Chapter 6

GEOCHEMISTRY OF ACID MINE WATERS

D. Kirk Nordstrom[1] and C.N. Alpers[2]
[1]*U.S. Geological Survey, 3215 Marine Street, Boulder, CO 80303-1066*
[2]*U.S. Geological Survey, Placer Hall, 6000 J Street, Sacramento, CA 95879-6129*

INTRODUCTION

There are about a dozen major hydrogeochemical processes that can account for the chemical composition of most natural waters. One of these is the oxidation of pyrite, a process at least as important a source of sulfate in natural waters as seawater and sea spray, gypsum dissolution, and atmospheric emissions. The natural process of pyrite oxidation is fundamental to the supergene alteration of ore deposits, the formation of acid-sulfate soils, and the development of acidity and metal mobilization in natural waters. As mineral deposits continue to be mined, and inactive or abandoned mines with their associated waste-rock and tailings piles continue to be exposed to weathering, large concentrations of sulfate and heavy metals will continue to be found in both surface waters and ground waters. Nearly 5×10^{10} tons of mining and mineral processing wastes had been generated in the United States as of 1985 and about 10^9 tons continue to be generated each year (U.S. Environmental Protection Agency, 1985). A more recent estimate indicates that there may be more than 500,000 inactive or abandoned mine sites in the U.S. (Lyon et al., 1993). Hazardous mine sites in serious need of remediation are probably much fewer but may still range in the thousands. Inventories of mineral resources, mine sites, and their associated environmental hazards are being assembled at various scales by federal and state agencies to better assess the magnitude of the problem.

The water-quality hazard produced by pyrite oxidation is known as "acid rock drainage," or if from a mined area, "acid mine drainage." We use the terms "acid mine drainage" and "acid mine water" synonymously, reflecting popular usage. These waters drain from waste rock, tailings, open pits, and underground mines into surface streams, rivers, and lakes. Acid mine waters typically have pH values in the range of 2–4 and high concentrations of metals known to be toxic to living organisms (Ash et al., 1951; Martin and Mills, 1976; Nordstrom and Ball, 1985). Natural waters acidified by mine drainage have killed enormous numbers of fish and benthic organisms, harmed livestock, and destroyed crops and have made many rivers, streams, and lakes turbid, colored, and unfit for most beneficial purposes. In the United States, 10^7 fish were reported killed during 1961–1975 from the effects of mining activities (Biernacki, 1978), and this number can safely be considered a gross underestimate. For example, the eighth annual report of the Federal Water Pollution Control Administration (1968) states that of the 11.59×10^6 fish reported killed in 1967 from all types of pollution only 16,413 were reported killed from the state of California. The California Department of Fish and Game (Nordstrom et al., 1977), however, recorded 47,100 fish killed from mine drainage at one site during a 7-day period in January of 1967. Many other mining-related fish kills may not be adequately recorded in federal or state archives.

Kleinmann (1989) has estimated that about 19,300 km of rivers and streams and more than 180,000 acres of lakes and reservoirs in the continental U.S. have been seriously damaged by acid mine drainage. Although a quantitative assessment of environmental damage from mining activities may be difficult or impossible, the volume of water bodies affected by acid mine drainage could be comparable to that affected by acid rain or other industrial sources of acidification.

It is important to note that pyrite oxidation also occurs in the absence of mining and there are numerous localities world-wide where naturally acidic waters containing high concentrations of metals are known (Runnells et al., 1992). The geochemical processes of weathering may be very similar in terms of mineral oxidation and dissolution but the hydrologic regime, the rates of reaction, and the environmental consequences can be quite different. Geochemical reactions in mined areas are more rapid because of:

1) greater accessibility of air through mine workings, wastes, and tailings,
2) greater surface areas for sulfides in mine workings, wastes, and especially tailings, and
3) different compositions of tailings as a result of mineral processing.

The presence of flues and flue dust piles (typically high in arsenic, zinc, and cadmium), slag piles, and soils and rocks contaminated by smelter fumes can be particularly detrimental to flora and fauna. Erosion of these materials by both aeolian and fluvial transport can contaminate drainage systems for very long distances (Moore and Luoma, 1990). The slower weathering of unmined mineral deposits occurs over longer time frames and tends to lead to more stable and insoluble mineral phases than those at mined deposits.

As an example of the extremes to which mine waters can develop acidity and high metal concentrations, the analyses of four of the most acidic mine waters ever reported are shown in Table 6.1. These waters were found in the Richmond mine workings at Iron Mountain, California (Nordstrom et al., 1991). Note that all samples have negative pH values and metal concentrations in grams per liter. These concentrations are some of the highest recorded metal and sulfate concentrations and the lowest pH values known. A survey of the literature indicates that only one known determination for copper, one for zinc, and one for arsenic have been found to be higher than those from the Richmond mine waters (Table 6.1). Although these extreme values are rare, they do indicate the dramatic changes in water quality caused by natural processes and enhanced by mining activities.

TABLE 6.1—Comparison of four of the most acidic mine waters at Iron Mountain, California with the most acidic and metal-rich mine waters reported in the world (pH values in standard units, concentrations in grams per liter, Nordstrom et al., 1991; Nordstrom and Alpers, 1999).

	Iron Mountain				Other sites	References
pH	-0.7	-2.5	-2.6	-3.6	0.67	Goleva et al. (1970)
Cu	2.3	4.8	3.2	n.d.	48	Clarke (1916)
Zn	7.7	23.5	20	n.d.	50	Braeuning (1977)
Cd	0.048	0.21	0.17	n.d.	0.041	Lindgren (1928)
As	0.15	0.34	0.22	n.d.	0.40	Goleva (1977)
Fe (total)	86.2	111	101	16.3	48	Blowes et al. (1991)
Fe (II)	79.7	34.5	34.9	9.8	48	Blowes et al. (1991)
SO_4	360	760	650	n.d.	209	Lindgren (1928)

The chemical reaction responsible for the formation of acid mine waters requires three basic ingredients: pyrite, oxygen, and water. The overall reaction is often written as:

$$FeS_{2(aq)_3} + 15/4\,O_{2(g)} + 7/2\,H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2\,H_2SO_{4(aq)} \quad [1]$$

where one mole of ferric hydroxide and 2 moles of sulfuric acid are produced for every mole of pyrite oxidized. For each mole of pyrite oxidized in equation [1], 1 electron is lost by oxidation of iron, 14 electrons are lost by oxidation of disulfide, and 15 electrons are gained by reduction of oxygen. Iron is also hydrolyzed and precipitated. All of these reactions cannot take place in a single step. Electron transfer reactions take place generally with only one or two electrons at a time (Basolo and Pearson, 1967). Hence, there could be 15 or more reactions with as many possible rate-determining steps to consider. To further complicate matters, several other oxidizing agents besides oxygen have been implicated in pyrite oxidation, e.g., ferric iron. Fortunately, all the intermediate reactions need not be determined to delineate the rate-controlling mechanisms involved with pyrite oxidation.

This chapter reviews the abiotic and microbial rates and mechanisms for sulfide mineral oxidation, the secondary minerals formed as a result of sulfide oxidation, and the major environmental factors that control the quality and quantity of acid water produced from mining activities.

HISTORICAL BACKGROUND

The history of mining and its environmental consequences, like technology in general, goes back several thousands of years, well before recorded history. Theophrastus (*ca.* 315 B.C.) mentions the degradation of pyrite to acid and salts (see Agricola, 1556). By the time of Pliny (23–79 A.D.), it was already well known that oil of vitriol (sulfuric acid), vitriol (ferrous sulfate), and alum (aluminum sulfates) were produced by the natural lixiviation (leaching) of pyritiferous rocks. Oil of vitriol was used to make other acids and compounds, vitriol was primarily used to blacken leather, and alum was used to tan hides. The acid waters and their associated efflorescent (or flowering) salts produced from pyrite oxidation were also known to be highly toxic. Georgius Agricola (1546) wrote "When moisture corrodes cupriferous and friable pyrite it produces an acid juice from which *atramentum sutorium* forms and also liquid alum.... Experiments show that when porous, friable pyrite is attacked by moisture such an acid juice is produced." *De Re Metallica* (Agricola, 1556), considered to be the first systematic book on mining and mineralogy, contains the following passage, "Since I have explained the nature of vitriol and its relatives which are attained from cupriferous pyrites I will next speak of an acrid solidified juice...; it is hard and white and so acrid that it kills mice, crickets and every kind of animal." The "solidified juice" was later identified (by Herbert Hoover, translator) as goslarite, a hydrated zinc sulfate that likely contained some cadmium. With the dawn of the industrial revolution, acid mine drainage became a major source of water pollution on a large scale.

In the United States, occasional effort was directed towards the problem of acid mine drainage in the Appalachian coal mining region before 1900 (Vranesh, 1979). The State of Indiana has had a land reclamation act for coal-stripping since 1942 and a history of concern with the adverse effects of strip mining that can be traced back to 1917 (Wilber, 1969). Western mines were originally exempt from regulations on mine drainage or other environmental hazards because of the interest in attracting businesses and people to the West. Mining and metallurgical engineers occasionally investigated the problem (e.g., Burke and Downs, 1938), but primarily with an aim to alleviate coal mine drainage problems. From the 1920s through the 1940s, government agencies and the mining industry investigated acid mine drainage produced in the Appalachians from coal mines (Ash et al., 1951). Twenty years later the Appalachian Regional Commission reviewed the coal mine drainage problems (Appalachian Regional Commission, 1969). From the late 1960s through the late 1970s the National Coal Association and Bituminous Coal Research, Inc. sponsored a series of Coal Mine Drainage Research Symposia that resulted in several useful publications on the problem. About the same time, considerable research was supported by the Federal Water Pollution Control Federation and, later, the Environmental Protection Agency (EPA) on both the causes of acid mine drainage and its remediation. Even more attention has been given to the problem with the advent of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) in 1980. Several mining sites around the country were put on EPA's National Priority List for Superfund investigation and remediation.

FORMATION OF ACID MINE WATERS

The general description of the weathering of pyrite will now be examined in more detail. Equation [1], the overall reaction for the breakdown of pyrite to ferric hydroxide and sulfuric acid, is a gross oversimplification. It gives the correct picture in that oxygen is the ultimate driving force for the oxidation of pyrite and the final products are an insoluble form of oxidized iron and an aqueous sulfuric acid solution. Some problems with equation [1] are that it does not explain geochemical mechanisms or rates, it does not explain that ferric hydroxide is a fictitious, idealized phase, and it does not reflect the slow oxidation of aqueous ferrous iron in acid solutions that often results in high ferrous iron concentrations in acid mine waters. Furthermore, factors such as microbial catalysis, neutralization reactions, sorption reactions, and climatic effects have an important influence on pyrite weathering, but are not considered explicitly in equation [1].

Mine operators as well as reclamation and remediation teams would like to know the potential or actual production of acid waters from a mine or from waste materials at a mine or a mineral processing facility. There is no simple, single test to assess metal and acid mobility in these settings because of the numerous variables that affect contaminant transport. The problem is multifaceted and we must emphasize that acid mine drainage forms within a complex environmental system where several factors need to be considered within the five general categories as shown in Table 6.2. These five categories are traditional scientific disciplines that must be integrated to characterize a field site.

TABLE 6.2—Environmental factors affecting acid mine water formation.

	Traditional Scientific Disciplines				
	Inorganic chemistry	Organic chemistry	Geology/ mineralogy	Hydrology	Microbiology
Sulfide oxidation	✓	✓	✓	✓	✓
$Fe^{(II)}_{(aq)} \rightarrow Fe^{(III)}_{(aq)}$	✓	✓		✓	✓
pH	✓	✓	✓	✓	✓
Temperature	✓		✓	✓	✓
Gangue dissolution	✓		✓	✓	
Rock type/structure	✓		✓	✓	
Porosity			✓	✓	
Permeability			✓	✓	
Flow paths (recharge/discharge)	✓		✓	✓	
Climate	✓			✓	
Evapoconcentration/ efflorescent salt formation	✓		✓	✓	
Efflorescent salt dissolution	✓		✓	✓	
Photochemistry	✓	✓		✓	✓

Stoichiometry and kinetics of abiotic pyrite oxidation

The voluminous literature on pyrite oxidation has been reviewed by Lowson (1982) with regard to abiotic chemical oxidation and by Nordstrom (1982a) with regard to biotic and abiotic geochemical oxidation. More recent contributions can be found in Goldhaber (1983), McKibben and Barnes (1986), Moses et al. (1987), Moses and Herman (1991), and Evangelou (1995). When pyrite oxidizes there are two species that can oxidize, the ferrous iron and the sulfidic sulfur. In studies on acid mine waters and pyrite oxidation, it has long been recognized that iron easily leaches out of pyrite but tends to stay in the ferrous state in acid solutions. Ancient history records the production of vitriol and oil of vitriol from washing pyritiferous ores and shales. During the last two centuries this vitriol was determined to be a mixture of ferrous sulfate and sulfuric acid. Hence, another common representation of the pyrite oxidation reaction is:

$$FeS_{2(s)} + 7/2O_{2(g)} + H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 2H^{+}_{(aq)} \qquad [2]$$

The sulfur moiety in pyrite oxidizes more quickly than the iron, but it must transfer a large number of electrons (14 times as many as iron per mole of pyrite). Consequently, there are several possible side reactions and sulfur intermediates that may occur during oxidation.

One side reaction is the formation of elemental sulfur during oxidation (Stokes, 1901; Bergholm, 1955; Clark, 1966). The yield is low and increases with higher temperatures, up to a maximum at about 100–150°C (Lowson, 1982). The lowest yield is at ambient temperatures but increases with increasing acidity. Field observations without laboratory identification are not reliable sources of information on elemental sulfur forming from pyrite oxidation because other minerals such as copiapite and jarosite may commonly be misidentified as elemental sulfur. Positive identification of elemental sulfur has been made at numerous inactive tailings impoundments (Blowes, 1995, written commun.). When acid waters react with minerals such as pyrrhotite and sphalerite they will produce H_2S, which readily oxidizes to elemental sulfur. Elemental sulfur is found commonly in nature where sulfur-rich, near-surface, hydrothermal solutions with temperatures around 100–150°C have oxidized or where H_2S-rich spring waters have oxidized on exposure to air.

Another side reaction, or group of reactions, is the formation of intermediate sulfoxyanions of lower oxidation state than that found in sulfate: i.e., thiosulfate ($S_2O_3^{2-}$), polythionates ($S_nO_6^{2-}$), and sulfite (SO_3^{2-}). Steger and Desjardins (1978) reported a thiosulfate compound on the surface of oxidizing pyrite but their method did not distinguish between thiosulfate, polythionate, and sulfite. Goldhaber (1983) measured rates of reaction and reaction products for the pH range 6–9 and found that polythionates, thiosulfate, sulfite, and sulfate formed but only at high stirring rates. The proportions of intermediate sulfoxyanions were sensitive to pH in Goldhaber's (1983) experiments. Polythionates were found to be dominant at low pH and thiosulfate was dominant at high pH, with some sulfite formed at the highest pH values. Some ambiguity exists in his determination of polythionates and thiosulfate. He used the colorimetric method of Nor and Tabatai (1976), which assumes tetrathionate is the dominant polythionate and does not completely distinguish between thiosulfate and polythionate. The pyrite and sphalerite oxidation experiments of Moses et al. (1987) included more direct determination of sulfate, sulfite, polythionates, and thiosulfate by ion chromatography (Moses et al., 1984). Their results were similar to those of Goldhaber (1983) except that additional experiments carried out in the presence of $Fe^{3+}_{(aq)}$ did not produce any detectable intermediate sulfoxyanions. These results are also similar to those of aqueous H_2S oxidation with oxygen (Chen and Morris, 1971, 1972; Zhang and Millero, 1994; Vairavamurthy et al., 1994).

Experiments documenting the formation of intermediate sulfoxyanions during pyrite oxidation should not be taken as evidence that the same oxyanions are to be found in natural waters during sulfide weathering. In experimental systems, these compounds can only be detected in solution when the aqueous layer next to the mineral surface is strongly sheared by high stirring rates so that these metastable products can not back-react by further electron exchange with the solid. Such strong shearing is not found generally in ground-water systems and even rapidly-moving surface waters rarely exhibit such shearing at the mineral surface. Luther (1987, 1990) has pointed out that species such as thiosulfate and sulfite would not be detected in solutions containing $Fe^{3+}_{(aq)}$ because they oxidize so rapidly; experiments by Williamson and Rimstidt (1993) and references therein confirmed that this reaction is rapid. Furthermore, intermediate sulfoxyanions are an excellent source of energy for chemoautotrophic bacteria of the *Thiobacillus* genus and may be quickly biodegraded before detectable concentrations can accumulate (Gould et al., 1994).

The experiments of Granger and Warren (1969) are often cited as evidence for the formation of sulfoxyanions from pyrite oxidation and the role of sulfoxyanions in the genesis of ore deposits. However, these authors admitted that the thiosulfate they found in their column experiments may have been formed by the oxidation of residual aqueous Na_2S solution. They had first added H_2O_2 solution in an effort to sterilize the column and then added Na_2S solution to reduce the iron oxide stains that had formed from the peroxide treatment. After such a traumatic chemical treatment, significant quantities of thiosulfate would have formed from the aqueous sulfide solution and would have been difficult to remove completely from the column. The thiosulfate thus formed may have had nothing to do with pyrite oxidation.

It has long been known that ferric iron rapidly oxidizes pyrite (Stokes, 1901). Experiments carried out by Garrels and Thompson (1960) and McKibben and Barnes (1986) have confirmed the balanced reaction stoichiometry:

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 16H^{+}_{(aq)} \qquad [3]$$

for the oxidation of pyrite by aqueous ferric ions. This reaction is considerably faster than the reaction with oxygen as the oxidant, but significant concentrations of oxidized iron only occur at low pH values because of the low solubility of hydrolyzed ferric iron at circumneutral pH values. Hence, it is thought that pyrite oxidation is initiated by oxygen at circumneutral pH (equation [2]) but as pH values reduce to about 4, the rate of oxidation becomes governed by equation [3]. Oxygen is still required to replenish the supply of ferric iron according to

$$Fe^{2+}_{(aq)} + 1/4O_{2(g)} + H^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 1/2H_2O_{(l)} \qquad [4]$$

but the oxygen does not have to diffuse all the way to the pyrite surfaces. It is quite possible for pyrite to oxidize in the absence of dissolved oxygen. Nevertheless, the overall rate of pyrite oxidation in a tailings pile, in a mine, or in a waste rock pile will largely be determined by the overall rate of oxygen transport (advection and diffusion).

Considerable speculation can be found in the literature on the question of the initiation and propagation of pyrite oxidation. Undoubtedly, during the initiation of pyrite oxidation, there are complex chemical and microbiological processes occurring in microenvironments (Williams et al., 1982), i.e., within a few tens of nanometers of the surface of a sulfide grain. These regions are inaccessible to normal sampling techniques and are not represented by the bulk aqueous phase. For example, when oxygen initially adsorbs to a pyrite surface and transfers electrons, an accumulation of protons will form at or near the surface. Acidophilic iron-oxidizing bacteria will begin to colonize and a film of acidic water will cover the mineral grain without affecting the bulk aqueous phase. Even before some acidic water develops, neutrophilic *Thiobacilli* will catalyze the initial stage of pyrite oxidation (Blowes et al., 1995; Gould et al., 1994). The extent to which these microenvironmental gradients affect the bulk properties are dependent on many factors, not the least of which is the pyrite concentration in the rock, soil, or waste material. The existence and importance of these microenvironments is well illustrated by the formation of jarosite, a mineral that can only form under acid conditions and has been found in soil waters of circumneutral pH (Carson et al., 1982).

The oxidation of at least 18 different sulfide minerals has been investigated (Table 6.3). Most of these have been studied with and without microbial catalysis by *Thiobacillus ferrooxidans*. The microbial oxidation rate is usually greater than the abiotic rate, all other conditions being equal. Unfortunately, most of the microbial studies were done without measurement of surface area and without a consistent procedure for removing small particles or otherwise cleaning the samples before the experiment. The lack of these characteristics prevents any direct comparison of microbial oxidation rates except in a qualitative manner. The results for abiotic and biotic oxidation of pyrite, however, are of considerably better quality than for other sulfide minerals and some quantitative comparisons are possible.

It should be noted that arsenic-rich minerals such as arsenopyrite and orpiment are also subject to bacterially catalyzed oxidation (Ehrlich, 1963a, 1964). Indeed, the occurrence of arsenite-oxidizing bacteria in acid mine waters has been reported by Wakao et al. (1988) and one of the first reports of arsenite oxidation by heterotrophic bacteria was that of Turner (1949).

There are now numerous reports on the oxidation rates of pyrite and marcasite by oxygen (Bergholm, 1955; McKay and Halpern, 1958; Smith and Shumate, 1970; Mathews and Robins, 1974; Goldhaber, 1983; McKibben and Barnes, 1986; Moses et al., 1987; Nicholson et al., 1988; Moses and Herman, 1991), by ferric iron (Bergholm, 1955; Garrels and Thompson, 1960; Smith and Shumate, 1970; Mathews and Robins, 1972; Wiersma and Rimstidt, 1984; McKibben and Barnes, 1986; Moses et al., 1987; Brown and Jurinak, 1989; Moses and Herman, 1991), and by hydrogen peroxide (McKibben and Barnes, 1986). The oxidation rates of pyrrhotite in the presence of oxygen (Nicholson and Scharer, 1994) and marcasite, covellite, galena, sphalerite, chalcopyrite, and arsenopyrite in the presence of ferric iron (Rimstidt et al., 1994) have been measured. Pyrite oxidation rates from different studies are generally comparable, but differences in experimental design, initial pH values, temperatures, grain size, mineral preparation, method for data reduction and rate law expression make a quantitative comparison difficult. For this paper, we use the results of McKibben and Barnes (1986) on pyrite to compare with the biotic rates in the next section. Table 6.4 summarizes the reaction rates from several studies cited above for a pH close to 2, $m_{Fe(III)} = 10^{-3}$, temperatures close to 25°C, and oxygen in equilibrium with the atmosphere.

The rates in Table 6.4 show that the oxidation of pyrite by ferric iron (according to the reaction stoichiometries given in equations [2] and [3]) can be about 2–3 orders of magnitude faster than by oxygen, that some minerals oxidize more rapidly than pyrite and some more slowly, and that oxidation rates can range over three orders of magnitude. These rates are demonstrably faster than the dissolution rates for aluminosilicate minerals (White and Brantley, 1995) by one to several orders of magnitude.

TABLE 6.3—Sulfide oxidation studies (more references can be found in Nordstrom and Southam, 1997).

Mineral	Formula	Oxidant	pH	Reference
Pyrite	FeS_2	O_2, Fe^{3+}, H_2O_2	0-10	See references in next sections
Marcasite	FeS_2	O_2, Fe^{3+}	2–3	Wiersma and Rimstidt (1984); Silverman et al. (1961)
Pyrrhotite	$Fe_{1-x}S$	O_2	2–6	Nicholson and Scharer (1994)
Sphalerite	(Zn, Fe)S	O_2, Fe^{3+}	2–7	Rimstidt et al. (1994); Torma et al. (1972); Khalid and Ralph (1977)
Galena	PbS	O_2, Fe^{3+}	2	Rimstidt et al. (1994); Torma and Subramanian (1974)
Chalcopyrite	$CuFeS_2$	O_2, Fe^{3+}	1.2–2.5	Rimstidt et al. (1994); Torma et al. (1976)
Arsenopyrite	FeAsS	O_2, Fe^{3+}	2	Rimstidt et al. (1994); Ehrlich (1964)
Covellite	CuS	O_2, Fe^{3+}	2	Walsh and Rimstidt (1986); Rickard and Vanselow (1978)
Chalcocite	Cu_2S	O_2	2–4.8	Beck (1977); Sakaguchi et al. (1976)
Greenockite	CdS	O_2	2.3	Torma et al. (1974)
Millerite	NiS	O_2	2.3	Torma et al. (1974)
Cobalt sulfide	CoS	O_2	2.3	Torma et al. (1974)
Klockmannite	CuSe	O_2	2.3	Torma and Habashi (1972)
Cinnabar	HgS	Fe^{3+}	2	Burkstaller et al. (1975)
Enargite	Cu_3AsS_4	O_2	3	Ehrlich (1964)
Orpiment	As_2S_3	O_2		Ehrlich (1963a)
Bornite	Cu_5FeS_4	O_2		Landesman et al. (1966)
Molybdenite	MoS_2	O_2	2.5	Brierley and Murr (1973)
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	O_2		Yakhontova et al. (1980)
Stibnite	Sb_2S_3	O_2		Torma et al. (1974)
Pentlandite	$(Fe, Ni)_9S_8$	O_2		Brierley and Le Roux (1977)

TABLE 6.4—Abiotic reaction rates (mol m^{-2} s^{-1}) for sulfide mineral oxidation.

Mineral/Oxidant	MB86[1]	BJ89[2]	R94[3,7]	N94[4]	NS94[5]
Pyrite/O_2	3.1×10^{-10}			5.3×10^{-10}	1.1×10^{-10}
Pyrite/Fe^{3+}	9.6×10^{-9}	1.8×10^{-8}	1.9×10^{-8}		
Pyrrhotite/O_2				1.4×10^{-8}	
Marcasite/Fe^{3+}			1.5×10^{-7}		
Arsenopyrite/Fe^{3+}			1.7×10^{-6}		
Galena/Fe^{3+}			1.6×10^{-6}		
Sphalerite/Fe^{3+}			7.0×10^{-8}		
Blau. covellite[6]/Fe^{3+}			7.1×10^{-8}		
Chalcopyrite/Fe^{3+}			9.6×10^{-9}		
Covellite/Fe^{3+}			9.1×10^{-9}		

[1] McKibben and Barnes (1986); because there appears to be an error in the stated value for pyrite oxidation by oxygen we have used the corrected value from Nicholson (1994).

[2] Brown and Jurinak (1989); average from oxidation rates measured in different electrolytes.

[3] Rimstidt et al. (1994).

[4] Nicholson (1994); the value for pyrite is an average from four studies covering a pH range of 1-8.

[5] Nicholson and Scharer (1994) and Tervari and Campbell (1976).

[6] "blau. covellite" is blaubleibender or "blue-remaining" covellite having slightly different optical and X-ray properties than ordinary covellite.

[7] The values listed for R94 are all given in terms of the amount of Fe(III) reduced except for pyrite. All values for pyrite are given in the same units, per mole of pyrite oxidized, for purposes of direct comparison.

Galvanic protection does occur during oxidative dissolution of coexisting sulfide minerals. This phenomenon is the same as that for galvanized iron. The more electroconductive metal sulfide (the one with the higher standard electrode reduction potential, see Sato, 1992) will oxidize at a slower rate and the less electroconductive sulfide will oxidize at a faster rate than either one would when not in contact. Sveshnikov and Dobychin (1956) reported that rates of metal release from different sulfides are related to their electrode potentials and that a mixture of sulfide minerals in contact releases more metals into solution and decreases the pH more than monomineralic samples. Sveshnikov and Ryss (1964) postulated that these electronic properties of co-existing conductive sulfides are important during the weathering of sulfide mineral deposits. Sato (1992) has used electrochemical data on metal sulfides, typical of heavy metal sulfide deposits, to explain the mineral assemblage that is found during supergene enrichment.

Nicholson and Scharer (1994) mixed pyrrhotite and pyrite in different proportions to see if there was any evidence for galvanic protection, but could not detect any such effect in their study. Kwong (1995) has done laboratory experiments to show the effect of galvanic protection during dissolution of multi-sulfide mineral assemblages. The relative rates of mineral dissolution follow the sequence indicated by standard electrode potentials as outlined by Sato (1992).

Because the oxidation rate for pyrite by $Fe^{3+}_{(aq)}$ is faster than that by oxygen, it is important to know the oxidation rate for ferrous to ferric iron according to equation [4]. Numerous studies on the ferrous iron oxidation rate show that, under acid conditions, the rate becomes very slow and independent of pH. Singer and Stumm (1968) reported an abiotic rate of 2.7×10^{-12} mol L^{-1} s^{-1} at pH values below 4. Similar rates have been reported elsewhere. Such rates are considerably slower than the rate of oxidation of pyrite by $Fe^{3+}_{(aq)}$; hence, equation [4] would be the rate-limiting step were it not for the catalytic effect of bacteria.

Microbial oxidation: Historical perspective

Microorganisms are abundant in natural waters containing acid mine drainage; indeed, they are often the *only* form of life under such conditions. Powell and Parr (1919) and later Carpentor and Herndon (1933) suggested that pyrite oxidation and the consequent acid mine drainage from coal deposits may be catalyzed by bacteria. Lackey (1938) observed flagellates, rhizopods, ciliates, and green algae in 62 West Virginia streams. Joseph (1953) found gram-positive and gram-negative bacilli and cocci, fungi, green algae, diatoms, and actinomyces in acidified surface waters and soils in West Virginia and Pennsylvania. Acid mine waters from a copper mine in the southwestern U.S. were found to contain yeasts, flagellates, protozoa, and amoebae (Ehrlich, 1963b). "Acid slime streamers" have often been observed in acid mine waters (Dugan et al., 1970; Dugan, 1972).

As long ago as 1888 it was recognized by S.N. Winogradsky that certain microbes could oxidize reduced inorganic compounds, such as sulfur, to gain energy for the reduction of carbon dioxide for metabolism and growth (see Sokolova and Karavaiko, 1968). Microorganisms that utilize reduced inorganic substances are known as chemolithotrophic (see Mills, 1999). Nathansohn (1902) first isolated a *Thiobacillus* species and the acidophilic bacterium, *Thiobacillus thiooxidans*, was isolated and identified by Waksman and Jåffe (1921, 1922) from soils containing free sulfur and phosphate. Colmer and Hinkle (1947), Colmer et al. (1950), Temple and Colmer (1951), and Temple and Delchamps (1953) isolated a new chemoautotrophic and acidophilic bacterium, *Thiobacillus ferrooxidans*, and showed that microbial degradation of pyrite was an important factor in the production of acid mine waters.

The nutritional requirements for *T. ferrooxidans* are ubiquitous. Nitrogen and carbon dioxide are available in the atmosphere. Sulfur is readily available in mined environments, and only small amounts of phosphorous are needed. *Thiobacilli* have several adaptive techniques that permit them to tolerate low pH and high metal concentrations (Tuovinen et al., 1971; Kushner, 1978). Some studies have shown that *T. ferrooxidans* can tolerate g/l concentrations of Zn, Ni, Cu, Co, Mn, and Al (Tuovinen et al., 1971). Scala et al. (1982) found consistent and roughly equal concentrations of *T. thiooxidans* and *T. ferrooxidans* in mine effluents of different compositions from quite different mines, in different geological and climatological environments, in different parts of the country (from California to Virginia). The diversity of microorganisms and their populations in mineral deposit and mine waste environments is complex and not well understood. Further investigations on the microbial ecology of mines and mine wastes are certainly needed.

T. thiooxidans oxidizes elemental sulfur but not iron, *T. ferrooxidans* oxidizes both iron and sulfur compounds, and a third species, *Leptospirillum ferrooxidans*, behaves metabolically like *T. ferrooxidans* but has a helical-rod morphology first described by Markosyan (1972). *L. ferrooxidans* is now thought to be equally important as the other two bacilli (Sand et al., 1992). Mixed cultures oxidize reduced iron and sulfur compounds faster than single-species cultures (Kelly et al., 1979; Wakao et al., 1982). Apparently, bacteria are preconditioned by the medium in which they are cultured and may have a synergistic association with other species. For example, *T. ferrooxidans* grown in ferrous-containing solutions exhibited different surface chemistry than those grown on minerals such as pyrite, elemental sulfur, and chalcopyrite (Devasia et al., 1993) as exhibited by hydrophobicity and electrophoretic mobility measurements. The bacilli grown on mineral sulfides developed a proteinaceous cell surface appendage that adhered to the solid surface whereas the cells grown in ferrous iron solutions contained no such characteristic. The importance of these features bears on the mechanism of microbial oxidation. Free-floating bacteria can catalyze the oxidation of iron from ferrous to ferric in aqueous solution, and then the ferric iron directly oxidizes the pyrite. Silverman (1967) calls this the indirect mechanism. The direct contact mechanism works by direct adhesion of the bacteria to the pyrite surface. There has been a long-standing debate over whether the direct or indirect mechanism is dominant. We contend that the indirect mechanism is the dominant one, but there is some evidence for enhancement of the pyrite oxidation rate by direct microbial contact. Surface-etch patterns may result from bacterial attachment (Bennett and Tributsch, 1978), and direct microbial growth on pyrite surfaces has been observed (Konishi et al., 1990).

Microbial oxidation: Kinetics

The catalytic effect of *T. ferrooxidans* on the aqueous oxidation of ferrous to ferric iron is well-established. Singer and Stumm (1968, 1970a, b) found that bacteria increased the ferrous iron oxidation rate by 10^5 over the abiotic rate, from about 3×10^{-12} mol L^{-1} s^{-1} to about 3×10^{-7} mol L^{-1} s^{-1}. Silverman and Lundgren (1959), Lundgren et al. (1964), and Lacey and Lawson (1977) grew *T. ferrooxidans* on culture media and typically measured oxidation rates of 2.8–8.3×10^{-7} mol L^{-1} s^{-1}. Wakao et al. (1977) measured field oxidation rates of ferrous iron oxidation in acid mine drainage and estimated 3×10^{-6} mol L^{-1} s^{-1} but the stream velocity was not measured. Nordstrom (1985) measured stream velocities and iron oxidation rates of 2 to 8×10^{-7} mol L^{-1} s^{-1} in a mountainous stream drainage containing acid mine waters, where the range of values depended on climatic conditions. From these studies we have chosen an average microbial oxidation rate for ferrous iron of 5×10^{-7} mol L^{-1} s^{-1} for the purpose of comparison with the abiotic rates.

Table 6.5 summarizes abiotic and microbial rates of oxidation for ferrous iron and pyrite under roughly comparable conditions (except for the field rates cited here and discussed later). The microbial oxidation rate of pyrite by oxygen is very similar to the abiotic oxidation rates of pyrite by either oxygen or ferric iron. Studies by Wakao et al. (1984) showed that adsorption of bacterial cells on pyrite surfaces actually inhibited pyrite oxidation and that it was the growth of free-floating ferrous-iron-oxidizing bacteria that contributed to pyrite oxidation. These results help to clarify the reaction mechanism. Pyrite oxidation is primarily accomplished by microbial catalysis by the indirect mechanism, as defined earlier.

Estimates of field oxidation rates of pyritiferous waste rock or tailings cover a wide range of values, from three orders of magnitude less than the microbial rate to two orders of magnitude greater (Table 6.5). The field rates are primarily based on flux rates of oxygen depletion upon reaction with pyrite in waste rock or tailings. There may be complications with the assumptions made in translating temperature and oxygen profiles into flux rates. The relation between flux rates and actual *in situ* rates of pyrite oxidation may be more difficult to quantify than previously realized. The main problem is estimating the reactive surface area of the sulfides. Other problems may include the consumption of oxygen by processes other than pyrite oxidation, the dependence of temperature profiles on the moisture content, the salinity of the moisture, the temperature dependence of the oxygen consumption rate, climatic variability in pressure and temperature, site heterogeneities, and variations in thermal conductivities of the various waste materials. Averaging hydrologic properties over spatial and temporal intervals may cause inaccurate estimations of flux rates and oxidation rates at some sites.

A direct comparison of the rates of microbial oxidation of aqueous ferrous iron with rates of microbial oxidation of pyrite would be helpful in discerning the rate-controlling step of these processes, but it is difficult to accomplish. Aqueous iron oxidation is expressed as a molar concentration change with respect to time (mol L^{-1} s^{-1}), whereas pyrite oxidation is a function of surface area and the ratio of pyrite mass to solution volume or porosity (mol m^{-2} s^{-1}). Two investigations make such a comparison possible: Southham and Beveridge (1992) described bacterial cell densities on pyrite surfaces and Olson (1991) conducted an interlaboratory comparison of pyrite bioleaching rates. Neither study reported pyrite surface area but both reported grain size, so that surface areas may be estimated from the relationship between surface area and grain size for sulfide minerals.

Figure 6.1 depicts the dependence of surface area (in cm^2 g^{-1}) on grain size for pyrite and other sulfide minerals. The solid line represents the diameter-to-surface-area relationship for an ideal sphere or cube of pyrite with a density of 5.0 g cm^{-3} (see Parks, 1990; Nicholson, 1994). The dashed line is a best fit for cleaned quartz grains from Parks (1990). Two suggestions are evident from Figure 6.1. More recent determinations demonstrate the effect of more carefully sized and cleaned pyrite grains (compare museum pyrite of Braley, 1954, with any of the more recent non-diagenetic pyrite). Secondly, the diagenetic or framboidal pyrite has much more surface area for a given mass than coarse-grained pyrite. Several of the data points on Figure 6.1 lie close to the best fit of Parks (1990), which will be used as a lower limit and as an estimate of the relationship of surface area to grain diameter.

Southam and Beveridge (1992) determined values of 10^7 to 10^9 cells g^{-1} for *Thiobacilli* on surfaces of Lemoine tailings at Chibougamau, Quebec, Canada, by the most probable number method. Their tailings samples were in the size range of 200 mesh and higher, hence about 50 micrometers (μm) in diameter or about 500 cm^2 g^{-1} in surface area. A cell count of 10^8 cells g^{-1} for a surface area of 500 cm^2 g^{-1} works out to 2 x 10^5 cells cm^{-2} or 2 x 10^9 cells m^{-2} on pyrite surfaces. For a tailings aquifer with 30% porosity and assuming only pure pyrite in the solids, the cell concentration in the slurry becomes (1 - porosity)(pyrite density)(cell count) = (0.7) x (5 g ml^{-1}) x (10^8 cells g^{-1}) = 3.5 x 10^8 cells ml^{-1}, which is the same concentration of cells in solution that would oxidize aqueous ferrous iron optimally at 5 x 10^{-7} mol L^{-1} s^{-1} (Silverman and Lundgren, 1959). It is also in the same range of cell concentration found in acid mine waters in the environment (Scala et al., 1982). Therefore, it appears that the observed concentration of *Thiobacilli* on pyrite surfaces would produce aqueous Fe^{III} concentrations of the same order of magnitude as those formed by microbial oxidation of ferrous iron in aqueous solution by free-floating bacteria.

A preferable method of estimating the microbial rate of pyrite oxidation can be obtained from the interlaboratory comparison of pyrite bioleaching rates coordinated by the National Institute of Science and Technology (Olson, 1991). Eight laboratories participated in tests using a standardized method with 1 gram of pyrite from the same source. The pyrite was cleaned and sterilized after sizing to -165/+250 mesh (58 to 91 μm). Then sample was inoculated with a standard culture of *Thiobacillus ferrooxidans*. From Figure 6.1, the surface area would have been about 350 cm^2 g^{-1}. The reported oxidation rate (12.4 mg Fe L^{-1} h^{-1} or about 6 x 10^{-8} mol L^{-1} s^{-1}) is about an order of magnitude lower than the microbial oxidation rate of aqueous ferrous iron (Table 6.5). Olson

TABLE 6.5—Comparison of abiotic, microbial, and field oxidation rates (pH ≈ 2, T ≈ 25°C).

Reaction or Process (references)	Abiotic rate	Microbial rate	Field rate
Oxidation of aqueous ferrous iron (Singer and Stumm, 1968; Lacey and Lawson, 1977; Nordstrom, 1985)	3 x 10^{-12} mol L^{-1} s^{-1}	5 x 10^{-7} mol L^{-1} s^{-1}	5 x 10^{-7} mol L^{-1} s^{-1}
Oxidation of pyrite by ferric iron (McKibben and Barnes, 1986; Rimstidt et al., 1994)	1 to 2 x 10^{-8} mol m^{-2} s^{-1}		
Oxidation of pyrite by oxygen (McKibben and Barnes, 1986; Olson, 1991)	0.3 to 3 x 10^{-9} mol m^{-2} s^{-1}	8.8 x 10^{-8} mol m^{-2} s^{-1}	
Oxidation of waste dump (Ritchie, 1994a, b)			0.03 x 10^{-8} mol m^{-2} s^{-1}
Oxidation of tailings (Elberling et al., 1993)			20 to 60 x 10^{-8} mol m^{-2} s^{-1}

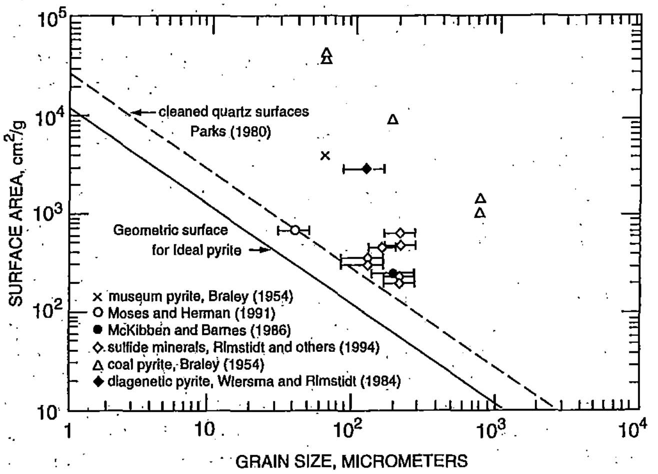

FIGURE 6.1—Surface area versus grain size for pyrite and other sulfide minerals.

(1991) used 1 g of pyrite in 50 ml of solution, so we can calculate the microbial oxidation rate of pyrite as

$$R = \frac{12.4 \text{ mg Fe L}^{-1}\text{h}^{-1}}{56 \text{ mg Fe mmol}^{-1}} \; \frac{50 \text{ ml}}{(1\text{g})\,(350 \text{ cm}^2\text{g}^{-1})}$$

$$\frac{1 \text{ mol}}{10^3 \text{ mmol}} \; \frac{1 \text{ L}}{10^3 \text{ ml}} \; \frac{10^4 \text{ cm}^2}{\text{m}^2} \; \frac{1 \text{ h}}{3{,}600 \text{ s}}$$

$$= 8.8 \times 10^{-8} \text{ mol m}^{-2}\text{ s}^{-1} \qquad [5]$$

This rate falls squarely between the abiotic oxidation of pyrite by ferric iron and the microbial oxidation of ferrous iron, i.e., within the uncertainty of the data, there is little difference between the oxidation rate of pyrite by ferric iron and the oxidation rate of ferrous iron by *T. ferrooxidans*. The lower rate of microbial pyrite oxidation compared to the oxidation rate of ferrous iron by *T. ferrooxidans* suggests that the heterogeneous reaction is the rate-determining step. We would suggest, however, that the uncertainties on the rates are large enough and the natural variation in the ferrous iron oxidation rate is large enough that there is not a significant difference. Hence, the rate of pyrite oxidation proceeds about as fast as the aqueous ferric iron can be produced from ferrous iron through microbial catalysis.

Field oxidation rates

What are the actual oxidation rates of pyritic mine waste in the field? What governs oxidation rates at field sites? Singer and Stumm (1970a) conceived of rates in the conventional sense of chemical kinetics. They described the abiotic oxidation of aqueous ferrous to ferric iron as the "rate-determining step" for the production of acid mine drainage because it is orders of magnitude slower than the oxidation of pyrite by ferric iron. This abiotic iron oxidation rate, however, has limited relevance because iron- and sulfur-oxidizing bacteria are ubiquitous in ground and surface waters, catalyzing aqueous iron and pyrite oxidation by orders of magnitude. Singer and Stumm (1970a, b) recognized that microbial catalysis greatly speeds up the oxidation of aqueous ferrous iron and that either the complete elimination of oxygen or the use of bactericides would be necessary to eliminate microbial activity. The microbial oxidation of aqueous ferrous iron, under optimal conditions of temperature, oxygen supply, and nutrient availability, is the fastest rate known in the system. This rate provides an upper limit to the pyrite oxidation rate. The lower limit is zero (or negative if sulfate reduction is considered) in the absence of oxygen and water. These extremes of rate cover a wide range over which actual rates may occur in the field.

The effects of sulfide surface area, degree of crystallinity, and purity cannot be overstated. One has only to compare the spontaneous oxidation of "framboidal," "microcrystalline," or "cryptocrystalline" pyrite (see Pabst, 1940; Caruccio, 1970) with untarnished, large, euhedral pyrite cubes that have survived in museums for several centuries to notice the difference in oxidation rates. The signatures of kings, queens, and other dignitaries over the last century can still be seen clearly on an exposed surface of massive chalcopyrite in the Falun mine in Sweden. Caruccio (1970) and Caruccio et al. (1976) pointed out that the grain size and surface area of pyrite in coal deposits has a considerable influence on the production rate of acid mine drainage, with framboidal pyrite being the most reactive. Normalizing reaction rates to unit surface area is now routinely done when reporting dissolution rates of minerals but differences in degree of crystallinity and purity (solid solution substitutions) may also affect reaction rates. Furthermore, the "reactive surface area" may be significantly less than the total measured surface area as measured by standard techniques (Dzombak and Morel, 1990). Reactive surface area refers to those sites on the surface that are actively available to adsorb and chemically bond with aqueous species, and can be reduced by intergranular contact or inclusion within other minerals. Another complication in the field is that not all exposed surface sites are in the flow path of the water, thereby reducing further the reactive surface area.

Field oxidation rates for pyrite are complicated by air and water transport processes, microbial growth kinetics, microbial ecology, organic compounds, temperature gradients, secondary mineral formation, neutralization reactions, climatic patterns, and the site-specific design of mine workings, waste dumps, and tailings. The production rate of acid mine drainage is governed by rates of transport and attenuation processes, which tend to be slower than rates of pyrite oxidation. Some confusion exists in the literature because the distinction between oxidation rates and transport/attenuation rates has not been made clear. In this sense, an obvious parallel or analogy can be made with silicate mineral weathering rates and discrepancies between laboratory and field studies (see Alpers and Nordstrom, 1999, and White and Brantley, 1995).

Ritchie (1994a, b) has reviewed and analyzed the physical factors that pertain to the acid production rate from waste piles. He has shown that the limiting factor is the transport and reaction of oxygen in the waste. Three main processes are dominant in these systems: convection of oxygen, diffusion of oxygen, and the intrinsic oxidation rate which he has calculated for two sites and compared with results compiled from other sites. Ritchie (1994 a, b) described the "global oxidation rate" as the overall flux rate of acid mine drainage from a waste dump and the "intrinsic oxidation rate" as the oxygen consumption rate, measured from oxygen profiles in units of mol kg^{-1} s^{-1} or mol m^{-3} s^{-1}. Several assumptions are involved in making these computations, including a stoichiometric relationship between oxygen consumed and pyrite oxidized (i.e., that oxygen is consumed only by pyrite).

The oxidation of pyrite is a highly exothermic reaction, which can cause thermal air convection in waste dumps and underground mines (Zverev et al., 1983). Air temperatures of 50 to 65°C are commonly achieved in waste-rock piles and copper heap-leach dumps (Cathles and Apps, 1975; Harries and Ritchie, 1981; Cathles, 1994; Ritchie, 1994a) and a water temperature of 47°C was reported from the Richmond Mine at Iron Mountain, California (Alpers and Nordstrom, 1991). Temperature and density gradients resulting from heat generation cause convective air transport, which can be a significant oxygen-supply mechanism (Ritchie, 1994a). Cathles (1994) indicated that convective gas flux driven by thermal gradients was dominant in the well-instrumented Midas Test Dump and other larger dumps at Kennecott's Bingham Canyon Mine (Cathles and Apps, 1975). However, Ritchie (1994a) asserted that the convective flux in a large dump generally applies over a much smaller area than the diffusive oxygen flux.

The relative importance of diffusion vs. convection depends primarily upon the range of air permeability. Ritchie (1994a) suggested a cutoff permeability value of 10^{-9} m^2. Above this value, convection should dominate and below this value, diffusion should dominate. Ritchie (1994a) also pointed out that he has found the global oxidation rate to be insensitive to changes in the intrinsic oxidation rate. Hence, for unsaturated waste rock, the dominant rate-limiting process should be oxygen diffusion, especially in a newly built waste-rock dump (Ritchie, 1994a). Parts of waste rock piles, usually located near the center, are typically dominated by diffusion whereas the outer edges may be dominated by convection. With time, convective gas transport will penetrate further into the dump as it ages (Ritchie 1994a).

Other factors that affect the ultimate release of acid drainage include the climate, hydrologic variables, mineralogy of the waste materials, physical structure of the waste and geological structure and setting of the mine site, historical evolution of mineral-processing practices, materials used and discarded in mineral processing, geomorphology of the terrain, and vegetation. Discussion of these subjects is beyond the scope of this chapter and can be found in other chapters of this volume or in other review papers. For example, Moore and Luoma (1990) have outlined the sources, transport mechanisms, and sinks for mining and mineral-processing wastes. They use the categories "primary," "secondary," and "tertiary" according to how many times the mining waste has been retransported. A comprehensive overview of tailings problems and their management has been published by Ritcey (1989).

REDOX CHEMISTRY AND MINERAL SOLUBILITIES

Eh-pH diagrams and redox chemistry

The traditional graphical method of delineating the stabilities of reduction-oxidation (or redox) species in geochemical systems (and in corrosion systems) has been through the use of Eh-pH (or pε-pH) diagrams. These are a type of master variable diagram where the independent or master variable is pH. Originally developed by Pourbaix (1945, 1966; also see Pourbaix and Pourbaix, 1992; Sato, 1992) to portray equilibrium relationships in metal corrosion systems, they were introduced and championed in the geochemical literature by Krumbein and Garrels (1952), Garrels (1954) and Garrels and Christ (1965). Hem (1961, 1985), Krauskopf (1967), Krauskopf and Bird (1995) and many others have used the concepts of Eh and pH as a convenient means of representing redox relationships for ions and minerals. The reader is referred to these sources as well as discussions by Stumm and Morgan (1981) and Nordstrom and Munoz (1994) for an introduction to the construction of these diagrams from thermodynamic data.

A pε-pH diagram for the Fe-S-K-O_2-H_2O system is shown on Figure 6.2 with the thermodynamic stability fields of several major ions and minerals of iron. The formation and occurrence of jarosite, goethite, and other secondary iron minerals are discussed in the next section. The stability boundary between goethite and jarosite can vary over several units of pH depending on the crystallinity and particle size of these minerals. Metastable phases such as ferrihydrite may form more readily than the thermodynamically stable phase in some conditions, and thus can play an important role in controlling aqueous metal concentrations.

Figure 6.2 indicates that goethite is stable under mildly acidic to basic oxidizing conditions, jarosite is stable under acidic oxidizing conditions, and pyrite is stable under a large range of strongly reducing conditions. Acidity tends to promote dissolution of minerals under a range of redox conditions. Additional iron minerals can be shown on diagrams similar to Figure 6.2, if additional components such as carbonate, silica, phosphate, and uranium are included, but such multi-component diagrams can become very cluttered and most of these additional minerals are not particularly relevant to acid mine waters.

These pε-pH diagrams can be very useful in showing the general stability relations among redox-sensitive ions and minerals but their limitations must be clearly understood:

1) The redox chemistry of a solution or a natural water cannot be measured by a simple "Eh" parameter. There is no such thing as a single representative redox potential or an Eh of a water. A measurement of electromotive force (EMF) with a platinum

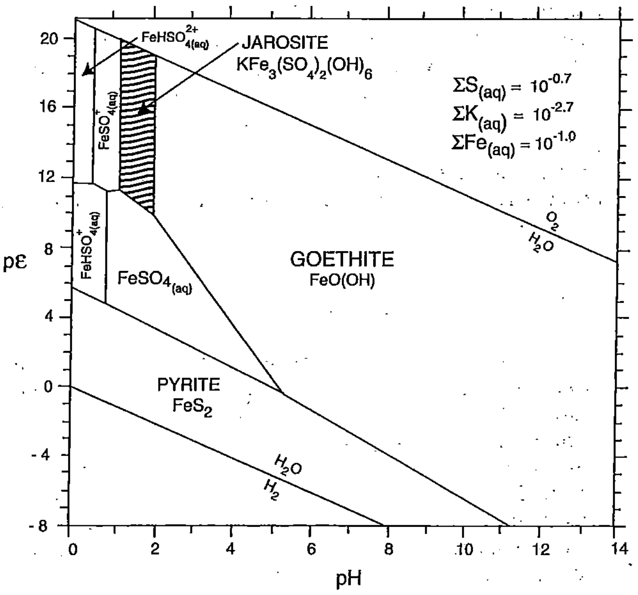

FIGURE 6.2—pε-pH diagram, showing stable solid phases in Fe-S-K-O-H system at 25°C (modified from Alpers et al., 1989).

electrode (converted to Eh by subtracting the reference electrode half-cell potential) for a water sample may or may not reflect an equilibrium potential for a single redox couple but there is no single Eh that represents the water (Thorstenson, 1984; Hostetler, 1984). Hence, Eh measurements may be quantitatively correlated to a specific redox couple such as Fe(II/III) but otherwise they are of little use.

2) Redox couples of different elements rarely, if ever, reach equilibrium at temperatures below 100°C. This fact is one of the reasons why a single Eh cannot be assigned to a water sample. Redox disequilibrium is the rule, not the exception. Lindberg and Runnells (1984) showed that when different redox couples are measured in the same water sample, none of them appear to be in equilibrium. The reasons for this are largely kinetic. Electrons transfer much more readily between redox-sensitive ions and surfaces such as electroconductive minerals (most sulfides) and bacteria than with other ions in solution.

3) Redox potential measurements respond to electroactive aqueous ions. To be electroactive an ion must have a sufficiently high exchange current density (Bricker, 1982) so that there is no kinetic hindrance to the transfer of electrons. This criterion requires both sufficiently high concentrations of the redox-sensitive ions as well as the lack of kinetic barriers to electron transfer. Only two common elements clearly meet this requirement: iron (II/III) and sulfur (sulfide). All other elements and ions found in natural waters (with the possible exception of uranium and cobalt under unusual circumstances) do not.

4) The redox conditions of a water sample are best characterized analytically by determining the concentrations of multiple redox species for each redox-active element in the sample. Acid mine waters are easily analyzed for Fe(II) and Fe(total) (with Fe(III) computed by difference or by direct determination, To et al., 1999) by visible spectrophotometry using a ferroin reagent such as bipyridine, orthophenanthroline, or ferrozine. The more precise and sensitive nature of methods using a colorimetric reagent such as ferrozine make them preferable to atomic absorption or inductively-coupled plasma atomic-emission spectroscopy (Ball and Nordstrom, 1994). Once the concentrations of redox species have been determined then the classification of Berner (1981) can be used to describe the redox chemistry. Berner suggests a practical lower limit of detection as 10^{-6} molar for oxygen, iron, sulfide, and methane. The presence of oxygen classifies a water as "oxic," the absence of oxygen and presence of ferrous iron classifies it as "post-oxic," the presence of sulfide classifies it as "sulfidic," and the presence of methane classifies it as "methanic." This general classification works well for the typical ground water evolving into more reducing conditions with time and depth, but not for acid mine waters. Acid mine waters and other types of surface waters are usually of a mixed redox chemistry and only be determining relevant redox species can you interpret the redox chemistry of the water.

Nordstrom et al. (1979) showed that acid mine waters typically have sufficient iron concentrations to give an equilibrium potential at the platinum electrode for the Fe (II/III) redox couple but that the O_2/H_2O redox couple was far from equilibrium with respect to the iron couple. Careful analyses of acid mine waters from the Leviathan/Bryant Creek system demonstrate the limits of redox measurements for mine waters even more clearly (Ball and Nordstrom, 1989, 1994). Figures 6.3a and 6.3b compare platinum electrode Eh measurements with Eh values calculated from Fe (II/III) determinations and speciated with the WATEQ4F code (Ball and Nordstrom, 1991; see Alpers and Nordstrom, 1999). The comparison of measured and calculated Eh on Figures 6.3a and 6.3b shows an excellent correlation for samples with total iron concentrations greater than 10^{-5} m. Most of the deviations are found at the lowest Eh values where the iron concentrations are so low (less than 10^{-6} m) that iron is no longer electroactive. Furthermore, these waters are saturated with atmospheric oxygen so that a mixed potential results from the oxygen competing with the low concentrations of iron. Poor comparisons of calculated and measured Eh are occasionally found at very high iron concentrations and low pH values because of inherent problems with the chemical model under these conditions (see Alpers and Nordstrom, 1999).

Iron photoreduction

Iron (II) concentrations in oxygenated surface waters have not only been detected but have been found to vary from night to day. The concentrations of Fe (II) reach a peak during midday, at the peak of insolation. The solar radiation reduces both dissolved Fe (III) and colloidal ferric hydroxide in natural waters (Waite and

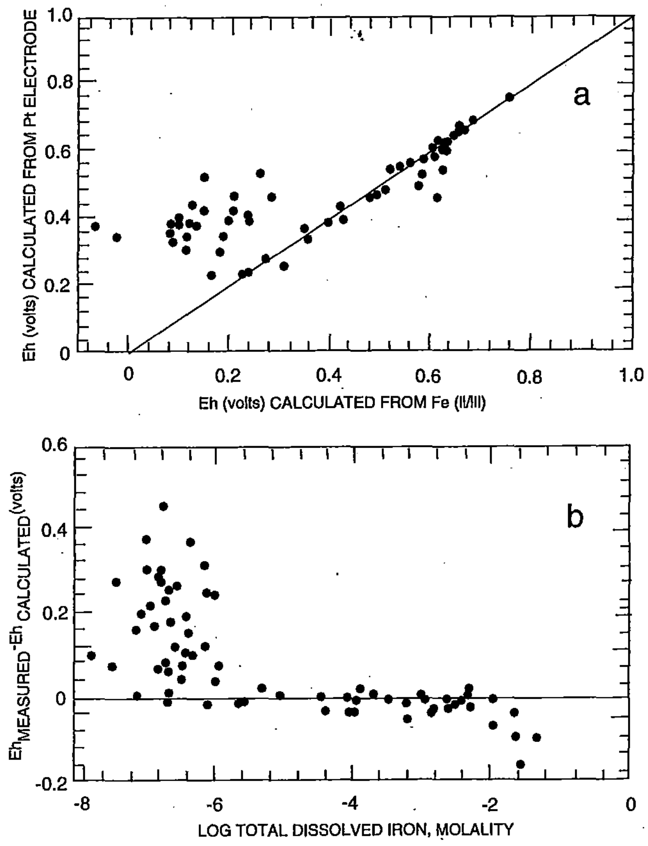

FIGURE 6.3—(a) Comparison of Eh calculated from the Fe (II/III) redox couple to Eh measured with a platinum electrode. (b) Difference between calculated and measured Eh plotted as function of total dissolved iron concentrations in molal units. Data from Leviathan/Bryant Creek watershed, California and Nevada (Ball and Nordstrom, 1989; 1994).

Morel, 1984). The same effect has been found for acid mine waters that have dissolved iron <5 mg/l (McKnight et al., 1988; McKnight and Bencala, 1988). McKnight et al. (1988) found the daytime production of Fe(II) to be nearly 4 times faster than the nighttime oxidation of Fe(II). These results might also be enhanced by light inhibition of iron- and sulfur-oxidizing bacteria (Le Roux and Marshall, 1977). The continual exposure of acid mine waters to the sun promotes recycling of the iron between dissolved and particulate phases and may have important consequences on the sorption of metals. Solar radiation could lead to Ostwald ripening of iron colloids which would increase the iron hydroxide particle size and decrease the reactive surface area. Alternatively, recycling of iron hydroxides and recreation of fresh colloidal surfaces would promote surface area and the opportunity for increased adsorption of metals (McKnight and Bencala, 1989). These effects, however, may only be detectable in streams with relatively small concentrations of iron. Acid mine waters with more typical iron concentrations of 20–1000 mg/l may not show this effect. In wetlands, an opposite effect has been observed, where Fe (II) concentrations reach a minimum during daylight hours; this effect has been attributed to daytime oxygenation by algae (Wieder, 1994).

Saturation indices (SI) and mineral solubilities

When complete water analyses for the major ions are available, a speciation computation can be done to determine the state of saturation with respect to any particular minerals for which thermodynamic data are available (see Alpers and Nordstrom, 1999). Numerous acid mine waters and tailings pore waters have been subject to these calculations to achieve more quantitative interpretations on the control of metal concentrations by mineral solubilities. Some brief examples of the usefulness of this approach are shown here.

Acid mine waters are characterized by low pH, high iron and aluminum concentrations, high metal concentrations, and high sulfate concentrations. Minerals that might be stable under these conditions should be hydrolyzed iron- and aluminum-sulfate minerals and insoluble metal-sulfate minerals. Prime candidates include jarosite, alunite, barite, anglesite, gypsum, and a suite of ferric- and aluminum-hydroxysulfate compounds. Figures 6.4a-d show two examples of SI values for barite, one for alunite, and one for anglesite. If equilibrium solubility is achieved and if it exerts the dominant control on the concentration of one or more elements, then the SI values should show a linear and horizontal trend close to zero. Such a pattern signifies that the water chemistry reflects the stoichiometry of the given mineral and may have reached equilibrium saturation. As expected, the values tend to plateau with the appropriate stoichiometry of the mineral but generally in the region of supersaturation. This effect might be explained by the particle size effect on solubility because the solubility product constant usually refers to a coarse-grained, well-crystallized material and it might also be due to solid solution substitution of trace components. Some of the apparent supersaturation could also be due to inadequacies in the chemical model, especially in the activity coefficient and stability constant expressions.

The behavior of aluminum and iron as reflected in saturation indices can be seen on Figures 6.5a-d. On Figure 6.5a, a plateau in the SI values for $Al(OH)_3$ is seen at pH values above about 4.5. At pH values above 4.5, solubility equilibrium is apparently reached with respect to microcrystalline or amorphous $Al(OH)_3$ and seems to be maintained at all higher pH values. This phenomenon was pointed out by Nordstrom and Ball (1986) and can be more clearly seen on Figure 6.5b in which the activity of the free aluminum ion is plotted against pH. The rate of aluminum leaching from common minerals at low pH is not generally fast enough relative to the flow rate of surface and ground waters to reach equilibrium with gibbsite. Furthermore, gibbsite solubility is so high at very low pH that it becomes an unstable or metastable phase with respect to other aluminous minerals, especially in the presence of high sulfate concentrations (Nordstrom, 1982b).

When acid mine drainage is diluted by neutral surface waters, the pH and aluminum concentrations eventually reach the gibbsite solubility curve and aluminum concentrations become controlled by one of 3 possibilities: (1) solubility of a solid phase (such as gibbsite), (2) a surface coating control with a stoichiometry similar to gibbsite, or (3) a common aluminosilicate mineral with an exchange ratio of Al^{3+} to H^+ of 1:3. A pH of 5 is also equal to the pK_1, the negative logarithm of the first hydrolysis constant for aluminum, and without hydrolysis the precipitation of hydrolyzed aluminum would not be possible. Hem and Roberson (1990) have shown that the rate of aluminum hydrolysis increases as pH values rise to about 5 so that the hydrolysis kinetics for dissolved aluminum favors the tendency toward equilibrium. Nordstrom et al. (1984) have shown that, when rapid mixing causes precipitation of aluminum in acid mine waters, the solid produced is an amorphous aluminum-hydroxysulfate material that might best be described as an amorphous basaluminite.

Comparable diagrams for iron are shown on Figures 6.5c-d. Apparent supersaturation with respect to ferric hydroxide or ferrihydrite occurs at pH values above about 4. The supersaturation might be explained by substitution of sulfate for hydroxide ions in the ferrihydrite and the formation of a schwertmannite-like phase. Schwertmannite [$Fe_8O_8(OH)_6(SO_4)$] was described by Bigham et al. (1990) and Bigham (1994) and is discussed in more detail in a later section of this chapter. The apparent supersaturation with respect to ferric hydroxide might also be explained by the formation of colloidal iron particles that cannot be filtered out by 0.1 micrometer pore size membranes. This apparent supersaturation behavior for ferric hydroxide is commonly seen for both surface waters and ground waters.

In general, the stoichiometry of a phase controlling the solubility of an aqueous constituent can be derived from an appropriately-selected ion-activity plot. For example, if pure ferric hydroxide were controlling the solubility of ferric iron, the reaction

$$Fe(OH)_3 + 3\,H^+ \rightleftharpoons Fe^{3+} + 3\,H_2O \qquad [6a]$$

and its log equilibrium constant expression

$$\log K = \log a_{Fe^{3+}} - 3 \log a_{H^+} + 3 \log a_{H_2O} \qquad [6b]$$

would indicate that a plot of Fe^{3+} activity versus pH (= $-\log a_{H+}$) should have a slope of -3.

The observed slope of -2.4 on Figure 6.5d is clearly inconsistent with solubility control by pure ferric hydroxide having a molar Fe:OH ratio of 1:3 (Nordstrom, 1991). Similar results (a

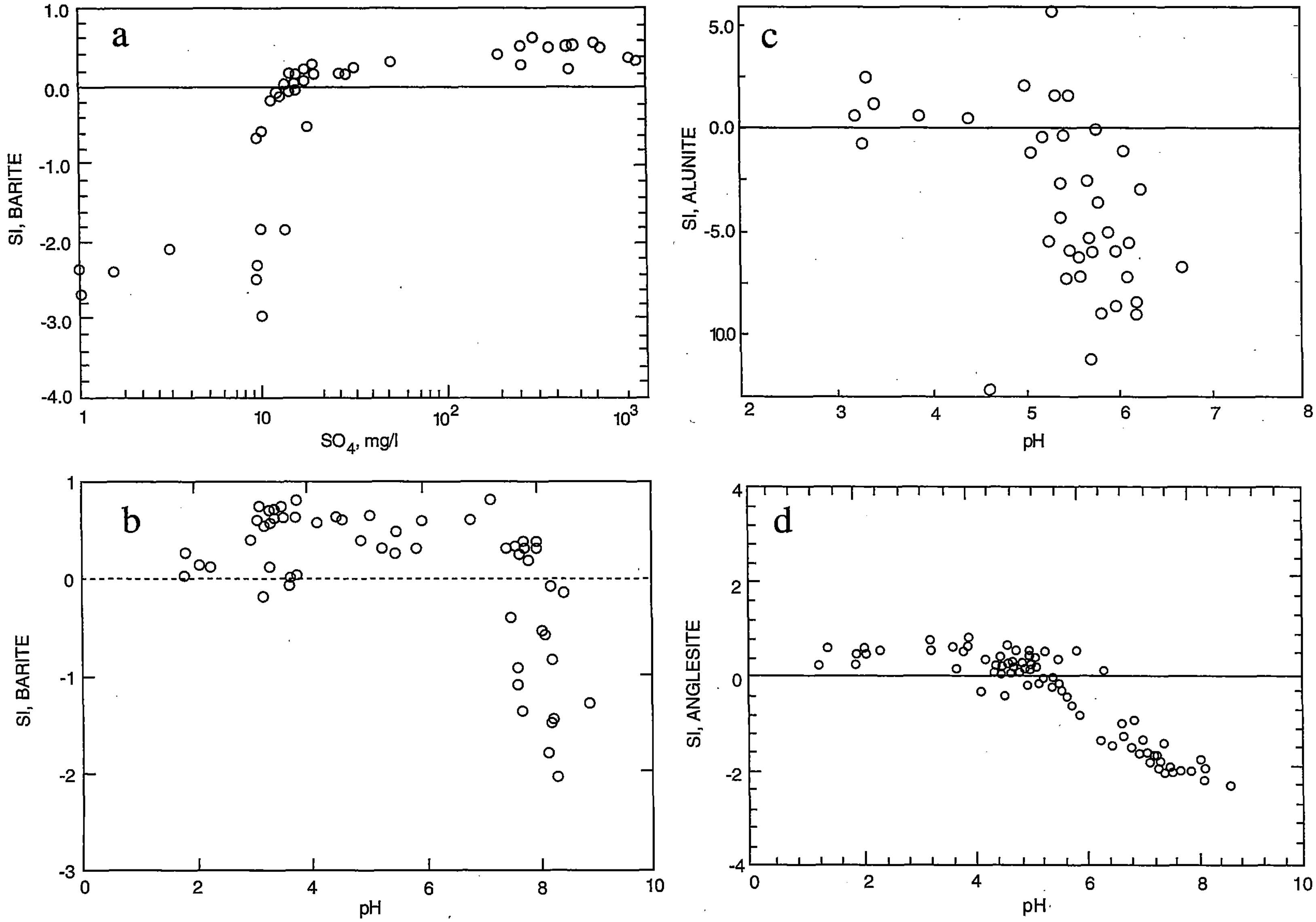

FIGURE 6.4—(a) Saturation indices for barite plotted as a function of sulfate concentration for data from the Osamu Utsumi mine site (Nordstrom et al., 1992). (b) Saturation indices for barite plotted as a function of pH for data from the Leviathan mine site (Ball and Nordstrom, 1989, 1994). (c) Saturation indices for alunite plotted as a function of pH for data from the Osamu Utsumi mine site (Nordstrom et al., 1992). (d) Saturation indices for anglesite plotted as function of pH for mine tailings based on data from Blowes (1990).

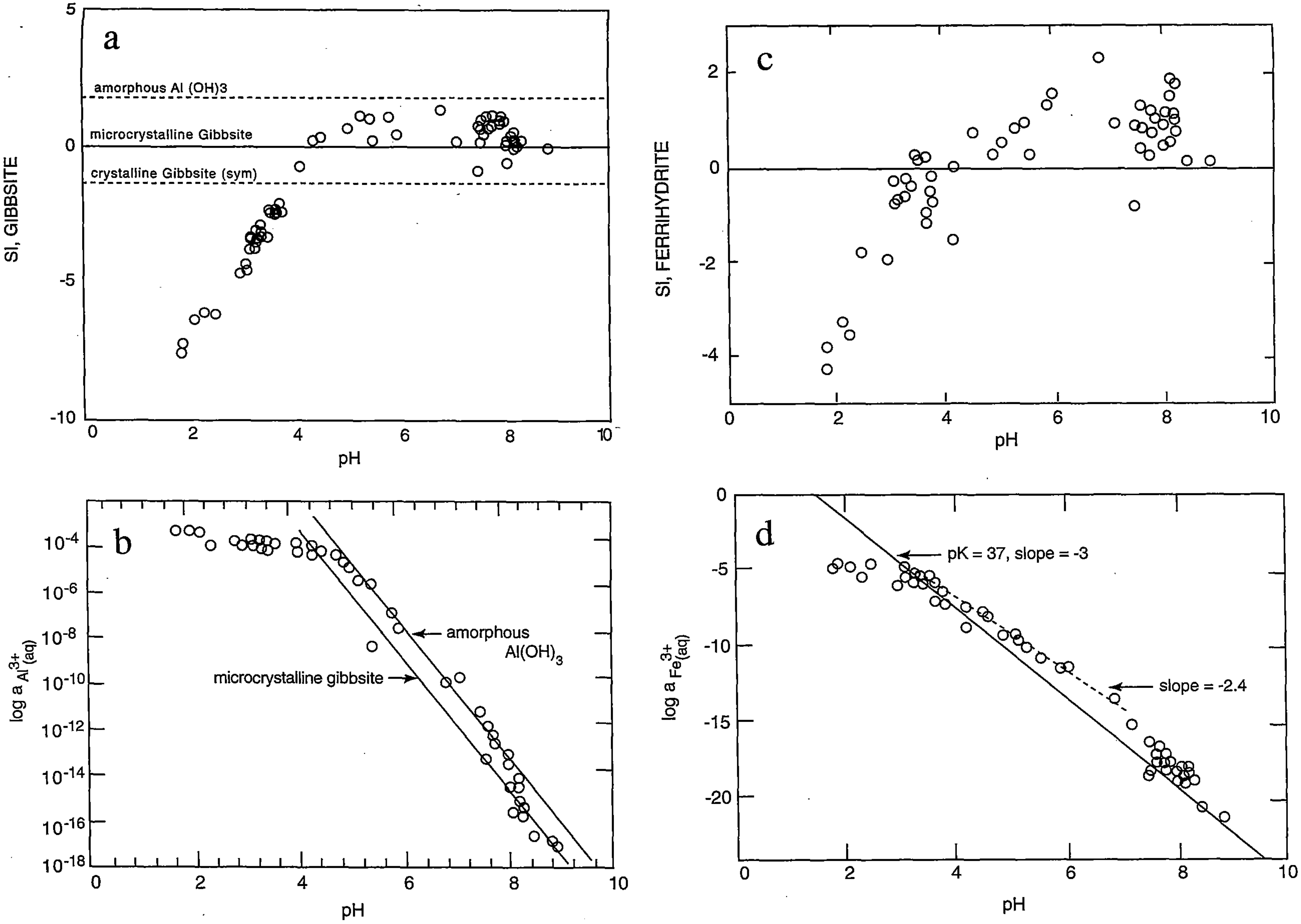

FIGURE 6.5—(a) Saturation indices for gibbsite as a function of pH for data from the Leviathan mine site (Ball and Nordstrom, 1989, 1994). (b) Logarithm of the activity of the aluminum ion plotted against pH with the equilibrium solubility lines for amorphous $Al(OH)_3$ and microcrystalline gibbsite shown (for 25°C). (c) Saturation indices for ferrihydrite ($\equiv Fe(OH)_3$) as a function of pH for data from the Leviathan mine site (Ball and Nordstrom, 1989, 1994). (d) Logarithm of the activity of the ferric ion plotted against pH with the equilibrium solubility for freshly precipitated ferrihydrite at 25°C shown as a solid line and the best fit for data in the pH range of 3.5 to 7 shown as a dashed line (Nordstrom, 1991). The higher slope from the fitted line suggests non-stoichiometric substitution of sulfate for hydroxide in the precipitating ferric phase.

slope of -2.35) in other surface-water environments and in laboratory experiments were interpreted by Fox (1988) to represent a ferric hydroxide in which nitrate has partially substituted for hydroxide, i.e., $Fe(OH)_{2.35}(NO_3)_{0.65}$. Kimball et al. (1994) found a regressed slope of -2.23 from iron data on the acid mine waters of St. Kevin Gulch, Colorado during a neutralization experiment.

The relation on Figure 6.5d could be caused by a reaction involving a hypothetical sulfate-substituted ferric hydroxide such as

$$Fe(OH)_{2.4}(SO_4)_{0.3} + 2.4\,H^+ \rightleftharpoons Fe^{3+} + 0.3\,SO_4^{2-} + 2.4\,H_2O \quad [7a]$$

with its log equilibrium constant expression

$$\log K = \log a_{Fe^{3+}} - 2.4 \log a_{H^+} + 0.3 \log a_{SO_4^{2-}} + 2.4 \log a_{H_2O} \quad [7b]$$

The data on Figure 6.5d do not indicate solubility with schwertmannite of the composition reported by Bigham (1994). The expected slope on a plot of a_{Fe3+} vs. pH showing schwertmannite solubility equilibrium would be -2.75, based on the reaction

$$FeO(OH)_{0.75}(SO_4)_{0.125} + 2.75H^+ \rightleftharpoons$$
$$Fe^{3+} + 0.125\,SO_4^{2-} + 1.75\,H_2O \quad [8a]$$

and its log equilibrium constant expression

$$\log K = \log a_{Fe^{3+}} - 2.75 \log a_{H^+} + 0.125 \log a_{SO_4^{2-}} + 1.75 \log a_{H_2O} \quad [8b]$$

Bigham (1994) reported that schwertmannite is associated with mine drainage ranging in pH from about 2.5 to 6, and is most commonly associated with "typical" mine effluents with pH from 3 to 4. Bigham (1994) also noted that ferrihydrite is associated with mine drainage in the pH range of about 5 to 8. The data on Figure 6.5d with slope of -2.4 span from pH of about 4 to about 7. This suggests that the apparent stoichiometry is more likely to represent a sulfate-substituted ferrihydrite, schwertmannite, or other hydrous ferric oxide with a molar Fe:OH ratio of 1:2.4. It is also possible that mixtures of different iron mineral phases are precipitating from these waters over this pH range and the slope is not clearly resolvable into a particular reaction. This complex chemistry needs more detailed work to quantitatively relate water chemistry to iron colloids and other precipitates.

In his thesis work (Blowes, 1990) and in subsequent papers (Blowes and Jambor, 1990; Blowes et al., 1991; Blowes and Ptacek, 1994; Ptacek and Blowes, 1994), Dr. Blowes and his colleagues have mapped the saturation indices for siderite, calcite, goethite, ferrihydrite, gypsum, melanterite, and anglesite with depth in tailings piles at Heath Steele, New Brunswick, and Waite Amulet, Quebec. Similar detailed hydrogeochemical studies are being completed at Kidd Creek and Copper Cliff, Ontario. In some of these studies, two aqueous models are compared: the ion association model and the specific ion interaction (Pitzer) model. For some minerals, the comparisons of saturation indices computed by both models are nearly identical, but for others the Pitzer model gives SI values that are more consistently at equilibrium. The mineralogy at these sites has also been studied in detail and it fully supports the interpretations based on the Pitzer model saturation index computations, which are more appropriate for solutions of high ionic strength. The strengths and limitations of these aqueous models as applied to acid mine waters are discussed by Alpers and Nordstrom (1999).

SECONDARY MINERALS

Acid mine waters are highly reactive solutions that can dissolve most primary minerals and form a wide variety of secondary minerals. The understanding of secondary mineral formation has important consequences for environmental management of mining wastes. Insoluble secondary minerals with large surface areas can effectively immobilize many of the major contaminants in acid mine waters, providing an important attenuation and detoxifying mechanism. Soluble secondary minerals also slow down toxic metal mobility but only temporarily until the next rainstorm or snowmelt event. Hence, the occurrence and properties of these minerals are equal in importance to the water chemistry and pyrite oxidation rates for the interpretation of chemical processes occurring in mine waste environments.

For the purpose of this discussion, secondary minerals are defined as those that form during weathering. A further distinction can be made between secondary minerals formed by natural processes prior to human disturbance and those formed after the commencement of mining, exploration, or other human activity. In this chapter we refer to these effects as pre-mining and post-mining.

There are clear similarities in the geochemistry of pre- and post-mining weathering processes, as well as in the nature of the associated aqueous solutions and secondary minerals; however, there are also some important differences. Mining tends to cause a dramatic increase in the rate of sulfide oxidation reactions because of rapid exposure of large volumes of reactive material to atmospheric oxygen. Blasting and crushing of ores and waste material leads to a considerable increase in the available surface area of reactive minerals. Hydrologic changes caused by mine dewatering in both underground and open-pit mines may expose large volumes of rock to atmospheric oxygen.

The type of secondary mineral formed depends on the composition of the water, the type and composition of the primary minerals, the temperature, and the moisture content. The initial minerals that precipitate in certain environments tend to be poorly crystalline, metastable phases that may transform to more stable phases over time. Therefore, those secondary minerals that are preserved in the geologic record in leached cappings, gossans, and zones of secondary enrichment may be quite different in their mineralogy compared with the secondary minerals that form over shorter time frames in mine drainage settings.

Four important processes lead to the formation of secondary minerals from acid mine waters: (1) iron oxidation and hydrolysis, (2) reaction of acid solutions with sulfides, gangue minerals, and country rock, (3) mixing of acid mine waters with more dilute waters, and (4) evaporation of acid mine waters.

A suite of Fe(III) minerals can form from iron oxidation and hydrolysis. Many of these phases have very low solubility, fall in the colloidal size range (less than 1.0 micrometer), and can adsorb or coprecipitate significant quantities of trace elements. Reaction of acid mine waters with country rock and some gangue minerals, such as calcite and dolomite, will cause neutralization and precipitation of metals. Evaporation concentrates the acid, sulfate, and metals found in acid mine waters until they reach mineral saturation, forming efflorescent sulfate salts, a common feature associated with oxidizing sulfide-bearing mine wastes.

This section describes five categories of secondary minerals: (1) metal oxides, hydroxides, and hydroxysulfates, (2) soluble sulfates, (3) less-soluble sulfates, (4) carbonates, and (5) secondary sulfides. For each category, one or more lists of mineral formulas are provided (Tables 6.6–6.13). These lists are intended to include the more common secondary minerals in each category, but it should not be inferred that all minerals on the lists have been demonstrated to control metal concentrations in acid mine waters on a large scale. A discussion of the secondary minerals that are likely to control metal concentrations in acid mine waters is included as the final part of this section.

Metal oxides, hydroxides, and hydroxysulfates

Most divalent and trivalent metals exhibit amphoterism, i.e., they produce a solubility minimum at circum-neutral pH values with enhanced solubilities under both acidic and basic conditions. Figure 6.6 shows both the amphoteric solubilities of ferrihydrite, gibbsite, and the hydroxides of Cu, Zn, Fe(II), and Cd at 25°C, as well as the importance of pH in controlling the dissolved concentration of these metals. Different metals reach their minimum solubility at different pH values. This phenomenon provides the basis for the removal of metals during rapid neutralization of acid mine drainage by alkaline treatment (lime, limestone, or sodium hydroxide). The pH-specific solubility minimum varies for each metal, causing a different efficiency of metal removal for neutralization to a given pH (Barton, 1978). At metal concentrations greater than 10^{-6} molar, metal hydroxides should precipitate in the following sequence with increasing pH: Fe(III), Pb, Al, Cu, Zn, Fe(II), and Cd. This sequence is also very closely followed by the pH-dependent sequence of adsorption of metals on hydrated ferric oxide surfaces (Dzombak and Morel, 1990).

Iron—The minerals discussed in this section are ferrous (Fe^{II}) and ferric (Fe^{III}) oxides, hydroxides, and hydroxysulfates. The list of minerals in Table 6.6 includes some that are not observed to form readily during weathering, but are included for completeness and for analogy with other metals, especially aluminum (Table 6.7; discussed in a later subsection).

Ferrous hydroxide is considerably more soluble than its ferric equivalent at a given pH (Fig. 6.6) and the former appears only rarely in nature. $Fe(OH)_2$, when slightly oxidized, takes on a green appearance and is also known as "green rust." It occurs when Fe^{II}-rich solutions are mixed with a highly alkaline solution and allowed to oxidize slightly. This material has been prepared in the laboratory and Ponnamperuma et al. (1967) have argued effectively for its occurrence in nature, but it is not credited as a mineral because it is unstable and poorly characterized.

Ferrihydrite is a poorly crystalline form of hydrous ferric oxide/hydroxide that seems to be the first phase to form upon neutralization of Fe(III)-bearing solutions at low temperature, surficial conditions. For many years, this phase was considered to be "amorphous $Fe^{III}(OH)_3$." However, careful examination by X-ray diffraction (XRD) and Mössbauer spectroscopy (e.g., Schwertmann, 1985a) has revealed that this material is commonly a poorly crystalline substance with a range of structural order, yielding an XRD pattern with two to six peaks (Carlson and Schwertmann, 1981). Ferrihydrite formed in mining environments tends to have two to four XRD peaks, and is associated with waters having pH values of 5 to 8 (Bigham, 1994). The "two-line" ferrihydrite is also referred to as "proto-ferrihydrite" (Chukhrov et al., 1973), although this is not an approved mineral name. At least two formulas for ferrihydrite have been reported: $Fe_5HO_8 \cdot 4H_2O$ (Towe and Bradley, 1967) and $Fe_2O_3 \cdot 2FeO(OH) \cdot 2.6H_2O$, a structural formula based on infrared spectroscopy (Russell, 1979). The latter formula can also be expressed as $Fe_2O_3 \cdot 1.8H_2O$.

Hematite (Fe_2O_3) and goethite [FeO(OH)] are the most common and most stable forms of ferric oxide and oxyhydroxide, respectively. The solubility and stability of hematite and goethite are sufficiently close that grain size and surface Gibbs free energy have important influence on the phase relations. With regard to coarse-grained minerals, goethite appears to be stable relative to hematite at temperatures below about 80°C (Langmuir, 1969, 1971, 1972). However, fresh goethite nearly always occurs in a particle size less than 0.1 micrometers in soils and sediments, so it is unstable relative to coarser-grained hematite under the geologic conditions that form sedimentary rocks. This conclusion is supported by both laboratory (Berner, 1969, 1971) and field evidence (Walker, 1967, 1974, 1976). Both goethite and hematite have slow growth kinetics at surficial temperatures, so the initial solid products from the hydrolysis of $Fe^{3+}_{(aq)}$ are poorly crystalline, metastable phases such as microcrystalline goethite or ferrihydrite. Thus, kinetic factors play an important role in determining the nature of the ferric precipitate(s) that may form as a result of ferrous iron oxidation and hydrolysis. Some progress has been made in understanding these factors and how they influence the distribution of hematite and goethite in soil profiles (Kämpf and Schwertmann, 1982; Schwertmann, 1985a, b). Ferrihydrite is known to convert to hematite if conditions are maintained between pH 5 and 9. Outside of this range, most of the ferrihydrite dissolves and reprecipitates as goethite (Schwertmann and Murad, 1983). Other factors may influence the formation of these phases, such as humidity, Al-content (Tardy and Nahon, 1985), grain size, and the presence of trace elements (Torrent and Guzman, 1982; Thornber, 1975). The preparation and characterization of iron oxides has been reviewed by Schwertmann and Cornell (1991).

Relatively little work has been done to understand the factors that influence the distribution of hematite and goethite in the weathered zone of mineral deposits. Leached cappings and gossans represent the *in situ* oxidized equivalents of porphyry copper and massive sulfide deposits, respectively. The mineralogy of iron in the oxidized zones of these deposits is dominated by hematite, goethite, and jarosite [$(K,Na,H_3O)Fe^{III}_3(SO_4)_2(OH)_6$]. The early literature (e.g., Locke, 1926; Tunell, 1930) documented the observation that "deep maroon to seal brown" hematitic iron oxide tends to remain in rocks after oxidation of supergene chalcocite-bearing ores, which form as the enrichment product of copper-iron sulfide protores. Increasing amounts of goethite and jarosite relative to hematite correlate with progressively higher ratios of pyrite to chalcocite at depth (Loghry, 1972; Alpers and Brimhall, 1989). The texture of the iron oxides (or "limonites") also reflects a systematic change from indigenous (in original sulfide cavities) to transported (outside sulfide cavities and in fractures) with increasing relative pyrite content prior to oxidation (Blanchard, 1968; Loghry, 1972).

Aluminum has been observed to substitute into goethite and

TABLE 6.6—Iron oxide, hydroxide, and hydroxysulfate minerals.

Mineral	Formula
Hematite	α-Fe_2O_3
Maghemite	γ-Fe_2O_3
Magnetite	$FeO \cdot Fe_2O_3$
Goethite	α-$FeO(OH)$
Akaganéite	β-$FeO(OH,Cl)$
Lepidocrocite	γ-$FeO(OH)$
Feroxyhyte	δ'-$FeO(OH)$
Ferrihydrite	$Fe_5HO_8 \cdot 4H_2O$ or $Fe_2O_3 \cdot 2FeO(OH) \cdot 2.6H_2O$
Schwertmannite	$Fe^{III}{}_8O_8(SO_4)(OH)_6$
Fibroferrite	$Fe^{III}(SO_4)(OH) \cdot 5H_2O$
Amarantite	$Fe^{III}(SO_4)(OH) \cdot 3H_2O$
Jarosite	$KFe^{III}{}_3(SO_4)_2(OH)_6$
Natrojarosite	$NaFe^{III}{}_3(SO_4)_2(OH)_6$
Hydronium Jarosite	$(H_3O)Fe^{III}{}_3(SO_4)_2(OH)_6$
Ammonium Jarosite	$(NH_4)Fe^{III}{}_3(SO_4)_2(OH)_6$
Argentojarosite	$AgFe^{III}{}_3(SO_4)_2(OH)_6$
Plumbojarosite	$Pb_{0.5}Fe^{III}{}_3(SO_4)_2(OH)_6$
Beaverite	$PbCuFe^{III}{}_2(SO_4)_2(OH)_6$
Chromate jarosite	$KFe^{III}{}_3(CrO_4)_2(OH)_6$

TABLE 6.7—Aluminum oxide, hydroxide, and hydroxysulfate minerals.

Mineral	Formula
Corundum	α-Al_2O_3
[γ-Alumina][1]	γ-Al_2O_3
Diaspore	α-$AlO(OH)$
Boehmite	γ-$AlO(OH)$
Gibbsite	γ-$Al(OH)_3$
Bayerite	α-$Al(OH)_3$
Doyleite	$Al(OH)_3$
Nordstrandite	$Al(OH)_3$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$
[Hydronium Alunite][2]	$(H_3O)Al_3(SO_4)_2(OH)_6$
Ammonium Alunite	$(NH_4)Al_3(SO_4)_2(OH)_6$
Osarizawaite	$PbCuAl_2(SO_4)_2(OH)_6$
Jurbanite	$Al(SO_4)(OH) \cdot 5H_2O$
Basaluminite	$Al_4(SO_4)(OH)_{10} \cdot 5H_2O$
Hydro-basaluminite	$Al_4(SO_4)(OH)_{10} \cdot 12\text{-}36H_2O$

[1] γ-Alumina is a synthetic compound, used as a catalyst in industry. Surface properties are reviewed by Goldberg et al. (1995).

[2] Hydronium alunite has not been found in nature and therefore is not considered a mineral.

TABLE 6.8—Some other oxide and hydroxide minerals and native metals.

Mineral	Formula
Pyrolusite	MnO_2
Hausmannite	Mn_3O_4
Manganite	γ-$MnO(OH)$
Pyrochroite	$Mn(OH)_2$
Todorokite	$(Mn^{II},Ca,Mg)Mn^{IV}{}_3O_7 \cdot H_2O$
Takanelite	$(Mn^{II},Ca)Mn^{IV}{}_4O_9 \cdot H_2O$
Rancieite	$(Ca,Mn^{II})Mn^{IV}{}_4O_9 \cdot 3H_2O$
Native copper	Cu
Tenorite	CuO
Cuprite	Cu_2O
Delafossite	$CuFeO_2$
Bunsenite	NiO
Theophrastite	$Ni(OH)_2$
Jamborite	$(Ni^{II},Ni^{III},Fe)(OH)^2(OH,S,H_2O)$
Native silver	Ag
Native gold	Au
Native mercury	Hg
Montroydite	HgO
Massicot litharge	PbO
Plattnerite	PbO_2

TABLE 6.9—Selected soluble iron-sulfate minerals.

Mineral	Formula
Melanterite	$Fe^{II}SO_4 \cdot 7H_2O$
Siderotil	$Fe^{II}SO_4 \cdot 5H_2O$
Rozenite	$Fe^{II}SO_4 \cdot 4H_2O$
Szomolnokite	$Fe^{II}SO_4 \cdot H_2O$
Halotrichite	$Fe^{II}Al_2(SO_4)_4 \cdot 22H_2O$
Roemerite	$Fe^{II}Fe^{III}{}_2(SO_4)_4 \cdot 14H_2O$
Coquimbite	$Fe^{III}{}_2(SO_4)_3 \cdot 9H_2O$
Kornelite	$Fe^{III}{}_2(SO_4)_3 \cdot 7H_2O$
Rhomboclase	$(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$
Ferricopiapite	$Fe^{III}{}_5(SO_4)_6O(OH) \cdot 20H_2O$
Copiapite	$Fe^{II}Fe^{III}{}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Voltaite	$K_2Fe^{II}{}_5Fe^{III}{}_4(SO_4)_{12} \cdot 18H_2O$

TABLE 6.10—Some other soluble sulfate minerals.

Mineral	Formula
Epsomite	$MgSO_4 \cdot 7H_2O$
Hexahydrite	$MgSO_4 \cdot 6H_2O$
Goslarite	$ZnSO_4 \cdot 7H_2O$
Bianchite	$ZnSO_4 \cdot 6H_2O$
Gunningite	$ZnSO_4 \cdot H_2O$
Zincosite	$ZnSO_4$
Gypsum	$CaSO_4 \cdot 2H_2O$
Anhydrite	$CaSO_4$
Morenosite	$NiSO_4 \cdot 7H_2O$
Retgersite	$NiSO_4 \cdot 6H_2O$
Boothite	$CuSO_4 \cdot 7H_2O$
Chalcanthite	$CuSO_4 \cdot 5H_2O$
Chalcocyanite	$CuSO_4$
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Thenardite	Na_2SO_4

TABLE 6.11—Some less-soluble sulfate and hydroxysulfate minerals.

Mineral	Formula
Celestite	$SrSO_4$
Anglesite	$PbSO_4$
Barite	$BaSO_4$
Radium sulfate	$RaSO_4$
Antlerite	$Cu_3(SO_4)(OH)_4$
Brochantite	$Cu_4(SO_4)(OH)_6$
Langite, Wroewolfeite	$Cu_4(SO_4)(OH)_6 \cdot 2H_2O$
Posnjakite	$Cu_4(SO_4)(OH)_6 \cdot H_2O$

TABLE 6.12—Some carbonate minerals.

Mineral	Formula
Rhombohedral	
Calcite	$CaCO_3$
Magnesite	$MgCO_3$
Siderite	$FeIICO_3$
Rhodochrosite	$MnCO_3$
Smithsonite	$ZnCO_3$
Otavite	$CdCO_3$
Gaspéite	$NiCO_3$
Sphaerocobaltite	$CoCO_3$
Orthorhombic	
Aragonite	$CaCO_3$
Strontianite	$SrCO_3$
Witherite	$BaCO_3$
Cerrusite	$PbCO_3$
Double	
Dolomite	$CaMg(CO_3)_2$
Kutnahorite	$Ca(Mn,Mg)(CO_3)_2$
Ankerite	$Ca(Fe^{II},Mg,Mn)(CO_3)_2$
Minrecordite	$CaZn(CO_3)_2$
Hydroxyl	
Malachite	$Cu_2(CO_3)(OH)_2$
Azurite	$Cu_3(CO_3)_2(OH)_2$
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$
Aurichalcite	$(Zn,Cu)_5(CO_3)_2(OH)_6$

TABLE 6.13—Supergene and diagenetic sulfide minerals.

Mineral	Formula
Supergene sulfide minerals	
Chalcocite	Cu_2S
Djurleite-I	$Cu_{1.965}S$
Djurleite-II	$Cu_{1.934}S$
Digenite	$(Cu,Fe)_9S_5$
Anilite	Cu_7S_4
Geerite	Cu_8S_5
Spionkopite	$Cu_{39}S_{28}$
Yarrowite	Cu_9S_8
Blue-remaining covellite	$Cu_{(1+x)}S$
Covellite	CuS
Violarite	Ni_2FeS_4
Millerite	NiS
Diagenetic sulfide minerals	
Amorphous FeS	FeS with coprecipitated Zn, Cd, Mn, Cu, Ni, As)
Mackinawite	$(Fe,Ni)_9S_8$
Smythite	$(Fe,Ni)_9S_{11}$
Greigite	$Fe^{II}Fe^{III}_2S_4$
Pyrite, marcasite	FeS_2

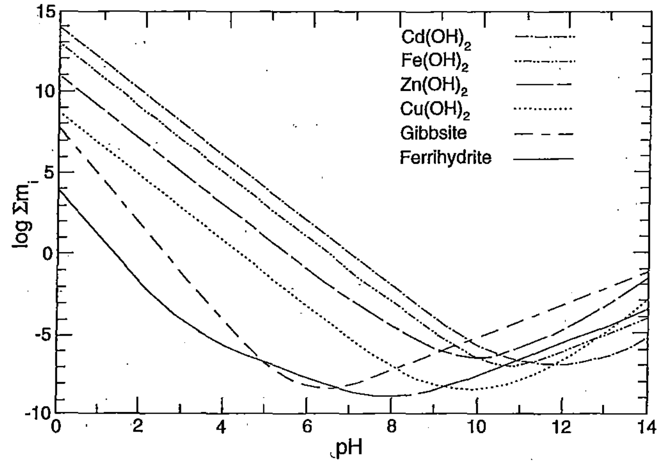

FIGURE 6.6—Solubility curves for gibbsite, ferrihydrite, and the hydroxides of Cu, Zn, Fe (II), and Cd shown as a function of pH.

hematite in certain soils, to maximum concentrations of 33 mole % AlO(OH) and 14 mole % Al_2O_3, respectively (Yapp, 1983; Tardy and Nahon, 1985; Schwertmann, 1985a). Although both iron and aluminum are highly soluble in acid mine waters, we are unaware of any data showing significant aluminum substitution in iron oxide minerals formed in mine drainage settings. Adsorption and precipitation of hydrolyzable metal ions tends to take place at pH values near the first hydrolysis pK for that metal. The first pK of hydrolysis for Fe^{III} is 2.2, and for Al is 5.0, so the coprecipitation of Al in hydrous Fe^{III} oxides formed at pH values less than about 4.5 is unlikely. This fundamental difference between iron and aluminum chemistry leads to spatial and temporal separation of precipitating phases of hydrolyzed iron and aluminum in oxidizing mineral deposits and mine waters.

Schwertmannite is a poorly crystalline iron-hydroxysulfate mineral that has recently been discovered to be a fairly common phase in ochres formed in mine drainage environments (Bigham et al., 1990; Bigham, 1994; Murad et al., 1994). The structure of schwertmannite appears to be related to that of akaganéite, an iron oxyhydroxide with essential chloride (Bigham, 1994; Murad et al., 1994). A combination of powder XRD and Mössbauer spectroscopy is necessary for definitive identification of schwertmannite (Murad et al., 1994). Schwertmannite or other sulfate-substituted, hydrous ferric oxides are most likely to control ferric iron solubility in acid mine drainage, as discussed previously (Fig. 6.5d).

Jarosite-alunite—The jarosite-alunite group of minerals shares a common crystal structure and stoichiometry, with many possible compositional substitutions. The general jarosite-alunite formula is $AB_3(SO_4)_2(OH)_6$ where the B sites are occupied by Fe^{III} to form jarosites and by Al to form alunites. Endmember formulas for some of the more common jarosite group minerals are given in Table 6.6, and the more common alunite endmember formulas in Table 6.7. The A site is occupied either by a monovalent cation or by a divalent cation alternating with a vacancy to maintain charge balance. The most common occupants of the A site in order of abundance in natural alunites and jarosites are $K^+ > Na^+ > H_3O^+$ (Kubisz, 1960, 1961, 1964; Brophy and Sheridan, 1965; Scott, 1987). The pure potassium-iron endmember is jarosite and the pure potassium-aluminum endmember is alunite. Pure endmembers are rare; jarosites and alunites formed during weathering and those synthesized at temperatures below 100°C tend to contain considerable hydronium ion in the A site (Dutrizac and Kaiman, 1976; Dutrizac, 1983; Alpers et al., 1989, 1992; Stoffregen and Alpers, 1992). Hydronium jarosite has been reported as a naturally occurring mineral (Kubisz, 1970), whereas hydronium alunite has not yet been found in nature. The hydronium endmembers can be synthesized readily (Ripmeester et al., 1986). Solid solutions between alunite and jarosite have also been synthesized (Parker, 1962; Brophy et al., 1962), but thermodynamic relations for iron-aluminum substitution have not been established and mineral compositions intermediate to alunite and jarosite are not commonly observed. This effect is probably caused by the different first hydrolysis constants for Fe^{III} ($pK_1 = 2.2$) and Al ($pK_1 = 5.0$), as discussed earlier regarding hematite and goethite. Further summaries on substitutional properties of the alunite-jarosite group were presented by Scott (1987), Stoffregen and Alpers (1987, 1992), and Alpers et al. (1989). Information on the relation between the crystallographic, chemical, and isotopic properties of alunite and jarosite was reported by Alpers et al. (1992) and by Stoffregen and Alpers (1992).

Aluminum—A list of some aluminum oxide, hydroxide, and hydroxysulfate minerals and their formulas is provided in Table 6.7. Thermodynamic properties of aluminous minerals have been reviewed, evaluated, and tabulated by Hemingway and Sposito (1996). Properties of aqueous aluminum ions and polymers have been reviewed and evaluated by Nordstrom and May (1996) and Bertsch and Parker (1996), respectively.

Solubility and stability relations among gibbsite, alunite, basaluminite, jurbanite, and alunogen were delineated by Nordstrom (1982b). In acid mine waters, aluminum-sulfate and -hydroxysulfate minerals become more stable than common soil minerals such as gibbsite and kaolinite. At pH values less than about 5.5 (depending on sulfate and potassium activities) gibbsite becomes unstable relative to alunite (Nordstrom, 1982b). Below pH values of about 4, jurbanite becomes most stable. Alunogen becomes stable only at pH values below 0 (i.e., hydrogen ion activities greater than 1.0). Some of these stability relationships need to be revised in light of the work by Reardon (1988), who applied the Pitzer approach to aluminum-sulfate solutions, and the recent revisions on thermodynamic properties of aluminum minerals and aqueous species (Hemingway and Sposito, 1996; Nordstrom and May, 1996). Despite its apparent thermodynamic stability, jurbanite tends to occur only rarely as a post-mining efflorescence (Anthony and MacLean, 1976), and has not been found commonly as a mineral precipitate from acid mine waters. We suspect that jurbanite has little significance as a solubility control in spite of the near-zero SI values commonly found, for three reasons:

1) recalculation of the solubility field is needed, based on revised thermodynamic properties for auxiliary species that may show the stability field of jurbanite to be at lower pH values,
2) jurbanite appears to be an efflorescent salt and most efflorescent salts in mine wastes form at pH values much less than 4,
3) other factors seem to govern aluminum and sulfate concentrations in acid mine waters (Nordstrom and Ball, 1986).

The behavior of aluminum in acid mine waters (and stream waters affected by acid rain) has been described by Nordstrom and Ball (1986). For waters with pH values less than 4.5 to 5.0, dissolved aluminum tends to behave as a conservative ion in surface waters, whereas for waters with pH values above 5.0, solubility control of dissolved aluminum by microcrystalline to amorphous

$Al(OH)_3$ is apparent, as described previously (Figs. 6.5a and 6.5b). Such control may be caused by equilibrium solubility or by a surface reaction involving the exchange of Al^{3+} for $3H^+$ on an aluminous surface. May and Nordstrom (1991) showed that a characteristic change of behavior for aluminum from conservative to non-conservative is common for a wide variety of sulfate-acidified waters. When the pH in an acid mine water increases to 5 or higher because of rapid mixing with circumneutral, dilute water, an aluminum-hydroxysulfate compound precipitates immediately. This precipitate is usually white, and is most commonly amorphous to XRD, electron diffraction, transmission electron microscopy, and scanning electron microscopy (Nordstrom et al., 1984). It seems to be of fairly constant composition, similar to the amorphous basaluminite reported by Adams and Rawajfih (1977). It has been observed many times by people working on acid mine waters and mine wastes. The occurrence of the white, aluminous precipitate at pH values of 5 or above is so consistent that one can frequently use its presence to predict the pH of the water when a pH electrode and meter are unavailable. A classic example is the caved portal at the Gem Mine (often called the Paradise portal), in the San Juan Mountains of southwestern Colorado, which has been discharging mine water continuously with a pH of 5.5 ± 0.3 for more than 30 years. This site has a striking white precipitate, affectionately known as "white death," that consists primarily of aluminum, sulfate, and water (Nordstrom et al., 1984); anomalous concentrations of lanthanide elements have been found in this precipitate (Carlson-Foscz, 1991; Nordstrom et al., 1995).

As with the iron minerals, thermodynamic stability relations among the aluminum minerals and their kinetic rates of formation can vary greatly, depending upon sulfate concentration, salinity, pH, particle size, and temperature. Precipitation rates for some of these aluminous minerals may be sluggish so that the equilibrium conditions are not often reached in surface waters. In soil and ground waters, longer residence times favor solubility control by mineral-solution equilibria.

Other metals—Native metals, oxides, and hydroxides of several other metals such as copper, nickel, manganese, silver, gold, and mercury may occur from the weathering and oxidation of primary sulfide minerals (Table 6.8). These minerals tend to occur as residual products in oxidized zones (gossans and leached cappings), where many pore volumes of water have reacted with the formerly mineralized rocks. It is unlikely that these phases exert solubility control on large volumes of water, but rather they are likely to form during dry periods when isolated microenvironments may reach saturation with a given native metal, oxide or hydroxide. The absence of discrete trace-metal-bearing oxides and hydroxides in most oxidized mine wastes suggests that other mechanisms, such as adsorption or coprecipitation with hydrous iron oxides, limit the concentrations of dissolved trace metals in mining environments (see Smith, 1999).

The behavior of nickel in tailings impoundments and acid-mine-drainage precipitates illustrates that the fate of trace metals in mine drainage settings is generally tied to that of the major elements, particularly iron. Mineralogical analysis and microanalysis by Jambor and co-workers as part of a study on the Copper Cliff tailings area at Sudbury, Ontario, has indicated that nickel tends to occur dispersed in hydrous iron oxides forming alteration rims on pentlandite and nickeliferous pyrrhotite, rather than as discreet nickel oxide or hydroxide phases (Alpers et al., 1994b). Overall, the bulk of the nickel liberated by oxidation of these sulfides ends up in goethite, a part of the nickel remains in solution and is transported from the site of oxidation, a small amount is taken up by vermiculite and associated mixed-layer silicates that replace biotite, and some may occur as secondary violarite (see Supergene and Diagenetic Sulfides section, below), which is expected to occur but has not yet been found in the Copper Cliff tailings (Alpers et al., 1994b).

Copper oxides, particularly tenorite and cuprite, are known to form in the oxidized zone of sulfide deposits and are indicative of low pyrite content and(or) a high wallrock neutralization capacity (Loghry, 1972; Anderson, 1982). The behavior of copper in tailings impoundments and waste-rock piles is similar to that of nickel in that discrete secondary copper oxides are rarely formed; rather the copper is either transported away from the oxidized zone in solution, is fixed in other secondary phases such as sulfates, carbonates, or silicates, or is coprecipitated and(or) adsorbed to hydrous iron oxides.

Manganese oxides and hydroxides are known to form from acid mine drainage, often at considerable distance from the source(s) of sulfide oxidation and acid formation. Krauskopf (1957) pointed out that the redox and hydrolysis properties of iron and manganese are such that they sometimes behave differently under changing conditions of oxidation and reduction. Hem (1978, 1980) considered the effects of manganese oxidation and disproportionation on the coprecipitation of other trace metals with manganese oxides. He demonstrated the effect of manganese on the coprecipitation of CoO(OH) (Hem et al., 1985) and on the precipitation of zinc as hetaerolite, $ZnMn_2O_4$, at 25°C (Hem et al., 1987). He further discussed the possibility that low-temperature "ferrite" compounds may be responsible for the low concentrations of trace metals found in uncontaminated natural waters. Hem also made many other significant contributions to our understanding of the hydrolysis and precipitation of trace metals (Hem, 1985).

Manganese oxides are actively precipitating at Pinal Creek, Arizona, in the Globe-Miami mining district, and so provide an opportunity for study of geochemical processes controlling manganese solubility in a mine drainage setting. At Pinal Creek, an alluvial ground-water aquifer was contaminated by acidic recharge (pH about 2.7) from copper mining and smelting activities (Eychaner, 1991). After neutralization by interaction with the alluvial material, the contaminated ground-water emerges at near-neutral pH in a perennial reach of Pinal Creek, about 15 km downgradient from the acid source, at which point manganese-rich crusts have developed in the streambed. Chemical and XRD analyses (Lind, 1991) suggest that the manganese occurs as a mixture of two related hydrous oxides, takanelite and rancieite (see Table 6.8), plus an Mn-bearing carbonate, probably kutnohorite (see Table 6.12). The overall oxidation state of the manganese in the less-than-75 micrometer size fraction of the Pinal Creek precipitates was 3.65 (Lind, 1991). To test the hypothesis that neutralization of acidic Mn-bearing water would lead to formation of similar Mn-bearing minerals, titrations were made of Mn-rich ground waters from the Pinal Creek area with a 0.1 molar NaOH solution with and without CO_2 present; these experiments yielded hausmannite (which aged to manganite), kutnohorite, and a mixed Ca-Mn species similar to todorokite (Hem and Lind, 1993).

Soluble sulfates

Soluble sulfate minerals, often occurring as efflorescent salts, are common in mines, on mine tailings and waste rock, and on sulfide mineralization exposed to the air. These phases store metals and sulfate during dry periods and dissolve readily during flushing events, a process that has an important influence on temporal variations of metals in surface waters affected by mine wastes.

Iron sulfates—The most common efflorescent minerals are hydrated iron sulfate salts (Table 6.9). Based both on laboratory experiments of evaporating acid mine waters as well as field observations, the hydrated iron sulfate minerals seem to follow a paragenetic sequence as shown below (Buurman, 1975; Nordstrom, 1982a; C. Maenz, written commun., 1995).

melanterite (rozenite, szomolnokite)
↘
copiapite
↘
roemerite, coquimbite, kornelite
↘
rhomboclase
↘
voltaite, halotrichite

The formation of melanterite as the first phase to precipitate from the evaporation of many acid mine waters is consistent with the preponderance of aqueous ferrous iron in these waters. Reactions (2) and (3) indicate that aqueous ferrous iron and sulfate are the initial products of pyrite oxidation, and it is these ions that combine to form melanterite. The remaining iron sulfates in the generalized paragenetic sequence form as the solutions evaporate and the ferrous iron oxidizes to ferric; however, a simple progression from ferrous to ferric salts is not observed because of differences in solubility among the various salts and the influence of other major elements which substitute to a variable degree for divalent and trivalent iron, such as copper and zinc for ferrous iron and aluminum for ferric iron.

Copper tends to partition into melanterite in preference to zinc (Alpers et al., 1994a). The result of this partitioning is a tendency toward higher ratios of zinc/copper in residual solutions as melanterite and related phases form in the dry season, and then lower ratios of zinc/copper as the salts are flushed in the wet season (Alpers et al., 1994a).

Another important role of the soluble iron sulfates is to store acidity and oxidation potential in the form of hydronium and ferric ions. The mineral rhomboclase is essentially a solid form of sulfuric acid plus ferric sulfate. Although generally considered rare, large quantities of rhomboclase and other iron sulfate salts were found at Iron Mountain, California, in inactive underground mine workings within a volcanogenic massive sulfide deposit (Alpers and Nordstrom, 1991). The salts were observed to be actively forming from waters with pH values from 1 to less than -3 (Nordstrom et al., 1991; Alpers et al., 1991; Nordstrom and Alpers, 1999). Rhomboclase may be present in trace amounts in other settings where acid waters evaporate to dryness, providing a storage mechanism for hydronium ions. Other ferric-sulfate and mixed ferrous-ferric-sulfate salts have been found associated with mine wastes and spoils in numerous localities including coal and metal mines (e.g., Zodrov and McCandlish, 1978a, b; Zodrov et al., 1979; Cravotta, 1994; Plumlee et al., 1995).

Dissolution of these salts can create large quantities of very acid mine waters. Flooding of underground mines and mine wastes as a remedial measure may not result in short-term improvements in water quality because the ferric salts will dissolve and the ferric iron will hydrolyze (if pH is above 2.2), providing an oxidant that will cause continued sulfide oxidation (e.g., Cravotta, 1994).

Other metal sulfates—There are a large number of additional metal sulfates that occur as efflorescent minerals in weathered mineral deposits and mining environments. Some of the more common ones are listed in Table 6.10. One of the important aspects of these salts is that they are a solid form of acid mine drainage that is stored until the next rainstorm event when the salts can quickly dissolve and be transported to a drainage system. Dagenhart (1980) demonstrated that the concentrations of copper, zinc, iron, and aluminum increase sharply during the rising limb of the discharge as rain dissolves and flushes efflorescent salts from oxidizing tailings into a receiving stream. This phenomenon is probably common at mined sites and may be an important factor in the association of fish kills during periods of high runoff, especially after a significant dry period.

Less-soluble sulfates

Although there are a great many metal sulfate minerals of low solubility known to occur, the most common ones are barite, celestite, and anglesite (Table 6.11). These are likely to provide solubility controls for the concentrations of barium, strontium, and lead (see previous section on mineral solubilities, Fig. 6.4). Their low solubilities tend to immobilize these elements in the environment and make them less bioavailable than many of the other hazardous metals at mine sites. In particular, lead concentrations in acid mine drainage and tailings pore waters appear to be controlled at relatively low levels by anglesite solubility (e.g., Blowes and Jambor, 1990).

Carbonates

Many carbonate minerals occur as either primary or secondary minerals in mine wastes. Examples are given in Table 6.12. Carbonates may originate as an accessory gangue mineral that accompanies the mineral deposit and mine waste (mine working residuum, waste piles, tailings), as an amended material for neutralization, or as a secondary product from weathering of wastes or amendments. Carbonate minerals are important as neutralizers of acid in mine drainage (Blowes and Ptacek, 1994). Siderite forms as a secondary phase in tailings impoundments where calcite reacts with Fe(II)-rich solutions (Ptacek and Blowes, 1994). The hydroxyl-bearing carbonates in Table 6.13 form as secondary minerals in the oxidation of Zn-Cu-Pb ores and related mine wastes.

Supergene and diagenetic sulfides

The supergene enrichment process that affects primary sulfide ores may also be a factor in redistribution of metals in mine waste environments, particularly tailings impoundments. Supergene alteration of copper- and nickel-sulfide deposits has resulted in enrichment of ore grades by oxidation and leaching of metals in the unsaturated zone above the water table followed by transport of metals to a zone of more reducing conditions where secondary sulfide minerals are formed (Anderson, 1982; Alpers and Brimhall, 1989). A list of some supergene copper and nickel minerals is given in Table 6.13. The two compositions for djurleite are based on the investigation by Potter (1977). An example of active supergene enrichment in a tailings impoundment is the presence of secondary covellite near the depth of active oxidation at Waite Amulet, Ontario (Blowes and Jambor, 1990).

Diagenetic processes affect mine drainage geochemistry in areas where reducing conditions can lead to sulfate reduction and the formation of secondary sulfides. The sulfides are generally insoluble, so this represents a plausible geochemical mechanism for metal fixation in mine workings, anoxic wetlands, and lake bottoms, if reducing conditions are maintained. Iron is commonly the most abundant transition metal and therefore is the most likely metal to combine with H_2S to produce secondary sulfides in environments affected by mine drainage. Other divalent metals present will also tend to form secondary sulfides, as indicated in Table 6.13. The relative solubility of metal sulfides, starting from the most soluble, is: $MnS > FeS > NiS \sim ZnS > CdS \sim PbS > CuS > HgS$ (DiToro et al., 1991).

A summary of mineralogic controls on metal concentrations

As a guide to the aqueous geochemistry for acid mine waters, we have compiled a list of minerals in Table 6.14 that might be important in governing metal concentrations. This list is drawn from our experience in modeling and interpreting mine water chemistry and is meant as a guide rather than a strict protocol. The two columns in Table 6.14 show those minerals most likely to have a solubility control and those less likely but possible.

SUMMARY

Physical, chemical, and biological processes all play important roles in the production, release, mobility, and attenuation of contaminants in acid mine waters. Physical aspects include the geology (geomorphology, structure, petrology, geophysical features), the hydrology (water budget, porosity, permeability, flow direction, flow rate, dispersion, mixing, surface transport characteristics), and the effects of mining and mineral processing. The specific processes that have been studied and found to contribute to the overall phenomenon of acid mine water geochemistry are:

1) pyrite oxidation
2) oxidation of other sulfides
3) oxidation and hydrolysis of aqueous iron and other elements
4) neutralizing capacity of gangue minerals and country rock
5) neutralizing capacity of bicarbonate-buffered waters
6) oxygen transport
7) fluid transport of water and water vapor
8) form and location of permeable zones relative to flow paths
9) climatic variations (diel, storm events, seasonal)
10) evaporation, efflorescence, redissolution
11) heating by conduction and radiation (due to a variety of exothermic reactions including pyrite oxidation, dissolution of soluble salts, and dilution of concentrated acid)
12) temperature
13) microbial catalysis of reaction rates
14) microbial sorption and uptake of metals
15) mineral precipitation and dissolution during transport
16) adsorption and desorption of metals during transport
17) photoreduction of iron
18) organic complexing
19) microenvironmental processes (surface films, microbial films, mineral coatings)

TABLE 6.14—Minerals whose solubilities might control metal concentrations in mine waters.

Solubility equilibrium likely	Solubility equilibrium difficult but possible
alunogen	alunite
anglesite	ankerite
barite	antlerite
basaluminite (amorphous)	atacamite, paratacamite
calcite	azurite
cerussite	bronchantite
chalcanthite	chrysocolla
epsomite	goethite
ferrihydrite	hemimorphite
gibbsite (amorphous to microcrystalline)	hematite
goslarite	hydrozincite
gypsum	jarosite
halotrichite-pickeringite	kaolinite
manganese oxides	kutnohorite
melanterite	malachite
otavite	natroalunite
rhodochrosite	natrojarosite
schwertmannite	plumbojarosite
scorodite	
siderite	
silica (microcrystalline)	
smithsonite	
witherite	

Many of these processes are represented schematically on Figure 6.7. Perhaps the most important factors affecting the production of acid mine waters are the amount, concentration, grain size, and distribution of pyrite present in a mine, tailings, or waste pile. The rate of oxidation can vary depending on the accessibility of air, moisture, and microbes to the pyrite surfaces and the neutralizing capacity of available buffering materials. These complex geochemical processes can be modeled with either equilibrium or kinetic principles to estimate the result of pyrite oxidation, carbonate buffering, and silicate hydrolysis (see Chapter 14 on geochemical modeling). Modeling calculations of this type have been done for pyritic rocks and waters of different initial compositions (e.g., Lichtner, 1994). Modeling calculations, however, are well-educated guesses. There will always be inadequate data and contentious ambiguities in the conclusions. The advantage of modeling is that it can take into account some of the complex interactions between hydrology, geochemistry, geology, and other site characteristics as well as performing database management. This advantage is a major step beyond various acid-base accounting, static, and kinetic tests for which comparison, evaluation, and agreement is lacking (White and Jeffers, 1994).

The geochemistry of acid mine waters is a complex subject that draws upon many technical disciplines. Although considerable

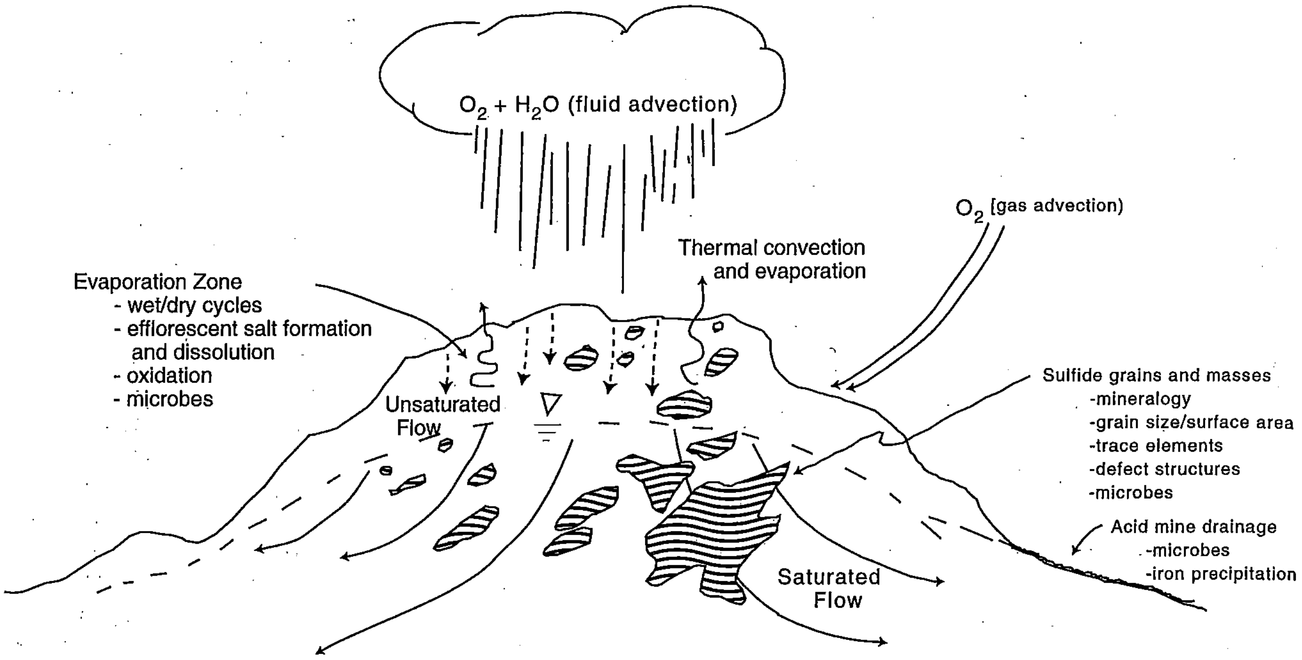

FIGURE 6.7—Schematic diagram depicting a hypothetical tailings or waste pile or mineralized site, showing the various materials and processes involving reaction and flow.

research has been accomplished on this subject, surprises and new challenges continue to appear. Inadequate recognition of the importance of the multi-disciplinary nature of the subject can result in inappropriate or even dangerous remediation measures. In this arena, as with many other environmental problems, the quick fixes are rare; complexity and heterogeneity of this environment along with high-cost, high-risk options are the rule. A cautious, phased, and iterative approach to both site characterization and remediation would seem most warranted.

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Volume Editors

G.S. PLUMLEE
U.S. Geological Survey
MS964 Denver Federal Center
Denver, CO 80225
gplumlee@usgs.gov

M.J. LOGSDON
Geochimica, Inc.
206 North Signal Street, Suite M
Ojai, CA 93023
mark.logsdon@worldnet.att.net

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