nickel	Copper, lead, and zinc	mg/L	0.1
pH	All	mg/L	6–9
Temperature increase	All	°C	<3°
Total suspended solids	All	mg/L	20
Toxicity	—To be determined on a case-specific basis—		
Zinc	Copper, lead, and zinc	mg/L	0.2

Source: World Bank Group 2007

Arsenic

The removal of arsenic from hydrometallurgical solutions, wastewaters, and AMD waters has been and continues to be an important research and regulatory topic. The EPA has promulgated regulations based on its determination of the BDAT to be used for listed and characteristic waste-containing arsenic. The chosen BDAT is ferrihydrite adsorption of arsenic (Rosengrant and Fargo 1990). Therefore, a guide to the literature is presented here that is focused on the removal of arsenic from aqueous solutions using ferric precipitation and subsequent adsorption of arsenic and on the long-term outdoor storage of the arsenic-bearing products (Twidwell and McCloskey 2011). The following guide is arranged in the following order: summary of current industrial processes, a presentation for those who want further detailed information on ferrihydrite formation and properties, and ferrihydrite/arsenic formation and stability of arsenic-bearing waste products.

Summary of current industrial processes. Two ferric precipitation arsenic removal technologies are presently practiced by industry throughout the world: ambient temperature ferrihydrite arsenic adsorption/co-precipitation and elevated temperature, elevated pressure precipitation of scorodite/ferric arsenate. The ambient temperature technology is relatively simple, and the presence of commonly associated metals (copper, lead, zinc) and gypsum have a stabilizing effect on the long-term stability of the outdoor storage of the product. The disadvantages of the adsorption technology include the following:

- A relatively large amount of waste material is created (Fe/As mole ratio varies; it is usually approximately 3–4 but can be as high as 10), which may be difficult to filter.
- The arsenic must be present in the fully oxidized state (arsenate).
- The presence of competitive associated anionic species may negatively influence the adsorption of arsenate.
- The long-term stability of the product in the presence of reducing substances and bacterial activity must be determined.

The second technology practiced at several copper smelting facilities is arsenic removal by precipitation of scorodite in autoclaves. The advantage of the scorodite process over the ferrihydrite technology is that less waste is formed (Fe/As mole ratio is one, greater density, and better thermodynamic stability). The disadvantages of scorodite/ferric arsenate precipitation are that the treatment process is more capital and energy intensive; the compound may dissolve incongruently if the pH is greater than 3; and its long-term storage may not be stable under reducing and/or anaerobic bacterial conditions (Erbs et al. 2010; Kocar et al. 2010; Jones et al. 2000; Xie et al. 2009).

Currently, the ambient temperature/ambient pressure ferrihydrite/arsenate process is more commonly applied throughout the world. However, recent research has shown that scorodite can be formed under less intense non-autoclave operating conditions, that is, elevated temperature but ambient pressure processing. This technique will likely be adopted in the future; to date, one smelter, the Dowa smelter in Japan (Fujita et al. 2012), has adopted this process. The various scorodite formation processes are summarized as follows (Twidwell 2014a, 2014b):

1. Autoclave hydrothermal precipitation of scorodite from acidic solutions (pH ~1, ~150°C) containing Fe(III) and As(V) (Gomez et al. 2011).
2. Elevated temperature ambient pressure precipitation from acidic solutions (pH ~1, 90°–95°C) containing Fe(III) and As(V) or As(III) (Demopoulos 2008, 2005).
3. Intermediate temperature ambient pressure precipitation by in situ oxidation of Fe(II) in the presence of As(V) from acidic solutions (pH ~1, ~70°C, 95°C) (Fujita et al. 2012).
4. Intermediate temperature ambient pressure precipitation by biogenic in situ oxidation of Fe(II) in the presence of As(V) from acidic solutions (pH ~1, ~70°C) (Okibe et al. 2013).
5. Intermediate temperature ambient pressure precipitation by biogenic in situ oxidation of Fe(II) and As(III) from acidic solutions (pH ~1, ~70°C) (Okibe et al. 2014).

Riveros et al. (2001) concluded the following from their extensive review of the literature:

> For practical purposes, arsenical ferrihydrite can be considered stable provided the Fe/As molar ratio is greater than 3, the pH is slightly acidic and that it does not come in contact with reducing substances such as reactive sulfides or reducing conditions such as deep water, bacteria or algae.

Swash et al. (2000) concluded that from the point of view of safe disposal of arsenic, there is no clear experimental evidence favoring the low-temperature precipitates over the high-temperature precipitates. A detailed review of the stability of scorodite, ferrihydrite, and ferrihydrite/arsenate adsorption is presented by Welham et al. (2000). Their conclusions are as follows:

> There are significant problems with the use of jarosite and scorodite as phases for the disposal of iron and/or arsenic from metallurgical systems. Neither phase is stable under typical atmospheric weathering conditions with transformation to goethite predicted to occur. The currently permitted discharge level of arsenic is only achieved due to the slow kinetics of the transformation releasing arsenic over time. Crystalline scorodite is two orders of magnitude less soluble than amorphous iron(III) arsenate precipitate often formed in low temperature systems.

Ferrihydrite formation and properties (Twidwell and McCloskey 2011). Important reviews detailing conditions for formation and the stability of ferrihydrite are presented by Jambor and Dutrizac (1998) and Cornell and Schwertmann (1996, 2003). The reviews by Jambor and Dutrizac (314 references) and Cornell and Schwertmann (approximately 1,500 references) are indeed excellent sources of information on ferrihydrite occurrence, structure, chemical composition, adsorptive capacity for cations and anions, and transformation rate as well as a summary of the factors that influence ferrihydrite's transformation to hematite or goethite. Schwertmann and Cornell (2000) have published a "recipe" book that details how to prepare iron oxides in the laboratory, including ferrihydrite, hematite, and goethite. Many of the experimental studies reported in the literature reference this publication.

Literature-reported characteristic features of ferrihydrite and its conversion to more crystalline forms (goethite and hematite) are briefly summarized here. Ferrihydrite is characterized by X-ray diffraction as having a two-line or six-line structure, which relates to the number of broad peaks present. Two-line ferrihydrite is formed by rapid hydrolysis to pH 7 at ambient temperature. Six-line ferrihydrite is formed by rapid hydrolysis at elevated temperature and is generally more crystalline than two-line ferrihydrite. However, Schwertmann and Cornell (2000) have demonstrated that either can be formed at ambient temperature by controlling the rate of hydrolysis (i.e., less crystalline two-line forms at rapid hydrolysis rates, whereas six-line forms if the precipitation is conducted at lower rates, and lepidocrocite forms if the rate of addition of sodium hydroxide is slow enough). Crystallite sizes have been reported to be 2–4 nm and 5–6 nm for two-line and six-line ferrihydrite, respectively. The surface area of freshly precipitated two-line ferrihydrite is greater than 340 m^2/g (Paktunc et al. 2008). The particle size of aggregated ferrihydrite is usually quoted in the range of 3–10 µm. Hohn et al. (2006) determined the mean minimum particle size to be 1.5–2.0 nm at pH 7. Hohn et al. also demonstrated that two-line ferrihydrite and arsenic-loaded (7%) ferrihydrite prepared at pH 4 and 7 self-flocculate to a mean agglomerate size of 5–10 µm.

The rate of transformation of ferrihydrite to hematite or goethite when suspended in an aqueous medium has been discussed in great detail by Cornell and Schwertmann (2003) and by Jambor and Dutrizac (1998) and many others. The rate of transformation is a function of time, temperature, and pH. For example, conversion of pure two-line ferrihydrite to hematite at 25°C is half complete in 280 days at pH 4 but is completely converted at 100°C in 4 hours (Cornell and Schwertzman 2003). Transformation of ferrihydrite results in a relatively large change in surface area (e.g., freshly prepared two-line ferrihydrite showed a surface area of about 150 m^2/g that when converted to goethite at 25°C was reduced to 92 m^2/g; when converted to goethite at 90°C, the area was reduced to 9 m^2/g). Many investigators have pointed out that pure ferrihydrite converts rapidly and the conversion results in a significant decrease in surface area. However, in real industrial systems, the ferrihydrite conversion rate may be mitigated (changed from days to perhaps years) by the presence of other species and solution conditions during precipitation and subsequent storage. General factors that have been shown to decrease the rate of conversion of two-line ferrihydrite to more crystalline forms include lower pH; lower temperatures; and presence of silicate, aluminum, arsenic, manganese, metals, sulfate, and organics.

Ferrihydrite/arsenic formation and stability of arsenic-bearing waste products (Twidwell and McCloskey 2011). The EPA promulgated rules for BDATs to be used for the following listed and characteristic waste-containing As and Se: K031, K084, K101, K102, As wastes (D004), Se wastes (D010), and P and U wastes (Rosengrant and Fargo 1990). The specified BDAT for treatment of effluent solutions is arsenic adsorption on ferrihydrite. This technology has also been selected as one of the best available technologies for removing arsenic from drinking water. A brief discussion of the arsenical ferrihydrite literature follows.

Removal from solution. Studies investigating the removal of anions on ferrihydrite surfaces are not new. Municipal water treatment systems have used ferric, ferrous, and aluminum hydroxide precipitation for many years to cleanse heavy metals and phosphates from solution as a final polishing stage. In fact, doping manuals are available for ferric chloride, ferric sulfate, or aluminum sulfate (AWWA 1988a, 1988b). A wide range of arsenic removal results are reported in the literature for the adsorption or co-precipitation of arsenic-bearing iron products. The relatively wide range of results is to be expected because there are several experimental factors that influence the removal. These influencing factors include the ferrihydrite formation procedure; the iron/arsenic mole ratio; pH, time, and initial concentration of arsenic; the anionic environment; the method of agitation; the presence of co-precipitants; and the arsenic valence.

The presence of arsenite, As(III), and other dissolved aqueous species are important aspects that need to be considered when discussing ferrihydrite technology. The normal approach when considering ferrihydrite removal of arsenic is to consider ways to oxidize the As(III) to As(V). It is often stated that As(V) is much more effectively removed by ferrihydrite than As(III). However, the relative removal of As(V) and As(III) depends upon the Fe/As ratio, pH, and whether the arsenic species are present individually or as mixtures. As(III) is often found in appreciable quantities in ambient temperature metallurgical operations and in groundwater and surface waters (Wilson et al. 2001; Borho and Wilderer 1996). In fact, Borho and Wilderer state that approximately 30% of the arsenic present in ground and surface waters used for drinking waters is As(III). The presence of associated ions such as phosphate, sulfate, carbonate, and dissolved organic species can greatly influence the removal of arsenic and the relative long-term stability of ferrihydrite.

Stability of products. Excellent examples of synthesis and transformation rates for scorodite, ferric arsenate, and arsenical ferrihydrite are provided in publications by Paktunc et al. (2008) and Paktunc and Bruggeman (2010). Drahota and Filippi (2009) present a recent review of arsenic mineralization and a description of primary and secondary minerals found at mine and industrial sites. Riveros et al. (2001) have presented a review of the disposal practices and long-term stability of arsenic products in the Canadian metallurgical industry. Paktunc et al. (2008) have investigated the structure of scorodite, ferric arsenate, and arsenical ferrihydrite, and results are presented in their publications. The authors have clarified the distinction between the three forms. For example, scorodite, $FeAsO_4$, is a fully crystallized phase containing a Fe/As mole ratio of 1 ($FeAsO_4$:$3.5H_2O$); ferric arsenate ($FeAsO_4$:4–$7H_2O$) is less crystalline than scorodite; and arsenical ferrihydrite ($5Fe_2O_3$:$9H_2O$) is X-ray amorphous. Ferric arsenate forms at low pH, has a Fe/As mole ratio of one, and is rapidly transformed to scorodite at pH levels below approximately 1.7. Above that pH, ferric arsenate and arsenical ferrihydrite form up to approximately a pH of 4.5 for Fe/As ratios from 1–10. Ferric arsenate was not present at Fe/As ratios of 5 and greater; ferrihydrite and arsenical ferrihydrite predominate. Ferrihydrite converts to a six-line product at these Fe/As ratios and the conversion is a function of aging time. Paktunc et al. (2008) discuss the implications for arsenic releases and controls:

> Common industrial practice is to remove and stabilize arsenic using Fe/As ratios of 3–4. Therefore, the solids are likely mixtures of ferric arsenate and arsenical ferrihydrite. The thought is that ferric arsenate forms and that phase dissolves to form arsenical ferrihydrite which has abundant surface sites for adsorbing arsenate. The applications at higher Fe/As ratios ensure that the more soluble ferric arsenate is dissolved to form the more insoluble arsenical ferrihydrite. At Fe/As ratios above five the two-line ferrihydrite converts to six-line (more crystalline) ferrihydrite but the presence of arsenic in the 2-line structure retards this conversion. Quoting the authors "the kinetics of phase transformations and its dependence on pH would facilitate the development of new technologies for the stabilization of As in mine wastes. Identification of ferric arsenate in mine wastes destined for disposal should be considered critical for the prediction of the short-term and long-term behavior of arsenic in wastes. Disposal options would then need to consider the changes in pH and redox conditions that may occur with time and their bearings on potential As releases.

Generally, arsenical ferrihydrite and scorodite pass the EPA TCLP test and the waste products do not have to follow EPA Subtitle C disposal regulations. However, an important unknown at this time is whether the product from ferrihydrite adsorption of arsenic will be stable if storage conditions are anaerobic or may become anaerobic or contain microbial agents. Erbs et al. (2010) demonstrated that induced reduction conditions using hydroquinone resulted in arsenic and iron reduction and that co-precipitated ferrihydrite showed less arsenic release than adsorbed arsenic on previously precipitated ferrihydrite. Pederson et al. (2006) found that arsenate remained with ferrihydrite when exposed to ascorbic acid until the surface area was insufficient to retain the arsenate. Brannon and Patrick (1987) have demonstrated that anaerobic lake sediments convert As(V) to As(III) (pH 5–8.0). However, when the anaerobic conditions were shifted by aerobic leaching, the previously reduced As(III) was reconverted to more immobile As(V), which was associated with aluminum and iron oxyhydroxides. Chatain et al. (2005a) investigated the effect of controlling the solution redox potential (normal hydrogen electrode reference) and pH using sodium ascorbate (–7 to 345 mV) and sodium borohydride (–500 to 140 mV) to treat an arsenic-bearing gold mining soil (2.8% As, 1.8% on ferrihydrite). The release of arsenic from the soil under oxidizing conditions (410 mV) showed the normal ferrihydrite release of As(V) (i.e., ~300 mg/L), whereas the treatment with 0.046 mole/L sodium ascorbate at an $E_H = -7$ mV (pH ~6) released ~80,000 mg/L As(III). Although different results were obtained with sodium borohydride, the release of arsenic was significant. Also, it is known that the effect of bacterial reduction of ferrihydrite and arsenate can be extensive. Kocar et al. (2010) found that the effect of sulfate-reducing bacteria (that produces dissolved sulfide species) was to reduce ferrihydrite to other iron solids along with the reduction of arsenate to arsenite. Chatain et al. (2005b) investigated the influence of anaerobic conditions (at pH ~7) with indigenous bacterial activity on the release of arsenic (and other metals) from a contaminated mining soil (3% As, 0.3% on ferrihydrite). The results showed <4,000 µg/L arsenic release from baseline soil/water leaches (80 days) and ~100,000 µg/L As(III) for nutrient-fed indigenous bacteria. Langer and Inskeep (2000) have investigated the possible reduction of As(V) to As(III) on ferrihydrite. They adsorbed arsenate onto previously precipitated two-line ferrihydrite solids, added a reducing fulcose fermenting microorganism to a suspended slurry containing the precipitated arsenate and arsenate species in solution at pH 6.8, and aged for 24 days. The solution arsenate was reduced to arsenite in less than one day, but the precipitated As(V) and ferrihydrite were not reduced. Langmuir et al. (2006) reported on analytical tests conducted for pore waters collected from various depths at a tailings impoundment (approximately five years aging). The results showed the following: pH = 7.76 ± 0.24, total arsenic = 4.1 ± 3.6 mg/L (which decreased to 1–2 mg/L in the older tailings), and E_H ~369 – 450 mV. The presence of several milligrams per liter of arsenite was noted in pore waters at some depths. Many more relatively recent studies are available that are not quoted here.

Removal of arsenic from solution by ferric precipitation has been and is or has been practiced at numerous extractive metallurgical facilities, for example, the Noranda Horne Smelter (Rouyn-Noranda, Quebec, Canada), the Giant mine and the Con mine (Yellowknife, Northwest Territories, Canada), and the Teck-Corona mine (Marathon, Ontario, Canada); the Kennecott Utah Smelter (Magna, Utah, United States), Placer Dome Lonetree and Getchell mines (Nevada, United States) (on a periodic basis), and Barrick's gold mining operations in Nevada. Harris (2000) has tabulated worldwide industrial operating practice (as of 2000/2001) for removal and stabilization of arsenic by the ferrihydrite, autoclave, or lime neutralization processes, or by production of copper arsenate. Harris (2000) states the following:

> By far the most popular approach is arsenical ferrihydrite, although possibly not always with the requisite level of understanding. Inco's CRED plant in Sudbury has been operating for close to thirty years, with no sign of ferrihydrite breakdown, or of arsenic release. As noted earlier, it is, however, well known that the incorporation of small amounts of cations and anions into the ferrihydrite matrix appreciably slows down any crystallization process to the formation of goethite/and or hematite, and hence the consequent release of adsorbed ions[54]. To all intents and purposes, it appears that recrystallization in these ferrihydrite materials in these situations is virtually non-existent. Certainly, the EPA regards the arsenical ferrihydrite process as the BDAT, and operations applying it correctly (molar Fe(III)/As(V) ratio >4) have not reported any contamination of local groundwater.

Drahota and Filippi (2009) present a review of secondary arsenic minerals in the environment (150 references). Important to this discussion is the authors' detailed presentation of information concerning the identification and presence of arsenic-bearing secondary solids in mining and industrial sites. This review is extensive and also includes the identification of calcium–iron–arsenate minerals in a wide variety of products such as "waste mine dumps, cyanidation tailings, naturally contaminated soils, stream bed sediments and altered rocks from arsenopyrite weathering." The authors suggest that further work needs to be performed to "clarify the formation conditions and stability of these minerals, in particular to evaluate their suitability for As sequestering under natural and lime/ferric precipitation conditions." The authors note the work of Demopoulos and colleagues on the synthesis, characterization, and solubility of calcium-containing compounds (Gomez et al. 2010; Bluteau et al. 2009; Jia and Demopoulos 2008). Building evidence shows that calcium Fe(III) As(V) compounds form during or with aging in lime precipitated arsenate removal systems or in pore waters saturated with gypsum. Several investigators have proposed that the presence of gypsum formed during ferric arsenate and/or ferrihydrite assists in maintaining long-term stability of the solids. Jia and Demopoulos (2008) have demonstrated that stability is enhanced by conducting arsenate removal, by ferric additions, using lime instead of sodium hydroxide. Bluteau et al. (2009) have continued work to determine the reason for the stabilizing effect by studying the dissolution of scorodite in gypsum-saturated solutions. Bluteau et al. and Gomez et al. have proposed that the mineral yukonite $[Ca_2Fe_3(AsO_4)_4(OH){:}12H_2O]$ likely forms from poorly crystalline scorodite with aging time, especially at pH levels of 7 and higher. Yukonite has been identified in mine tailings by other investigators as presented by Drahota and Filippi (2009). In their review, Johnston and Singer (2007) have evaluated the characteristics of ferrous arsenate (or symplesite) formation, and they suggest the following:

> Symplesite or other ferrous arsenate solid phases could be a significant sink for As(V) and Fe(II) in Bangladesh and other countries with similar geochemical environments. Symplesite could also control As(V) solubility in extreme environments such as alkaline lakes or in brines used for regeneration of anion exchange resins.

McCloskey et al. (2014) have developed and implemented an industrial application using ferrous arsenate formation for the removal of arsenate concentrations from 100 mg/L to <25 µg/L.

Paktunc and Bruggeman (2010) concluded the following from their extensive study of phase transformations of arsenic-bearing solids:

> Industrial practice to stabilize arsenic in metallurgical circuits is to form precipitates having Fe/As molar ratios than 3 or 4. Despite its important practical implication, the meaning of this ratio in terms of controlling arsenic releases has remained unknown. As described above, the precipitates with different Fe/As ratios, variably referred to as ferric arsenate or arsenical ferrihydrite, are not composed of a single phase. Instead, they are mixtures of ferric arsenate and ferrihydrite. Following the precipitation of ferric arsenate from arsenic-rich solutions, ferrihydrite forms at pH 2 and above. Its formation drives the solution composition to under saturation with respect to ferric arsenate and promotes dissolution of ferric arsenate. With this, the ferrihydrite content would increase at the expense of ferric arsenate. The increasing relative abundance of ferrihydrite would impose control on the As concentration in solution by providing additional sites for arsenate adsorption Accordingly, formation of ferrihydrite coupled with ferric arsenate dissolution would be considered as an efficient process in terms of minimizing As release.

Because of the extensive research performed during the last decade, important influencing factors for the removal of arsenic from solution are known and well characterized. Therefore, after the specific solution composition and conditions that exist at a treatment site are known, appropriate and effective removal systems can be designed. However, careful evaluation of the storage site must be performed with regard to the local conditions and what the local conditions will be in the future so that environmentally safe storage systems can be implemented and maintained.

Selenium

Selenium frequently occurs in natural and industrial waters throughout the world. Industrial sources include metals production activities, coal and mountaintop coal mining, coal-fired power plant effluents, oil refinery effluents, and agriculture activities. Examples of selenium sources are presented in Table 8. Selenium is often associated with metal sulfide mining and coal mining because of its occurrence with pyrite and other metal sulfides.

The EPA promulgated rules for the BDATs to be used for the following listed and characteristic waste containing As and Se: K031, K084, K101, K102, As wastes (D004), Se wastes (D010), and P and U wastes (Rosengrant and Fargo 1990). The specified BDAT for treatment of effluent solutions is selenium adsorption on ferrihydrite. The problem with this BDAT is that selenium removal is effective if it is present as selenite. However, selenium is usually present in natural and wastewaters as selenate; therefore, ferrihydrite adsorption is seldom used as the preferred treatment option because reduction of selenate to selenite is chemically and kinetically difficult. However, if the selenium is present as selenite, then the use of ferrihydrite is recommended. In general, the valence of selenium that occurs in some industry sectors is summarized in Table 9 (EPA 2016).

Recent reviews detailing process technologies for removing selenium from wastewaters include EPA (2000), Golder Associates (2009), North American Metals Council (NAMC) (Sandy and DiSante 2010), and Santos et al. (2015). Many of the referenced technologies have only been demonstrated in a laboratory or small pilot-scale application. Data are often lacking for large-scale treatments; costs are seldom presented. The most comprehensive recent review of selenium removal technologies was conducted for the NAMC. Pilot- and full-scale treatment technologies are discussed for four industrial sectors: mining, agriculture, power generation, and oil and gas industries (Sandy and DiSante 2010):

> While these physical, chemical, and biological treatment technologies have the potential to remove selenium, there are very few technologies that have successfully and/or consistently removed selenium in water to less than 5 µg/L at any scale. There are still fewer technologies that have been demonstrated at full-scale to remove selenium to less than 5 µg/L, or have been in full-scale for sufficient time to determine the long-term feasibility of selenium removal technology. No single technology has been demonstrated at full-scale to cost-effectively remove selenium to less than 5 µg/L for waters associated with all industry sectors. Therefore, performance of the technology must be demonstrated on a case-specific basis.

Technologies that have been demonstrated at a full-scale level are included in Table 10, which is based on NAMC Table ES-1 (Sandy and DiSante 2010). More detail is available in their summary table, including key design considerations and estimated capital and operating costs. Extensive discussions are presented in their text covering individual technologies such as physical (membranes, filtration), chemical (precipitation and adsorption), and biological (adsorption by biomasses and biological precipitation of selenium) treatments. For further information on laboratory and pilot studies, refer to the referenced publication.

Technologies for treating metals and nonmetal species in mine waters and hydrometallurgical effluent solutions. The EPA has recently published a report to provide a reference guide for the treatment of mining-influenced water (EPA 2014b).

> This report provides an overview of select mining-influenced water (MIW) treatment technologies used or piloted as part of remediation efforts at mine sites. The report is intended to provide information on treatment technologies for MIW to federal, state and local regulators, site owners and operators, consultants, and other stakeholders. The technologies described in this report are applicable to treatment of water from both coal and hard-rock mine operations. The report provides short descriptions of treatment technologies and presents information on the contaminants treated, pre-treatment requirements, long-term maintenance needs, performance and costs. Sample sites illustrate considerations associated with

Table 8 Total selenium concentrations in different contaminated waters and wastewaters

Water/Wastewater	Se Concentration	Reference*
Agricultural drainage water	140–1,400 µg/L	Y.Q. Zhang et al. 2005
Mining wastewaters	3 µg/L to >12 mg/L	Wasewar et al. 2009a
Coal mining pond water	8.8–389 µg/L	Mar Systems 2012
Uranium mine discharge	1,600 µg/L	Twidwell et al. 2005
Gold mines wastewater	0.2–33 mg/L	Twidwell et al. 2005
Petrochemical industries wastewater	7.5–55.9 µg/L	Cassella et al. 2009
Flue gas desulfurization wastewaters	1–10 mg/L	Vance et al. 2009
	0.2–1.8 mg/L	Sonstegard et al. 2010
Lead smelter scrubber water	3–7 mg/L	McCloskey et al. 2008

Source: Santos et al. 2015

*References as cited in Santos et al. 2015.

selecting a technology. Website links and sources for more information on each topic are also included.

This report focuses on passive treatment methods, but also includes recently developed or not widely utilized active treatment systems and passive-active hybrid systems. The report does not include all traditional active technologies, such as lime precipitation or high-density sludge systems.

The technologies discussed in the preceding EPA report for active treatments (the technologies applicable to mineral processing and extractive metallurgical processes) include

Table 9 Presence of selenium in various wastewater sources

Selenium Form	Sources
Selenate	Agricultural irrigation drainage Treated oil refinery effluent Mountaintop coal mining/valley fill leachate Copper mining discharge
Selenite	Oil refinery effluent Fly ash disposal effluent Phosphate mining overburden leachate
Organoselenium	Treated agricultural drainage (in ponds or lagoons)

Source: Presser and Ohlendorf 1987, Zhang and Moore 1996, and Cutter and Diego-McGlone 1990, as cited in EPA 2016

Table 10 Technology summary for full-scale demonstration projects*

Technology	Brief Description	Advantages	Disadvantages
ABMet	System is a bioreactor that is an attached growth (comprised of a biofilm, or a layer of microorganisms that grow on the surface of a solid phase media) down flow granular active carbon bed filter.	• Commercially available technology that has been demonstrated to remove selenium to low levels in pilot-scale and full-scale applications. *This process is capable of achieving EPA guideline concentrations of <5 μg/L for both selenate and selenite.* • Uses naturally occurring microbes and molasses-based nutrient feed to maintain biomass; *removes selenite and selenate.* • Biologically reduced elemental selenium is in an insoluble form as nanoparticles integral to the biological solids. • *Also removes nitrate, metals, mercury, and arsenic.*	• Potential need for pretreatment to remove suspended solids. • Large footprint required. • External carbon source is required if soluble influent organic content or chemical oxygen demand is insufficient. • Wasted biomass residuals contain elemental selenium that may be hazardous depending on toxicity characterization leach procedure (TCLP) results. • Biological residuals will need to be thickened and dewatered for landfill disposal.
Ferrihydrite adsorption or iron co-precipitation	Two-step physical adsorption process in which a ferric salt is added to the water source at proper conditions such that a ferric hydroxide and ferrihydrite precipitate results in concurrent adsorption of selenium on the surface; also known as iron co-precipitation.	• Widely implemented at full scale throughout the industry. • Established by EPA as the best demonstrated available technology of selenium (e.g., selenite) removal. • Relatively simple and low-cost chemical adsorption technology. • *Ferrihydrite is an adsorbent that can concurrently remove selenium and other species present in the wastewater such as arsenic, cadmium, copper, lead [illegible].*	• Selenium removal not proven to low μg/L (less than 5 μg/L). • Produces relatively large quantities of sludge that may need to be disposed as a hazardous waste depending upon outcome of TCLP testing. • pH dependent with optimal conditions in the range of pH 4 to 6; *Fe/As mole ratio 3–4.* • Not able to remove selenite effectively. • Potential release of selenium from ferrihydrite residuals. *Long-term outdoor storage stability unknown.*
Ferrous hydroxide	A two-step reduction oxidation and physical adsorption process where ferrous iron is added resulting in the reduction of selenite to selenite and subsequent physical adsorption of co-precipitation of selenite by ferrihydrite or ferric hydroxide.	• Widely implemented at full scale throughout the industry. • Relatively simple and low-cost chemical adsorption technology.	• Selenium removal not proven to low μg/L (less than 5 μg/L). • Large quantities of sludge that may need to be disposed as a hazardous waste. • Reduction and subsequent adsorption is pH dependent with optimal conditions in the range of pH 8 to 9. *Huge excess of ferrous may be required.* • Not as effective at the reduction of selenate to selenite as zero-valent iron. • *Green rust may form in the presence of high-sulfate solutions, which may not be stable for outdoor storage.* • *Potential release of selenium from ferrihydrite residuals. Long-term outdoor storage stability unknown.*
Reverse osmosis	A membrane separation process that uses high pressure to force a solution through a membrane that retains the soluble selenium (e.g., selenite and selenate) and other dissolved salts less than 0.001 μm on the reject side of the membrane and allows the purified water to pass to the permeate side.	• Demonstrated at full scale to remove selenium (selenite or selenate) to <5 μg/L. • Can remove high levels of total dissolved solids (TDS), approximately 90%–98% removal. • Produces a high water quality with relatively high recoveries as a function of scale treatment. • Small space requirements, modular-type construction, and easy expansion. • Concentrates the selenium reducing the volume for ultimate reduction treatment.	• Higher capital cost to purchase, install, and operate than other membrane separation processes. • Requirements for pretreatment and chemical addition to reduce scaling or fouling. • Pressure, temperature, and pH requirements to meet membrane tolerances. • Frequent membrane monitoring and maintenance. • Requires treatment and disposal of the brine. • Permeate stream will require treatment (pH and TDS buffering) prior to discharge to receiving waters to meet aquatic toxicity test. • Operating issues will result from viscosity changes at extreme low and high temperatures.

Adapted from Sandy and DiSante 2010

*Italic has been added by the chapter author.

fluidized bed reactors, reverse osmosis, zero-valent iron, ferrihydrite adsorption, electrocoagulation, ion exchange, biological reduction, and ceramic microfiltration. Sixteen applications are discussed that include the topics technology description, constituent treated, long-term maintenance, system limitations, costs, and effectiveness.

Technologies that have been demonstrated at a full-scale level are included in Table 11, which is based on Appendix A from EPA 2014b. Additional information is available in the EPA (2014b) summary table, including entries for pilot and laboratory research. Additional descriptive information is presented for the topics, including operations, long-term maintenance, and costs. The appendix presents extensive discussions on individual technologies such as physical (membranes, filtration), chemical (precipitation and adsorption) and biological (adsorption by biomasses and biological precipitation of selenium) treatments. For further information on laboratory and pilot studies, refer to the referenced publication.

SUMMARY

All effluent wastewaters have their own characteristics, such as hazardous constituent concentration, associated constituents, physical properties (pH, oxidation–reduction potential, temperature, turbidity) and chemical properties (element speciation, associated ions speciation, biological oxygen demand, dissolved oxygen, etc.). Therefore, each effluent wastewater must be fully characterized before a treatment process can be selected, and a treatment process must be tailored for that specific water. The implementation of a successful technology depends on several variables that can have a great influence on which technology is chosen. A few examples are presented in the following examples.

Example 1: Adsorption Technology

Many influencing factors should be considered when choosing to use an adsorption technology; for example, the removal of arsenic from an effluent solution is dependent on the following:

- pH: Less than neutral is better.
- Fe/As loading ratio: The higher the ratio, the more effective the removal, but 3–4 is usually selected to limit excessive sludge formation.
- Species of arsenic present: Hydrated oxyanions are better adsorbed than arsenate anions.
- Valence of the arsenic specie present: Arsenates are favored over arsenites.
- Method of exposure to the adsorbent: Methods include addition of ferric to the solution or oxidation of ferrous in situ within the solution.
- Presence of other dissolved species: Sulfate, phosphate, and carbonate all compete with arsenic for adsorption sites.
- Presence of cations: Ferrihydrite has an affinity for cupric, nickel, and lead species so they complete for adsorption sites.

Storage disposal of the adsorbent/adsorbed specie product must be considered. Careful consideration must be given to the long-term stability of the product within the chosen repository. Consideration also must be given to the oxidation–reduction potential (will the waste matrix retain the constituent or constituents of interest?), pH (will the stability be maintained at a pH different than that used to form the product?), bacterial reduction (is the microbial environment suitable?), and comingling with other waste products (such as mixing with sulfide-bearing tailings). Many adsorbents have been and are presently being investigated for removal of specific constituents, and essentially the same considerations apply.

Example 2: Microbiological Technology

Two widely used industrial microbial-based bioreactor technologies are available: microbial-induced reduction (ABMet and BioSolve; Sandy and Disante 2010) and microbial-induced sulfide precipitation processes (Blumenstein et al. 2008). The microbial-induced reduction is via the establishment of a biofilm on activated carbon or plastic sponges to produce an anoxic/anaerobic reducing environment that locally transforms an oxyanion specie to its elemental state that is embedded within the biofilm matrix. The microbial-induced sulfide precipitation is via the b iological reduction of sulfate to sulfide with subsequent reaction with metallic and nonmetallic species to form sulfide solids.

Microbial-Induced Reduction

This process is conducted in a bioreactor where the conditions must be conducive for the establishment of biofilms (on various substrates) to form and to remain stable. Influencing factors include the following:

- Pretreatment of effluent wastewater to remove suspended solids
- Establishment of anoxic/anaerobic conditions
- Elevated temperature (10°C and 38°C)
- Sufficient concentration of oxyanions (selenates, selenites, nitrates) to supply oxygen during bacterial respiration
- Addition of an organic material as a carbon source to supply energy to the bacteria
- Residence time
- Circumneutral pH

The resulting exiting effluent water must be treated aerobically to increase dissolved oxygen and solubilize organic species. The constituent loaded biomass must be periodically stripped, dried, and disposed of in a proper repository. In general, the recovered biomass is considered nonhazardous.

Microbial-Induced Sulfide Precipitation

This process is conducted in a bioreactor or in large-scale passive systems for treatment of acid mine waters. Bioreactors have been operated effectively to remove arsenic, chromium, copper, lead, selenium, thallium, zinc, and uranium (EPA 2014b). The conditions must be conducive for the establishment of anoxic-reducing conditions sufficient for sulfate-reducing bacteria to form and to remain stable. Influencing factors include the following:

- Pretreatment of effluent wastewater to remove suspended solids
- Establishment of anoxic/anaerobic conditions
- Sulfate concentration (1–3 g/L required; sulfate additions may be required)
- An organic source to promote organism growth (usually acetic acid or ethanol)
- pH (usually 5–7 where metal sulfides are stable)
- Residence time (usually requires a few to several hours).

Table 11 Full-scale treatment of active technologies as applied to the removal of various constituents

Technology	Brief Description	Treated Constituents	Limitations	Effectiveness
Bioreactors (active systems)	Biochemical reactors (BCRs), or bioreactors, treat mining-influenced water (MIW) by using microorganisms to transform contaminants and to increase pH in the treated water. BCRs can be designed as open ponds and buried ponds or within tanks or even in trenches between mine waste and a surface water body. The most commonly used BCRs for treating MIW are operated anaerobically. They are also called "sulfate-reducing" bioreactors.	Selenium, cadmium, copper, nickel, lead, zinc, arsenic, chromium	The primary target metals for sulfate-reducing BCRs are those that precipitate as a metal sulfide at pH values between 5 and 7. Additionally, some active metals and metalloids such as arsenic, chromium, selenium, thallium, and uranium may undergo a change in oxidation state, which is more amenable to precipitation in a neutral anaerobic environment. The size of the system is a function of metal loading rate, which includes factors such as flow, metals concentration, and required retention time. For example, a higher metal loading rate necessitates a larger system that requires more retention time and, in most cases, a lower flow rate. BCRs are most effective in conditions where relatively steady flow rates and loading rates can be maintained and pH levels balanced to optimize overall treatment efficiency. Thus, flow equalization or pH adjustment may be required as a pretreatment step.	The use of active BCRs to treat MIW would allow for the treatment of relatively high flows in a small footprint. The use of active BCRs, with low energy and chemical input but which recycle (semipassively) like the rock-based system at the Leviathan mine (California, United States), is an attractive alternative. The amount of human intervention varies with the type of reactor. The use of an active BCR allows various design configurations because the MIW may be piped into different chambers or the sulfate reduction occurs in one cell while the precipitation occurs in another chamber. When it comes to sludge or precipitate removal, the main cell is not affected, so the system maintains its sulfide-generating capacity with little or no interruption in operation.
Biological reduction of selenium (BSeR and GE's ABMet)	This process uses specially developed biofilms that contain specific proprietary microorganisms in anaerobic bioreactors to reduce selenium (in the form of selenite and selenate) to elemental selenium. The end product is a fine precipitate of elemental selenium that is removed from the bioreactor with back flushing.	Selenium, mercury, complete nitrate removal and removal of a variety of other metals	Requires pre- and post-treatment steps to remove suspended solids, backwashing to prevent plugging and short-circuiting of flow, and temperature dependence.	Process can treat flow rates as low as 5 gpm and as high as 1,400 gpm, while achieving up to 99% removal rates and discharging a treated effluent containing 5 µg/L of selenium. Nitrate (typical feed of 10–25 mg/L), possible effluent: not detectable <1 mg/L. Selenium (typical feed of 10,000 µg/L), possible effluent: <0.005 µg/L. Mercury (typical feed of 5 µg/L), possible effluent: <0.012 µg/L.
EcoBond	EcoBond forms a chemical chain that binds with metal ions forming insoluble metal complexes, reducing bioavailability. It produces a reaction that proceeds at ambient temperatures and does not produce secondary waste streams or gases.	Arsenic, aluminum, cadmium, chromium, lead, mercury, selenium, zinc, radionuclides	The EcoBond was not effective at reducing zinc and copper. Since the chemicals are applied with water, the reactions and subsequent effectiveness are limited to the surfaces that can be contacted. This makes treatment at depth or in large stockpiles difficult, since the flow paths in mine waste are complex.	Reduced Al by 7%, Fe by 26%, Mn by 55%, Ni by 64%, and sulfate by 31%. Limited inhibition of copper and zinc. The maximum percent reduction of total metals from the EcoBond-treated plot was less than 50%.
Electrodialysis reversal (EDR)	Electrodialysis (ED) is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of a direct current voltage. EDR is a variation on the ED process, which uses electrode polarity reversal to automatically clean membrane surfaces.	Arsenic, radium, nitrate, dissolved solids	Total dissolved solids (TDS) economical up to 8,000 mg/L, but often run at waters of 1,200 mg/L • pH: 2.0 to 11.0 • Iron (Fe^{+2}): 0.3 ppm • Mn (+2): 0.1 ppm • H_2S: up to 1 ppm	When combined with reverse osmosis at a South African mine, the system treats MIW with 5,000 mg/L TDS with high calcium sulfate content down to <40 mg/L TDS.
Ferrihydrite adsorption (iron co-precipitation)	Ferrihydrite adsorption is a two-step physical adsorption process in which a ferric salt is added to the water source at proper conditions such that a ferric hydroxide and ferrihydrite precipitate results in concurrent adsorption of selenium on the surface. Also known as iron co-precipitation.	Selenium, arsenic	Consistent removal to regulatory levels of selenium has not been proven. Potential release of selenium from ferrihydrite residuals. Gravity sedimentation may be required to separate iron solids and adsorbed metals from the water matrix. High operational costs are typical of chemical treatment. Ion exchange capacity for selenium can be greatly reduced by competing ions (e.g., sulfates, nitrates).	At the Garfield Wetlands-Kessler Springs site Salt Lake City, Utah (United States), water contained 1,950 µg/L selenium, primarily as selenite. Using an iron concentration of 4,800 mg/L, the mean effluent selenium concentration was 90 µg/L. The minimum reported selenium concentration was 35 µg/L. Selenium removal is not proven to less than 5 µg/L.

(continues)

Table 11 Full-scale treatment of active technologies as applied to the removal of various constituents (continued)

Technology	Brief Description	Treated Constituents	Limitations	Effectiveness
Chemical precipitation	Hydroxide precipitation: Raising the pH with the use of alkaline agents causes certain dissolved metals (e.g., cadmium, copper, iron, lead, manganese, and zinc) to precipitate as hydroxides. A polymer may be added to enhance flocculation, and the solution may be transferred to a clarifier to separate the solids from the cleaned overflow effluent. The resultant metal-hydroxide sludge extracted from the bottom of the clarifier usually contains a large percentage of bound water, limiting the potential for reuse, and is disposed of as a solid waste. The amount of sludge generated can be reduced by employing a high-density sludge (HDS) treatment technique. In HDS processes, the precipitated hydroxide sludge is recycled to a conditioning tank where it is mixed with the alkali reagent. The sludge/alkali slurry is then metered into the MIW to raise the pH and cause additional metal precipitation. This reconditioning of the sludge provides for precipitation sites for the dissolved metals to bond, increasing the overall density of the sludge in the clarifier underflow. Sulfide precipitation: The addition of a sulfide induces precipitation of dissolved metals as metal sulfides. This treatment is very effective for many metals, including zinc and cadmium. It is less effective for some contaminants such as manganese. pH adjustment may be required prior to the sulfide precipitation. Benefits of sulfide precipitation include a reduction over hydroxide precipitation of the quantity of sludge generated. The sludge is more easily reprocessed to recover the metals and may offset the cost of treatment.	Cadmium, copper, iron, lead, manganese, and zinc	Limitations: • High cost • Not applicable for all cases • Requires operation and maintenance • Requires power • May generates a waste product Depending on the volume of water necessary for treatment, the cost of this technology can be high. Metal hydroxide sludge typically contains water bound in the chemical matrix and results in a large volume of waste requiring disposal. Generation of large volumes of sludge may be problematic. Lined impoundments must be considered if there is potentially hazardous waste that can migrate from the sludge disposal site. The waste product may contain free liquids or fail testing by the toxicity characterization leaching procedure and may necessitate subsequent disposal at an approved hazardous waste facility, incurring more costs.	Chemical precipitation is a proven, large-scale technology that offers permanent results. It can be used solo or in conjunction with other treatment technologies. Chemical precipitation has demonstrated achievement of stringent water quality limits. The performance and results are specific to initial water quality and site limitations.
Reverse osmosis	Reverse osmosis is the pressure-driven separation through a semipermeable membrane that allows water to pass through while rejecting contaminants.	Metals, sulfate, selenium, arsenic	Requires high operating pressure. Not practical above 10,000 mg/L TDS. Requirements for pretreatment and chemical addition to reduce scaling/fouling. Reverse osmosis permeate steam will require treatment before discharge to receiving waters to meet aquatic toxicity test. Frequent membrane monitoring and maintenance. May require temperature control at low and high temperatures to minimize viscosity effects.	Kennecott's Bingham Canyon Water Treatment Plant (Utah, United States) has consistently seen permeate production efficiencies in the range of 71% to 72%. Demonstrated at full scale to remove selenium to <5 µg/L. Can remove 90%–98% TDS. A TDS removal efficiency of 98.5% was observed during pilot testing of the membranes tested.

Source: EPA 2014b

In general, the sulfide product must be considered hazardous, and if the product cannot be recycled to a system that treats metal sulfides, then the waste must follow hazardous waste handling, transport, and disposal regulations.

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PART 10

Hydrometallurgy