Robert Kleinmann · Christian Wolkersdorfer Editors

# Acidic Pit Lakes

The Legacy of Coal and Metal Surface Mines



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Venæ metallicæ lavantur, quæ lotura, quia venenis inficit rivos & fluvios, pisces aut necat, aut ex eis abigit.

Further, when the ores are washed, the water which has been used poisons the brooks and streams, and either destroys the fish or drives them away.

Georgius Agricola De re metallica libris XII 1551 First book, page 5

English translation: Hoover & Hoover 1912

an expression of the percentage of Fe sequestered in  $\text{FeS}_x$  form, as an essential indicator for P mobility.

Groundwater seepage into MLs largely determines water geochemistry due to the import of elevated quantities of dissolved metals and sulfur associated with mining activities (Blodau et al. 2006; Graupner et al. 2005; Wisotzky and Obermann 2001). As the cycling of P relates to the quantity of this mining impact, various indicators for P mobility have been used, reflecting the interconnections between P, Fe, Al, and S (Fig. 3.27). A high mining impact (metal import and their pelagic precipitation as oxyhydroxides) leads to very low benthic P mobility in acid MLs. Under anoxic conditions, P mobility remains low due to: a) upward propagation of the aforementioned 'ferrous wheel,' which leads to a high P binding capacity of Fe-rich ML sediments beyond the period of a massive AMD, despite decreasing Fe- and Al-import and ongoing deposition of organic and P-rich sediment; b) the possibility of vivianite formation as a permanent P sink concurrent with sulfide formation, given a  $Fe^{2+}$  surplus; and c) the higher thermodynamic stability of the Fe(OH)<sub>3</sub>-P complex, compared to Fe(OH)<sub>3</sub>, so that an almost complete transformation of ferric Fe to  $FeS_x$  (>75%) is required before P release becomes significant (Golterman 1995).

A high pore-water Fe:P ratio and low SRP concentrations was found to assure efficient adsorption onto re-precipitated Fe oxyhydroxides, an indicator concept also suggested for natural lakes (e.g. Baccini 1985). The surface sediment Fe:P ratio, suggested as an indicator for shallow oxic lakes (Jensen et al. 1992; Sondergaard et al. 1993), can be used for MLs only when the DOP is low. Analogously, the Al:P ratio (Rydin et al. 2000; Welch and Cooke 1999) may be used with Al hydroxide as the binding partner. Kopáček et al. (2005) proposed the ratio NaOH-Al: BD + H<sub>2</sub>O-P > 25 as an indicator for efficient Al-based P sorption. Maaßen (2003) and Jin et al. (2006) suggested combined Al and Fe indicators, a concept not tested for MLs yet. We recommend the application of the Fe:S ratio or log(Fe:S) × log(Fe:P) ratio to account for the fact that DOP determines the availability of Fe as binding partner.

# Phosphorus Retention in Mining Lakes and Prognosis of Trophic State

Acid MLs exhibit a high availability of P binding partners as a result of mining activities, as indicated by sediment Fe:P ratios up to 370 (Fig. 3.23). Even neutral MLs (without unusually high P loading) have significantly higher sediment Fe:P ratios (17–148) than natural lakes ( $\approx 8$ ; Fig. 3.23). As a consequence of this elevated sediment-based P binding capacity, whole lake P retention for a set of eight Lusatian MLs was 14.7  $\pm$  5.5% higher than predicted from the empirical OECD (1982) model (Grüneberg, unpublished). Data indicate that even a slight mining impact (e.g. Fe surplus) leads to significantly increased P retention. We suggest that empirical P retention models be adapted for MLs since this underestimation of permissible loading may, for instance, lead to usage restrictions.





Fig. 3.26 Concentration of total P of water ( $TP_{water}$ ) and sediment ( $TP_{sediment}$ ) versus indicators (ratios in water and sediment) supposed to indicate conditions of low and high P concentrations in MLs (n = 27, see Fig. 3.23) compared to natural lakes (n = 5)

# 3.2.2 Hardrock Metal Mine Pit Lakes: Occurrence and Geochemical Characteristics

L. Edmond Eary and Devin N. Castendyk

## 3.2.2.1 Introduction

Pit lakes are an increasingly common legacy of modern, large-scale surface mining operations. Pit lakes formed in open pit metal mines, where base and precious metals are extracted from ore deposits hosted in predominantly igneous and metamorphic silicate rocks, comprise one category of pit lakes. This category is referred to as hardrock metal-mine pit lakes, to distinguish them from pit lakes formed in above-ground hydrocarbon, industrial minerals, and aggregate mining operations.

Ore deposits exploited by mining consist of rock assemblages with naturally elevated concentrations of metals. These include the base metals (e.g. Co, Cu, Pb, Mo, Ni, and Zn) and precious metals (e.g. Ag and Au). Base metals are typically

				P mo	bility
	process / mec	hanism		Low	High
Fe, Al, S Figure (mining impact)	Import	al present: future: Fe, river floodir	Fe, Al >> P Al decrease; P, C increase ng → burlal of Fe/Al-layer	<b>X</b>	×
Para	Sedimentation	Fe/Al-oxide	es high sorption capacity	×	<u></u>
S Fe~C <sub>org</sub> ~P	and sediment P binding	C <sub>org</sub> scaver complexati	nging, metal-organic on	×	
oxic	Diagenesis and release	Fe(OH <sub>3</sub> ) re formation	ductive dissolution, FeS <sub>x</sub>		x
= / ]		Fe2+ upwar	d diffusion and re-oxidation	x	
ē ('iron wheel')		vivianite fo	rmation due to Fe <sup>2+</sup> surplus	x	
	Indication for	pore water	: Fe:P *	~10.000	0.04 - 4
<sup>∞</sup> , <sup>×</sup> FeS, FeS,	P mobility	sediment:	Fe:P **	< 5.5-8.3	
moxic			AI:P ***	4.6-27.5	
Fe (PO)			Fe:S	2 - 12	< 2
THE THE AVE			log(Fe:P)xlog(Fe:S)	0.7 - 2	< 0.7

Fig. 3.27 Processes in MLs with implications for low or high P mobility and indicators for P mobility; (\*) no quantitative relation for P mobility versus pore water Fe:P or threshold value for MLs established yet; (\*\*) only if Fe is not immobilized as  $FeS_x$ ; (\*\*\*) only as Al hydroxide, not as clay constituent

found as metal sulfides and sulfosalt minerals, and precious metals as sulfide minerals (e.g. acanthite— $Ag_2S$ ) or as native metals (gold, silver, electrum), in association with iron sulfides. Accessory minerals containing As and Se are common. Due to the ubiquitous presence of iron sulfides, acid rock drainage is a major water quality problem in metal-mine pit lakes. Thus, the environmental problems with metal-mine pit lakes are similar to those at coal and lignite pit lakes, where acid rock drainage from iron sulfide oxidation occurs, but hardrock metal-mines often have a more diverse set of metals at high concentrations available for dissolution and release to surface and groundwater systems, compared to coal and lignite pit lakes.

Water quality in pit lakes is often an important issue that affects permitting of new mines, expansion of existing mines, and planning for closure. There are numerous approaches for using numerical models to predict future water quality in pit lakes (e.g. Balistrieri et al. 2006; Castendyk and Webster-Brown 2007a, b; Eary et al. 2008; Kempton et al. 1997; Schafer et al. 2006). However, one of the best ways to assess whether predictions are credible is to compare them to water quality patterns that occur in existing pit lakes located in ore deposits with similar geoenvironmental characteristics. This chapter provides an overview of the geoenvironmental characteristics and associated water quality patterns for metal-mine pit lakes that provides a starting point for comparative purposes. The frequency of occurrence of metal-mine pit lakes is also discussed. These topics are fundamental to understanding the importance of geoenvironmental models for guiding the setup of numerical models of future pit lake water quality and assessing the credibility of the resulting numerical predictions.

# 3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes

#### 3.2.2.2 Occurrence of Hardrock Metal-Mine Pit Lakes

The metal mining industry has faced an increasing challenge of meeting society's demand for metals to maintain economic growth while ore grades in metallic ore deposits have steadily declined. For example, worldwide production of copper has steadily increased at an annual rate of about 4% since 1910 while average ore grades have declined by about 50% (Fig. 3.28). The long term trends in worldwide gold production and ore grade are similar to copper (Fig. 3.29), although the trend data for gold show more ups and downs due to various factors, such as economic disruptions, opening of new mining districts, and improvements in extraction technologies. Since 1910, worldwide gold production has increased from about 700–2,500 t/year in 2006. This increase in production has taken place even though ore grades have decreased by 50–75% since the early 1900s (Fig. 3.29). Obviously, gold recovery from lower and lower grade ores has become increasingly important for maintaining production rates.

An important technology for efficiently extracting gold from low grade oxide ores is heap leaching with cyanide. In this process, crushed ore is saturated with a cyanide solution which dissolves microscopic grains of gold. The solution is recovered and processed to extract the gold. First trialed in New Zealand at the turn of the 20th century, gold heap leaching became a primary extraction method for oxide ores starting in the 1970s. By 1986, about 30% of the world's production of gold was through heap leaching with cyanide (Dore'y et al. 1988).

Increasing metal production from decreasing ore grades requires processing more material. Thus, open pit mining has become the dominant method for metal recovery over time because it is a more efficient method of excavating huge amounts of ore. The dominance of open pit mining can be seen in a compilation of data on yearly worldwide investments in mining projects from 2001 to 2007, which was a period of rapid increase in mine production. Figure 3.30 shows these data for all base metals, precious metals, iron, and diamonds. Figure 3.31 shows data specifically for gold and copper. Each of these charts shows that the proportion of mines planned to be operated as open pits has increased coincident with the recent increase in mining activity. This trend is especially evident for gold and copper mines (Fig. 3.31). For all metal mines, the proportion planned to be operated as open pits increased from 61% in 2001 to 79% in 2007 (Fig. 3.31). For copper and gold mines, the proportion planned as open pits increased from 63% in 2001 to 87% in 2007 (Fig. 3.31). While these data represent only a short time span, they show how open pits have become the dominant mining method for metals due to the need to increase production while ore grades have decreased.

The data on mining project investments also provides a good depiction of where metal mines are located and where they will be located in the future. Figure 3.32 shows the trends in investment by region. Australia (included as part of Oceania) has consistently been the leading country for investments in metal mining projects since 2001. Overall, investments are distributed across all geographic regions, and the proportions of investments by region have remained roughly constant, except for small increases for Latin America at the expense of other regions.

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Fig. 3.28 Trends in worldwide copper production (Kelly and Matos 2008a) and ore grades (Kelly and Matos 2008a; Gerst 2008) since 1910







Fig. 3.30 Trends in major mining projects (copper, gold, iron, lead, nickel, platinum group metals, silver, diamonds, zinc; E&MJ 2002-2008)

The global distribution of pit lakes can be expected to resemble the distribution of investments in mining (Fig. 3.32) because the trends shown in Figs. 3.30 and 3.31 indicate that a high percentage of metal mines will be open pit operations. Given the past exploitation of many prospects in the established mining districts of Canada, the United States, and South Africa, it is anticipated that the number of open pit mines (and therefore pit lakes) in East and Central Africa, Central Asia, and Latin America will increase in the future (Castro and Moore 2000).

Metal-mine pit lakes have the potential to cause long-term changes to hydrologic systems and water quality (National Research Council 1999). The creation of lakes in areas where no lake existed prior to mining can potentially affect the viability of nearby water resources. Given their potential volumes, mine pit lakes comprise a potentially large water resource in arid to semi-arid regions and mountainous areas, where potable water is a valuable commodity. For example, Miller (2002) estimated that 35 pit lakes in Nevada have the potential to store  $1.85 \times 10^9$  m<sup>3</sup> of water, compared to  $0.74 \times 10^9$  m<sup>3</sup> of water in all the reservoirs in Nevada constructed for water storage. However, the resource value of water in pit lakes is greatly diminished if the water is of poor quality or lost to evaporation. Evaporative loss from large-surface-area pit lakes in arid regions effectively "pumps" stored groundwater from aquifers to the atmosphere while simultaneously increasing the concentration of dissolved metals in residual lake water. Conversely, pit lakes in humid climates may undergo more extensive sulfide oxidation and generate larger volumes of acidic discharge owing to higher inputs of direct precipitation, runoff, and groundwater.

The sections below describe the typical causes of poor water quality at metalmine pit lakes based on known geochemical processes and observed trends in chemical compositions of existing pit lakes. While these descriptions are useful for making generalizations about the characteristics of metal-mine pit lakes, there are







Fig. 3.32 Annual investments in metal mining projects by region (E&MJ 2002-2008)

many deviations from such generalizations due to differences in the geoenvironmental characteristics of specific mine sites.

#### 3.2.2.3 Hydrogeochemical Processes in Metal-Mine Pit Lakes

There are a number of hydrochemical processes that can affect water quality in metal-mine pit lakes over the long term, including:

- 3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes
- · Geoenvironmental characteristics
- Sulfide mineral oxidation
- Water balance
- Mineral solubility
- Surface adsorption
- Water column dynamics
- · Sediment biogeochemical processes
- Mitigation and remediation efforts

This list of processes is not meant to imply rank in importance but is merely a generalized compilation of the numerous factors that influence water quality in pit lakes. The following sections discuss the importance of these processes in more detail.

## 3.2.2.4 Geoenvironmental Characteristics

The geoenvironmental characteristics of an ore deposit generally exerts the primary influence on water quality in pit lakes in the absence of remedial measures. The characteristics of ore deposits are often discussed in terms of geoenvironmental models, which are a convenient way to categorize geologically similar mineral deposits and their wastes with respect to their geochemical, mineralogical, geological, geophysical, hydrological, and climatic properties. Summaries and examples of geoenvironmental models can be found in duBray (1995), Plumlee (1999), Plumlee and Nash (1995), Plumlee et al. (1999) and Seal et al. (2007).

Two of the more important aspects of geoenvironmental models are host rock reactivity and alteration mineralogy. Host rock reactivity is important because a portion of the wallrock that surrounds a pit lake is usually comprised of partially mineralized and/or sub-ore grade host rocks that typically contain metal sulfides. Alteration mineralogy is important because the secondary minerals left exposed in the pit walls (host rocks, remnant ore, and adjacent rocks) after mining is completed represent potential sources of leachable metals and acidity. Table 3.6 provides a list of ore deposit types arranged by major metal commodity and their typical assemblages of host rocks. The reactivities of the host rocks are also indicated for each deposit type in terms of typical acid neutralization potential and acid generation potential. The predominant theme that can be gained from the data in Table 3.6 is that most metal ore deposits are contained in silicate rock types that typically have more acid generation potential than acid neutralization potential. The few exceptions to this generalization, such as the lead-zinc Mississippi Valley deposits and Carlin-type gold deposits, are hosted in carbonate rocks, and hence tend to have moderate to high acid neutralization potential. However, the host rocks of most metal ore deposits have an excess of acid generation potential relative to acid neutralization potential.

Table 3.7 lists typical alteration types and secondary mineral assemblages that may be overprinted on host and ore rocks at metal ore deposits. The effects of the secondary minerals on acid neutralization and acid generation potential are also qualitatively estimated in Table 3.7. Most types of alteration result in a decreased potential for acid neutralization because the metasomatic processes involved in secondary mineral formation usually remove or replace reactive primary carbonate and silicates with less reactive silicates and, in some cases, iron sulfides and metal sulfates (e.g. alunite, jarosite), depending on redox conditions. The primary exception to this generalization is carbonitization, in which primary minerals are replaced by carbonate minerals.

The geoenvironmental characteristics of an ore deposit, such as those listed in Tables 3.6 and 3.7, cannot be used to predict absolute values of water quality parameters, such as pH or metal concentration, but they can provide a useful qualitative guide about what type of water quality should be expected in a pit lake. For example, a prediction of neutral pH and low metal concentrations for a future pit lake in a porphyry copper deposit with pervasive argillic alteration should be questioned to identify what mitigating characteristics make it an exception when its geoenvironmental characteristics would predict that acidic water quality should occur. For existing pit lakes, an examination of the geoenvironmental characteristics of the deposit can provide context for explaining observed water qualities. This information may be used to identify the range of conditions that may occur based on comparison to pit lakes in similar deposit and host rock types, which may be useful in the design of remedial strategies for final closure of the pit lake.

# 3.2.2.5 Sulfide Mineral Oxidation

The primary processes responsible for poor water quality in metal-mine pit lakes is acid mine drainage due to the oxidation of iron sulfide minerals, such as pyrite, marcasite, and pyrrhotite. Sulfides are present in the floors and wallrocks of most metal-mine pit lakes and in the groundwater flow paths leading to pit lakes. In the groundwater flow paths, oxidation may take place in dewatered aquifers, providing a potential source of solutes that could be rinsed and transported into a mine (above and below ground) after mining has ended and the groundwater level recovers to its natural elevation. Sulfides may also be present in waste rock and ore stockpiles sometimes left in the pits after closure.

Iron sulfide is oxidized by molecular oxygen and ferric iron through reactions such as:

$$FeS_2 + 7/2 O_2 + H_2 O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (3.10)

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$
 (3.11)

A similar type of reaction can be written for pyrrhotite oxidation. Depending on pH conditions, dissolved oxygen concentrations, and microbial activity, ferrous

Deposit type	Typical host rocks	Host rock acid-base character <sup>a</sup>	Expected lake water quality
Adularia-sericite epithermal vein	Silicic-volcanics: rhyolite, dacite, latite, andesite	Low NP; moderate to high AGP	Acidic to circumneutral
Epithermal quartz- alunite	Silicic—volcanics	Low NP; high AGP	Acidiç
Carlin type (silicic)	Silicic—siltstone, sandstone, shale, $\pm$ igneous intrusive	Low NP; low to moderate AGP	Mildly acidic to circumneutral
Carlin type (calcareous)	Carbonates—calcareous siltstone, silty, cherty or dolomitic limestone, siltstone, limestone	Moderate to high NP; low to moderate AGP	Circumneutral to alkaline
Low sulfide quartz- gold veins	Silicic-granitic intrusives, greenstone, gneiss	Low NP; moderate AGP	Acidic
Au-Ag telluride veins	Silicic—alkalic porphyritic igneous (syenite, monzonite diorite, phonolite), volcanic breccia, diatremes, stockworks	Low NP; moderate AGP	Acidic
Quartz-pebble conglomerate	Silicic—Clastic sediment, igneous (granite, greenstone, ± volcanics)	Low NP; moderate AGP	Acidic
Skarn	Carbonates—limestone, dolomite, marble, metasediments	Moderate to high NP; moderate AGP	Acidic to alkaline
Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Low NP; moderate AGP	Acidic
Adularia-sericite epithermal vein	Silicicvolcanics (rhyolite, dacite, latite, andesite)	Low NP; moderate to high AGP	Acidic
Polymetallic veins	Silicic—igneous intrusives (diorite, granodiorite, monzonite), volcanics (andesite to rhyolite), metasediments	Low NP; moderate to high AGP	Acidic
Au-Ag telluride veins	Silicic—alkalic porphyritic igneous (syenite, monzonite diorite, phonolite), volcanic breccias, diatremes, stockworks	Low to moderate NP; moderate to high AGP	Acidic

Ag

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Summary of major ore types and acid-base characteristics for hardrock metal-mine pit lakes

Primary

metal Αu

Table 3.6

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(continued)

Primary metal	Deposit type	Typical host rocks	Host rock acid-base character <sup>a</sup>	Expected lake water quality
Cu	Seafloor massive sulfide	Silicic-mafic to felsic volcanics, metasediments	Low to moderate NP depending on mineral assemblage; high AGP	Acidic
	Magmatic massive sulfide	Silicic-mafic volcanic: diabase, gabbro, pyroxenite	Low to moderate NP depending on mineral assemblage; high AGP	Acidic to neutral
	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Low to moderate NP; moderate AGP	Acidic
	Porphyry	Silicic—igneous intrusives (tonalite to monzogranite, syenite porphyries)	Low NP; moderate to high AGP	Acidic
	Sediment hosted	Silicic—red-beds (green shale, gray shale, siltstone, sandstone, $\pm$ carbonates, evaporites)	Low to moderate NP; low to moderate AGP	Acidic to neutral
	Skarn	Carbonate—Limestone, dolomite, marble, calc- silicate metasomatic, igneous intrusives (tonalite to monzogranite, syenite porphyries)	Moderate to high NP; moderate AGP	Neutral
Лo	Porphyry	Silicic—igneous intrusive: granitic-rhyolitic porphyries	Low NP; moderate AGP	Acidic
b-Zn	Seafloor massive sulfide	Silicic-mafic to felsic volcanics, metasediments	Low to moderate NP depending on mineral assemblage, High AGP	Acidic
	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Moderate NP; low to moderate AGP	Acidic
	Mississippi Valley type	Carbonate—dolostone, $\pm$ limestone, sandstone– siltstone, shale	Moderate to high NP; moderate AGP	Neutral to alkaline
	Manto/skarn	Carbonate—limestone, dolomite, sandstone- siltstone	Moderate to high NP; moderate AGP	Acidic to alkaline

NP neutralization potential, AGP acid generation potential

Table 3.7 Summary of acid-base characteristics of major alteration types found in metallic ore deposits based on the summary in Plumlee (1999)

Alteration	Secondary minerals	Acid-base characteristics <sup>a</sup>
Acid sulfate (alunite)/ advanced argillic	Quartz/chalcedony, pyrite, alunite, jarosite, kaolinite, $\pm$ pyrophyllite, dickite	Greatly decreases NP, increases AGP; increases potential for rapid initial release of acid + sulfate
Argillic	Kaolinite, illite, <sup>*†</sup> nontmorillonite, ±pyrite, ±chlorite	Decreased NP; possible increase in AGP
Phyllic	Quartz, sericite, pyrite	Decreased NP; increased AGP
Potassic	K-feldspar, biotite, ±anhydrite	Decreased NP; possible rapid release of sulfate
Propylitic	Epidote, chlorite, calcite, albite, $\pm$ pyrite	Increased NP depending on amount of calcite formed; Possible increase in AGI from pyrite
Silica	Silica (quartz, chalcedony)	Decreased NP; AGP not substantially changed
Jasperoid	Silica (quartz, chalcedony)	Greatly decreased NP due to replacement of sedimentary carbonates with silica AGP not substantially changed
Greisen	Quartz, muscovite, fluorite, cassiterite, magnetite	Potential for decreased NP; AGP not substantially changed
Skarn	Ca silicates, silica, magnetite, ±pyrite	Decreased NP; increased AGP
Dolomitization	Dolomite .	Decreased effective NP due to formation of potentially less reactive dolomite; AGP not substantially changed
Carbonitization	Calcite, dolomite, siderite, rhodochrosite	Potentially large increase in NP (but neutralization from siderite is countered by oxidation of $Fe^{2+}$ ; AGP not substantially changed)
Sulfidation	Pyrite	Decreased NP; increased AGP

NP neutralization potential, AGP acid generation potential

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## 3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes

iron is fairly rapidly oxidized to ferric and precipitated as ferric hydroxide and schwertmannite, producing more acid, as in:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3 + 2H^+$$
 (3.12)

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$$8Fe^{2+} + SO_4^{2-} + 2O_2 + 10 H_2O \rightarrow Fe_8O_8(SO_4)(OH)_6 + 14H^+$$
(3.13)

It is generally recognized that dissolution reactions involving carbonates (calcite and dolomite) have a high potential to neutralize the acid generated by sulfide oxidation through reactions such as:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$
(3.14)

Silicates also have the capacity to neutralize acidity through dissolution reactions, such as the following reaction for anorthite:

$$CaAl_2Si_2O_8 + 2H^+ + 6H_2O \rightarrow Ca^{2+} + 2Al(OH)_3 + 2H_4SiO_4$$
(3.15)

There are numerous detailed descriptions of the above types of reactions involved in sulfide mineral oxidation in the literature (e.g. Nordstrom and Alpers 1999; White et al. 1999) and it is not the purpose of this paper to discuss them in detail. However, a comparison of the kinetics of acid generation reactions (Eqs. 3.10 and 3.11) to the rates of acid neutralization (Eqs. 3.14 and 3.15) is useful for illustrating why some metal-mine pit lakes become acidic and some do not.

Williamson and Rimstidt (1994) describe the abiotic rate of pyrite oxidation by oxygen for a reference system with a surface area to water ratio of  $1 \text{ m}^2$  pyrite/ 1 kg of solution:

Rate(mol pyrite 
$$m^{-2}s^{-1}$$
) =  $10^{-8.19} \left(\frac{m_{O_2}^{0.5}}{m_{H^+}^{0.11}}\right)$  (3.16)

These authors also describe the abiotic rate of pyrite oxidation by ferric iron for conditions where both dissolved oxygen and ferric iron are present in solution for a reference system (Williamson and Rimstidt 1994):

Rate(mol pyrite 
$$m^{-2}s^{-1}$$
) =  $10^{-6.07} \left( \frac{m_{Pe^{2+}}^{0.93}}{m_{Pe^{2+}}^{0.4}} \right)$  (3.17)

For carbonate minerals, Palandri and Karaka (2004) describe the rates of calcite and dolomite dissolution:

Rate(mol calcite 
$$m^{-2}s^{-1}$$
) =  $10^{-0.3}[H^+]^{1.0} + 10^{-5.81} + 10^{-3.48}P_{CO_2}$  (3.18)

Finally, the rates of dissolution of silicates can be described by the general form of the following rate expression (Casey and Ludwig 1995; Chou and Wollast 1985; Palandri and Karaka 2004):

Rate(mol silicate  $m^{-2}s^{-1}$ ) =  $k_H[H^+]^a + k_w + k_{OH}[OH^-]^b$  (3.19)

Palandri and Karaka (2004) provide a detailed summary of the values of rate constants and exponents for Eq. 3.19 for silicate minerals.

Figure 3.33 shows a comparison of the above reaction rates for a range of pH for equivalent quantities and surface areas. The rates of pyrite oxidation by both oxygen and ferric iron are more rapid than neutralization by the types of silicates most commonly found in silicic intrusive rocks hosting metal sulfide ores, such as quartz, feldspars, clays, and micas. The dissolution rates of some mafic silicates (e.g. olivine and anorthite) approximate the rate of pyrite oxidation by oxygen, suggesting that they may be good sources of neutralization. However, few economic grade metallic ore deposits mined in open pits are hosted in mafic silicates; hence, their importance for preventing acid generation for most pit lakes is minimal.

In comparison, the rates of carbonate mineral (calcite and dolomite) reactions are more rapid than pyrite oxidation (Fig. 3.33). That is why carbonate minerals, when present in sufficient quantities, can prevent acid generation in metal-mine pit lakes; they react rapidly enough to keep up with the rate of iron sulfide oxidation, assuming that they are not completely consumed before the sulfides.

The conclusion that can be drawn from Fig. 3.33 is that most silicate minerals generally do not dissolve fast enough to preclude acid generation under most circumstances, in contrast to carbonate minerals. This conclusion is not surprising; otherwise, acid rock drainage would not be the common phenomena that it is given the predominance of silicate rock types over carbonates in most mineralized districts. Similar observations have been made for natural, closed-basin lakes located in volcanic terrains with high sulfur contents where the buffering capacities of silicate minerals have been overwhelmed by pervasive acid alteration from sulfur and sulfide oxidation, resulting in naturally acidic, saline lakes (Risacher et al. 2002).

#### 3.2.2.6 Water Balance

Water balance, which describes the inputs and outputs of water and their associated solute loads to a pit lake, has a fundamental control on water quality in metalmine pit lakes, especially during the initial period of infilling. Solutes enter the lake primarily through groundwater inflow, leaching of wallrocks, leaching of backfill material (if present), and the dissolution of secondary minerals and metalsalts, some of which may exist as efflorescence on pit walls and in pore spaces prior to lake filling. Salts may also exist in the dewatered parts of aquifers surrounding a mine due to oxidation processes. Because solute influxes are functions of flow rates, they are directly dependent on the rates of water inflow from the different hydrologic sources that make up the water balance of the pit lake watershed. Sources may include groundwater, pit wall runoff, direct rainfall, and





possibly surface water diverted into the open pit to accelerate lake filling. The rates of inflow of different hydrologic sources may change over time as the pit lake fills. For example, the proportion of the water balance from groundwater inflow may decrease over time as the local groundwater table recovers and hydrologic gradients diminish, whereas the relative proportions of water from runoff and direct precipitation may increase, depending on the pit morphology and catchment area. Sulfide mineral oxidation will slow as the wallrocks are increasingly inundated, thereby slowing the rates of acid and metals release. In some cases, the rinsing of sulfide oxidation products from wallrocks and backfill materials may provide a short-term high influx of solutes during the early stages of pit filling (see also case study 5.1). If evaporation is the only route for water loss from the pit lake, many solute concentrations not affected by solubility will increase slowly over time due to evapoconcentration. Biogeochemical processes and surface adsorption reactions taking place in the water column and sediments may moderate the concentrations of some solutes, but for the most part, the water and chemical balance will primarily control water quality.

The water balances for most hardrock mining pit lakes can be categorized in general terms as either: terminal pit lakes, in which outflow occurs only as evaporation or; flow-through pit lakes, in which surface and/or groundwater flow into and out of the pit lake (see also Sect. 4.1.2). The typical trends in water quality

#### 3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes

dynamics for each type are likely to be different for different water balance scenarios.

A common situation for many hardrock mining pit lakes is that the wallrock leachates are acidic due to sulfide mineral oxidation, whereas the inflowing groundwater has a circumneutral to alkaline pH and some amount of acid-buffering capacity. As a result, the dynamics in water quality are controlled by the relative influx proportions from these two sources. For example, most terminal pit lakes with low influxes of acid solutes from wallrock leaching and high influxes of alkalinity from groundwater will evolve to water qualities with one of the following sets of characteristics: (1) circumneutral pH values, gypsum saturation, and low cationic and anionic metal concentrations due to solubility and adsorption constraints, or (2) alkaline pH values, calcite saturation, and low cationic metal concentrations but potentially elevated concentrations of arsenic and selenium (Davis and Eary 1997; Eary 1998). In either case, the total dissolved solids concentrations will continue to increase over time in terminal pit lakes due to evapoconcentration (Fig. 3.34). Pit lakes formed in Carlin-type gold deposits are examples of circumneutral to alkaline pit lakes with occasional instances of elevated arsenic and selenium (Davis and Eary 1997; Eary 1998).

For pit lakes with high influxes of acid equivalents from wallrocks compared to groundwater inflow, the initial and long-term water quality can be expected to be acidic, with high total dissolved solids (TDS) due to elevated metal concentrations and sulfate (Fig. 3.34; Eary 1999). The pH will most commonly stabilize over time between 2.5 and 4, but the TDS will continue to increase due to evapoconcentration (Fig. 3.34). Over the long-term, some amount of microbial activity in the sediments of anoxic lower layers of meromictic lakes may produce small increases in pH and decreases in metal concentrations due to sulfate reduction, but the lakes are likely to remain acidic in the absence of remedial measures due to their large volume and the isolation of meromictic waters from shallower lake layers. The acidic pit lakes of the Iberian Pyrite Belt (Sánchez-España et al. 2008) associated with polymetallic massive sulfide deposits and the former Spenceville pit lake (Levy et al. 1997), which formed in a silicic polymetallic vein deposit, are examples of terminal pit lakes with high rates of acid influx and evapoconcentration.

Bowell and Parshley (2005) documented the existence of a variety of secondary iron sulfates and arsenic oxyhydroxides on pit wallrocks that may act as sources of easily leachable metals to pit lakes during the initial stages of pit infilling and potentially on a seasonal basis thereafter. Pit lakes receiving high initial loads of metals and sulfate from the wash off of oxidation products may initially have acidic pH values that eventually rise as the effects of the wash off of acidic solutes diminish and the pit walls become inundated, slowing further sulfide mineral oxidation (Fig. 3.34). The TDS trends for this situation may show an initial period of decrease due to dilution from inflowing groundwater with lower TDS concentrations, but over time, the trend for TDS will be upward (Fig. 3.34). This type of TDS trend may be most applicable to arid climate pit lakes.

Flow-through and terminal pit lakes with high influxes of acidity from wallrocks relative to groundwater inflow are likely to remain acidic in the absence of

#### 3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes





remedial measures (Fig. 3.35). Conversely, flow-through pit lakes with low acid loads from wallrocks and high influxes of alkalinity from groundwater are most likely to have circumneutral pH values. An important difference with terminal pit lakes is that TDS concentrations in flow-through pit lakes will only increase until the lake reaches hydrologic steady state with the groundwater system (Fig. 3.35). At that point in time, the TDS should stabilize as a balance is reached between chemical inputs and losses to and from the pit lake. The Berkeley pit lake is an example of an eventual flow-through system in which total solute concentrations have slowly increased over time as the lake approaches its hydrologic spill-over point (Gammons and Duaime 2006), although its water quality dynamics are also affected by water management systems associated with metal extraction and inflows from underground workings. An important consideration for both terminal and flow-through pit lakes is that the time scale for the dynamics in chemical processes may be different from hydrologic processes (Schafer and Eary 2009). A flow-through pit lake may reach hydrologic equilibrium in a relatively short period of time, but various chemical processes and water column dynamics in terminal pit lakes may continue to evolve and result in changes in water quality.

#### 3.2.2.7 Water Column Dynamics

It is generally recognized that metal-mine pit lakes have substantially different shapes than natural lakes. Pit lakes tend to have lower ratios of surface area to depth and are steep-sided compared to natural lakes. This difference is evident in a comparison of relative depths for pit lakes. (Relative depth is defined by Wetzel (2001) as the ratio of the maximum depth to the average diameter, in percent.



Fig. 3.35 Generalized time trends in pH and TDS for flow-through pit lakes

See also Sect. 2.1) Natural lakes usually have relative depths in the range of 2% or less, whereas metal-mine pit lakes have much higher values, from 15 to 45% (Castendyk 2009). Highwalls, which are common on one or more sides of pit lakes, may also decrease the transfer of wind energy to the lake surface, decreasing the potential for mixing of the water column.

Based on these general characteristics, it has been thought that pit lakes should be more likely to be permanently stratified (meromictic) than natural lakes, which commonly experience seasonal overturn (holomictic), and that a calculation of relative depth may be sufficient to predict water column dynamics (Castro and Moore 2000; Doyle and Runnells 1997; Lyons et al. 1994). However, Schultze and Boehrer (2009) and Castendyk (2009) independently showed that relative depth is a poor predictor at best of the tendency for stratification in pit lakes. For example, a plot of maximum depths against surface areas for metal-mine pit lakes shows that, as might be expected, meromictic lakes tend to have slightly higher depths than holomictic lakes, there is a great deal of overlap between the two sets of data (Fig. 3.36). Many steep-sided pit lakes have high depths and small surface areas yet show holomictic water column dynamics. These data indicate that while the shape of a pit lake undoubtedly has an important influence on the water column dynamics, numerous other factors, such as the chemistry and density of lake water inputs, climate, and hydrology, are also important (see also Sect. 3.1).

The data in Fig. 3.36 show that predicting whether a pit lake will become permanently stratified or experience seasonal or occasional overturn cannot be based solely on shape. Knowledge of water column dynamics is important for predicting long term water quality and designing mitigation strategies to improve water quality. For example, a lake that experiences seasonal overturn may be expected to remain oxygenated for most of the year. This factor that can be used to parameterize predictive models for future pit lakes or interpret water quality models of existing pit lakes where redox processes are important for controlling metal concentrations. In comparison, a pit lake that experiences permanent





stratification may have substantially different redox conditions and water qualities in different lake layers. Oxygenated conditions may exist near the surface whereas anoxic conditions may exist at depth, leading to sulfate reduction and alkalinity production in bottom sediments.

Permanent stratification and associated effects on biogeochemical processes may be incorporated into approaches for improving water quality. For example, the strategies employed at the Island Copper pit lake in British Columbia have resulted in greatly improved water quality in surface layers, even though the lake experienced inputs of acid mine drainage water (Pelletier et al. 2009). In a different study, Colarusso et al. (2003) determined that density stratification of the water column in the South Mine Pit lake at the Copper Basin Mine, Tennessee would be stable for a range of potential conditions. This result was used by Wyatt et al. (2006) to justify development of an in-pit lime treatment system to improve the water quality of discharges from the top, low-TDS water layers.

#### 3.2.2.8 Mineral Solubilities

Mineral and gas solubilities play an important role in affecting rates of solute release in pit lakes similar to contaminant attenuation processes observed in some surface groundwater systems. Numerical models of pit lakes typically rely at least in part on thermodynamic-based geochemical models of aqueous speciation, solubility, and surface adsorption, as well as kinetic formulations for predicting water quality trends in future pit lakes and interpreting water quality conditions in existing pit lakes. Pit lakes, however, are dynamic systems in which both kinetically controlled abiotic and biotic chemical processes occur, producing conditions

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of disequilibrium that may metastably persist. Eary (1999) reviewed equilibrium trends in pit lakes to provide guidance to numerical modelers about which solubility reactions are reasonably well represented by chemical equilibrium and which are more likely to be affected by kinetic processes.

A summary of potential solubility controls for different solutes from Eary (1999) and supplemented by a few more recent studies is given in Table 3.8. The review by Eary (1999) showed that sulfate is the dominant solute in most metalmine pit lakes, especially acidic pit lakes, and sulfate concentrations are typically limited by gypsum solubility. Gypsum is indicated to be a solubility control based on its trend in saturation indices calculated for a number of metal-mine pit lakes as a function of sulfate concentration (Fig. 3.37). Other important solubility controls for major ions indicated from saturation indices were calcite, fluorite, and barite. In addition, the data trends from numerous acidic pit lakes indicated that reasonably well defined solubility controls include alunite for aluminum, ferrihydrite for iron, and manganite and birnessite for manganese. Schwertmannite may also be an important solubility control for iron in acidic pit lakes, based on evaluations provided by Nordstrom and Alpers (1999) and Sánchez-España et al. (2009).

Solubility controls for divalent minor metals are much less well established, but data trends suggest otavite for cadmium, brochantite and malachite for copper, cerrusite and pyromorphite for lead, and hydrozincite and zinc silicate for zinc (Table 3.8). Concentrations of As and Se are not represented by any established mineral solubilities and may be primarily affected by adsorption to aluminum and iron oxyhydroxide minerals under acidic conditions. For example, Sánchez-España et al. (2008) report that arsenic concentrations are significantly lower in acidic pit lakes that have pH values within the pH stability field of schwertmannite (i.e.  $pH < \approx 4$ ) compared to pit lakes in which schwertmannite is not stable. Arsenic may also be incorporated into uncommon mixed hydroxyl sulfate minerals, such as beudantite [PbFe<sub>3</sub>(AsO<sub>4</sub>)(SO<sub>4</sub>)(OH)<sub>6</sub>] (Romero et al. 2007). Adsorption processes are less effective for removing arsenic and selenium from solution in high sulfate concentrations or in higher pH (i.e. >pH 6) solutions and their concentrations can be expected to increase linearly with evapoconcentration.

In summary, mineral solubilities provide reasonable representations of maximum concentrations for many major solutes (e.g. Ca, Mg,  $HCO_3^-$ ,  $SO_4^{2+}$ , F, Al, Fe<sup>3+</sup>, and Mn) in metal-mine pit lakes (Eary 1999; Eary and Schafer 2009), but they are much less reliable for predicting the concentrations of divalent minor metals (e.g. Cd, Cu, Pb, and Zn) and metalloids (e.g. As and Se). In most cases, predictive models will need to rely on empirical formulations to represent metal and metalloid concentrations derived from either experimental, field data, and/or comparisons to existing pit lakes in similar geoenvironmental settings.

Trend data for  $CO_{2(g)}$  partial pressures as a function of pH for metal-mine pit lakes are shown in Fig. 3.38. These  $CO_{2(g)}$  levels are calculated from measurements of pH and bicarbonate alkalinity and carbonate equilibrium speciation. They show that most acidic metal-mine pit lakes can be expected to be oversaturated with  $CO_{2(g)}$  compared to the atmospheric level of  $10^{-3.5}$  atm (Fig. 3.38). The degree of oversaturation increases in acidic pH conditions and reaches about

Table 3.8	Summary of potential solubility controlling minerals for metal-mine pit lake:	(Bowell and Parshley 2005; Eary 1999	
	Acidic (pH $< \approx 4.5$ )	Circumneutral (pH $\approx 4.5$ to $\approx 7.5$ )	Alkaline (pH $> \approx 7.5$ )
AI	Alunite, basaluminite	Gibbsite, kaolinite, allophane, sericite	Gibbsite, kaolinite, allophone, sericite
Alkalinity	Not applicable	Calcite <sup>b</sup>	Calcite <sup>b</sup>
As	Adsorption to ferrihydrite and schwertmannite <sup>h</sup> , scorodite <sup>j</sup> , bukovskyite <sup>k</sup> , scorodite-mansfieldite <sup>k</sup> , weilite <sup>k</sup> , pharmacolite <sup>k</sup>	Adsorption to ferrihydrite <sup>h</sup>	None identified
Ba	Barite	Barite, witherite	Barite, witherite
Cd	None identified	Adsorption to ferrihydrite	Otavite
Ca	Gypsum	Gypsum	Gypsum, calcite
Cī	Copper sulfates <sup>j</sup>	Brochantite <sup>g</sup>	Malachite, brochantite <sup>g</sup>
FI	Fluorite	Fluorite	Fluorite
Fe <sup>c</sup>	Ferrihydrite, schwertmannite, melanterite <sup>j</sup>	Siderite (Fe <sup>2+</sup> ) <sup>j</sup>	Siderite (Fe <sup>2+</sup> ) <sup>j</sup>
$\mathbf{P}\mathbf{P}$	Anglesite <sup>f</sup> , chloropyromorphite <sup>d</sup> , plumbojarosite <sup>j</sup> ,	Anglesite <sup>f</sup> , chloropyromorphite <sup>d</sup> ,	Cerrusite,
		adsorption to ferrihydrite	chloropyromorphite <sup>d</sup>
Mn	Manganite, birnessite	MnHPO₄ <sup>d</sup>	Rhodochrosite
Se	Adsorption to ferrihydrite <sup>1</sup>	Adsorption to ferrihydrite	None identified
Strontium	Celestite	Celestite, strontianite	Celestite, strontianite
Sulfate	Gypsum, copiapite <sup>k</sup> , melanterite <sup>k</sup> , mirabolite <sup>k</sup> , halotrichite-pickeringite <sup>k</sup>	Gypsum	Gypsum
Zinc	None identified	Hydrozincite <sup>e</sup> , ZnSiO <sub>4</sub> <sup>g</sup>	ZnSiO4 <sup>g</sup> , zincite,
			smithsonite
<sup>a</sup> Oversatur pH > 8.5; <sup>6</sup> sulfate conc	ation with calcite is typical in most pit lakes; <sup>b</sup> Oversaturation with $CO_2$ at 1 Assumed to be ferric iron; <sup>d</sup> Dependent on the presence of phosphate; <sup>e</sup> Requi tentration such as those reached at gypsum saturation; <sup>g</sup> Requires the presence of in efficiency with increases in outflete concentration. <sup>1</sup> Medicible for suffete con-	$^{-3.5}$ atm typically occurs for pH < 8.5 es the presence of carbonate alkalinity; <sup>1</sup> f dissolved silica near or approaching sat	5 and undersaturation for Requires relatively high uration with chalcedony;
in Nordstro	m and Alpers (1999) <sup>k</sup> From compilation of Bowell and Parshley (2005)		

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 $10^{-2}$  atm or about 30 times atmospheric  $CO_{2(g)}$  for pH less than 7. These data are important for providing information on the levels of oversaturation that should be expected to occur when parameterizing geochemical models of pit lakes. Models of metal-mine pit lakes should expect conditions of disequilibria with respect to  $CO_{2(g)}$ , particularly for lakes with pH less than the circumneutral range. This is an important point for modelers to remember when predicting pit lake geochemistry. By specifying  $CO_{2(g)}$  in equilibrium with the atmosphere, the model will force  $CO_{2(g)}$  out of solution, resulting in a higher pH than would otherwise be calculated. This can lead to predicted higher pH values than observed pH values.

## 3.2.2.9 Surface Adsorption

At a microscopic scale, charged ions and molecules are attracted to electricallycharged surfaces of suspended particulate matter (SPM) within pit lake water. Positively-charged cations (e.g.  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ) are attracted to negatively-charged surfaces, whereas negatively-charged anionic metalloids (e.g.  $SeO_4^{2-}$ ,  $SeO_3^{2-}$ ,  $AsO_3^{3-}$ ,  $AsO_4^{3-}$ ) are attracted to positively-charged surfaces. Once the ion or molecule adsorbs onto a surface, it will remain there until the pH of the surrounding solution changes or the SPM decomposes. Under optimal conditions, the water quality of a pit lake may improve due to metal adsorption to SPM and the SPM settles to the bottom of the pit lake where it is buried. With this goal in mind, improving water quality via surface adsorption forms the basis of many contemporary remediation strategies for pit lakes (Kalin and Wheeler 2009; Pelletier et al. 2009).

Hydrous ferric oxides (HFO), such as ferrihydrite and schwertmanite, which are produced by the oxidation of iron sulfides in acidic pit lakes, typically provide abundant surface area for adsorption. Webster et al. (1998) discuss the effects of surface adsorption on the water quality of acid mine drainage. Castendyk and Webster-Brown (2007b) demonstrate the effects of surface adsorption on predicted pit lake water quality by comparing As, Cd; and Cu concentrations modeled Fig. 3.38 Trends in equilibrium partial pressures of  $CO_{2(g)}$  in metal-mine pit lakes (Eary 1999)



without surface adsorption to concentrations modeled with surface adsorption onto freshly precipitated ferrihydrite.

The surfaces of other particles, such as Al and Mn hydroxides and clays minerals (e.g. smectite, illite, kaolinite) that develop surface charges in response to cation substitutions may also be adsorption substrates. Furthermore, the surfaces of suspended organic matter, such as phytoplankton and diatoms spines, provide adsorption sites; hence, some remediation strategies endeavor to stimulate biological productivity of pit lakes by the addition of nutrients (Kalin and Wheeler 2009; Pelletier et al. 2009).

General depictions of percent adsorption of various dissolved cations and anionic metalloids onto a sample of HFO as a function of pH (Figs. 3.39 and 3.40 partially explain why low pH pit lakes tend to have elevated concentrations of cationic metals whereas high pH pit lakes may exhibit elevated concentrations of anionic metalloids (see below). However, these diagrams should only be used as general indicators of adsorption trends as each pit lake will contain different surface adsorption surfaces and different water chemistry.

#### 3.2.2.10 Sediment Biogeochemical Processes

Geochemical processes occurring in bottom sediments have the potential to affect metal cycling in metal-mine pit lakes in ways similar to natural water bodies. These reactions are driven in large part by the oxidation of carbon catalyzed by microbial processes. In simple terms, the oxidation of organic carbon can be described by:

$$C_{\text{organic}} + 2H_2O = CO_2 + 4H^+ + 4e^-$$
(3.20)

In the anaerobic environment at the bottom of a pit lake, anaerobic microorganisms derive energy from the oxidation of organic carbon coupled with the following reduction reactions, which are listed in order of decreasing redox potential: Fig. 3.39 Approximate adsorption of cations onto generic HFO as a function of lake pH (after Drever 2002, with data from Dzombak and Morel 1990)



Fig. 3.40 Approximate adsorption of anionic metals onto generic HFO as a function of lake pH (after Drever 2002, with data from Dzombak and Morel 1990)



 $2NO_3^- + 10e^- + 12H^+ = N_2 + 6H_2O$  (denitrification) (3.21)

 $MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O$  (manganese reduction) (3.22)

$$Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O$$
 (iron reduction) (3.23)

$$SO_4^{2-} + 8e^- + 10H^+ = H_2S + 4H_2O$$
 (sulfate reduction) (3.24)

When combined with reaction 3.20, the net oxidation-reduction reactions for iron and sulfate by organic carbon may be written as follows:

$$C_{\text{organic}} + 4Fe(OH)_3 + 8H^+ = CO_2 + 4Fe^{2+} + 10H_2O$$
 (3.25)

$$2C_{\text{organic}} + SO_4^{2-} + 2H_2O = H_2S + 2HCO_3^{-}$$
(3.26)

While these types of reactions are well established as important controls on sediment chemistry, there are few investigations specific to metal-mine pit lakes available in the literature that can be used to develop detailed understanding of sediment mineralogy, chemical composition, pore water chemistry, biogeochemistry, and their effects on water quality. Information gleaned from a few available studies is summarized in Table 3.9; although most of these studies were focused

on acidic, stratified (i.e. meromictic) pit lakes. The common characteristics of the lakes summarized in Table 3.9 are acidic compositions, seasonal or permanent stratification, oxygenated upper portion of the water column, and anoxic conditions at depth and in sediments. Iron and aluminum oxyhydroxide and sulfate minerals are commonly found in sediments along with gypsum. These minerals are most likely to have formed as secondary phases in wallrocks and carried into the pit lakes by erosion or formed in the water column and subsequently settled to the bottom. Triantafyllidis and Skarpelis (2006) also report the presence of a number of metal sulfate minerals present as a thin layer of precipitants in the bottom of a shallow, highly acidic pit lake that is oxygenated throughout the water column.

Accompanying the anoxic conditions at depth are increases in pH in the sediment pore water relative to the overlying water column and occasional presence of hydrogen sulfide (Table 3.9). These characteristics are indicative of biologicallymediated reduction of sulfate and Fe<sup>3+</sup>, potential for release of metals due to reductive dissolution of metal oxyhydroxides, and potential for re-precipitation of some metals as metal sulfides. Biological reduction of sulfate requires an energy source for microbial activity in the form of organic carbon. However, there are few data on organic carbon levels in metal-mine pit lakes. Levy et al. (1997) found low concentrations of dissolved organic carbon (DOC) in the water column of the acidic Spenceville pit lake, although concentrations were greater in the sediment pore water (Table 3.9). Levy et al. (1997) speculated that the low DOC levels in combination with high Fe<sup>3+</sup> levels limited the extent to which microbial processes resulted in sulfate reduction in the sediments of the Spenceville pit lake. Cameron et al. (2006) reported low DOC concentrations in the water column but relatively high concentrations in the sediment pore water from the acidic Berkeley pit lake (Table 3.9). However, there is little evidence of sulfate reduction in the Berkeley pit lake sediments, which Cameron et al. (2006) interpreted as an indication that highly acidic, metal laden conditions are hostile to supporting high populations of sulfate-reduction bacteria. In contrast, the less acidic Udden pit lake shows low TOC and evidence of some amount of sulfate reduction. Some of the highly acidic pit lakes of the Iberian Pyrite Belt also show increased pH values in sediments compared to the overlying water column and hydrogen sulfide has been detected in some deep water samples, indicative of sulfate reduction (Sánchez-España et al. 2009).

It is important to note that biogeochemical reactions do not always improve pit lake water quality. Wendt-Pottoff et al. (2004) observed that stimulation of sediment biogeochemical processes in an acidic pit lake in Germany released Fe<sup>2+</sup> to the overlying water column, which in turn oxidized and counteracted neutralization.

Also, the concepts and data discussed in this chapter are directed at natural factors that affect water quality in metal-mine pit lakes in the absence of mitigation and remediation efforts. Many different remedial approaches exist for improving water quality in pit lakes. The reader is referred to the appropriate chapters or sections in this volume and also discussions in Kalin and Wheeler (2009), Pelletier et al. (2009), and Wielinga (2009).

(2006) Rytuba et al. (2000)

Ferrihydrite floc in water column adsorbs As and Sb

pH 4 in water column; anoxic Not reported

Holomictic

McLaughlin South Pit, California

in lower lake layers

Triantafyllidis and Skarpelis

Jarosite, wroewolfeite, beaverite, gypsum, anglesite, scorodite, bukovskyite, goethite, melanterite, rozenite, butlerite

Levy et al. (1997) Reference

Secondary minerals in sediments

Jarosite, gypsum<sup>a</sup>, unidentified amorphous Al phase

DOC: 7 mg/L water column; DOC: 110 mg/L in sediment pore water

pH 2:4-2.9 in water column; pH 3:42 in sediment pore water; DOC and H<sub>2</sub>S in

Not reported

pH 2.9-3.1 in water column;

Not reported

Kirki (Agios Filippos) Pit,

Greece

sediments oxidizing

Organic carbon

Fable 3.9 Summary of sediment geochemistry characteristics for acidic, metal-mine pit lakes

pH/Redox conditions

Meromictic

Spenceville Pit, California<sup>b</sup>

Limnology

Pit lake

Ramstedt et al. (2003)

Ferrihydrite<sup>a</sup>, gibbsite<sup>a</sup>

TOC: 0.4-0.6 mg/L in surface layers

4.8 in surface increasing water column; anoxic in

Hd

Dimictic

Udden Pit, Sweden

to 6.4 at the bottom of

increasing to 2.7 mg/L at depth

Sánchez-España et al. (2008; 2009)

schwertmannite, jarosite, gibbsite, jurbanite)°, Efflorescent minerals on shorelines include gypsum, pickeringite, and hexahydrite

(Ferrihydrite, alunite,

Twidwell et al. (2006; Cameron et al. 2006)

schwertmannite (water column)<sup>a</sup>

Jarosite, gypsum, AlOHSO4,

TOC: 0.3-0.4% in sediments; DOC:

increased Fe, As, and Mn

with depth

lower lake layers;

pH 3.1-3.4 in sediment pore

Meromictic (may

holomictic in

have been the past)

Montana Berkeley Pit,

water; anoxic at depth

2.5-4.5 mg/L in water column and 50-380 mg/L in sediment

pore water

Not reported

pH 1.2-4.7 in water column;

Meromictic and holomictic

Numerous pit lakes of the Iberian Pyrite Belt

typically oxidizing in

surface water layers and anoxic at depth; evidence of Fe<sup>3+</sup> and SO<sub>4</sub> reduction

in sediments in the form of H<sub>2</sub>S odor

99

Inferred from solubility calculations
Spenceville pit was backfilled in 2001
Inferred from elemental analyses of colloids collected from the water column and solubility calculations

## 3.2.2.11 Water Quality Trends

Inspection and analysis of data trends from existing metal-mine pit lakes can provide useful knowledge about important factors affecting water quality, such as ore deposit type, geochemical processes, and hydrologic cycles. However, there are no publicly accessible, comprehensive international databases on pit lake water quality currently in existence that can be used for thorough assessment of chemical trends. Various amounts and detail on water quality data are available in open literature reports and scientific papers for individual and collections of pit lakes. The water quality data collected for this paper and discussed below are summarized in Table 3.10. Data from these sources were compiled for the purpose of summarizing trends in water quality and comprise 144 water quality analyses for 49 pit lakes. This dataset is predominantly reflective of pit lakes formed in gold mines in the western U.S. and is relatively old. Hence, it is recognized that these data represent, at best, only snapshots of water quality at the time of study and thus not a completely accurate representation of all types and variabilities of all types of metal-mine pit lakes. However, taken together, these water quality data do provide useful context for identifying trends generally common to metal-mine pit lakes.

TDS is an important parameter in the evaluation of water quality trends to provide context for more detailed inspection of other solutes, such as metals (discussed below). Figure 3.41 shows a plot of TDS as a function of pH for metalmine pit lakes where the data are categorized according to the ore deposit type. The TDS concentration can be strongly affected by evapoconcentration; hence, the age of the pit lake may be an important factor. The data shown in Fig. 3.41 represent lakes at all ages of maturity. While the factor of age may obscure some details in TDS trends, the data in Fig. 3.41 indicate that elevated TDS concentrations occur most frequently under acidic conditions (pH <  $\approx$  4.5), although a few alkaline (pH >  $\approx$  7.5) pit lakes also show elevated TDS (Fig. 3.41). Lakes with a pH between pH 4.5 and 7.5 generally have low TDS concentrations. Overall, the highest TDS concentrations occur for acidic pit lakes formed at mines of massive sulfide, high sulfidation polymetallic vein, and porphyry types of deposits.

A closer inspection of the major components of TDS indicates that the percentage comprised of sulfate increases as TDS increases (Fig. 3.42). The percentage of TDS as alkalinity decreases as TDS is increased as it is increasingly supplanted by sulfate. Sulfate is, by far, the dominant solute in nearly all pit lakes with highly elevated TDS concentrations. The majority of the high TDS, high sulfate pit lakes included in the datasets shown in Figs. 3.41 and 3.42 are acidic. A direct reflection of high acidity can be seen by the increase in the percentage of TDS comprised of metals (Al + Fe + Mn) with an increase in TDS. These metals comprise 5–20% of the TDS concentrations in most acidic pit lakes, such as those of the Iberian Pyrite Belt in Spain (Sánchez-España et al. 2008) and the Berkeley pit lake in Montana (Pellicori et al. 2005). These highly acidic pit lakes contain predominantly acidic sulfate solutions in which metals, sulfate, hydrogen ion, and to a lesser extent, base cations, make up most of the TDS concentrations.

et al. Bird et al. (1994; Davis and Ashenburg 1989; MacDonald 1993; Price et al. 1995; Sánchez-España et al. (2008; Ramstedt 2003; Seal et al. 2006) Levy et al. (1997; Rytuba et al. 2000; Triantafyllidis and Skarpelis 2006) Ashley and Savage (2001) Pellicori et al. 2005) Dowling et al. (2004) Price et al. (1995) Price et al. (1995) Price et al. (1995) Price et al. (1995) Reference Number of water quality values 25 16 6 16 35 ∞ 34 Spain Sweden Vermont, New Hampshire Nevada California California Nevada Montana Greece California Location Nevada Nevada Nevada Nevada Summary of water quality data sources for metal-mine pit lakes Cortez, Big Springs, Adelaide, Getchell (south, center, north) 22 Iberian District pit lakes, Udden, Elizabeth Spenceville McLaughlin (south, north), Kirki ington, Liberty, Ruth, Kimbley, Cypress-Tonapah, Anaconda, Berkeley Yerington, Liberty, Ruth, Tuscora (south, north) Boss, Aurora, Ketchup Flat Pit lakes Fortitude Harvard Sleeper Volcanogenic low Low sulfide goldquartz deposit polymetallic vein High sulfidation Quartz adularia Massive sulfide Quartz alunite sulfidation Carlin-type Table 3.10 Porphyry Deposit Skarn



Fig. 3.41 Trends in total dissolved solids in metal-mine pit lakes

Iron, Al, and Mn are most commonly the dominant dissolved metals in acidic pit lakes due to the increased solubilities of the minerals that contain these elements. This effect can be seen in plots of Fe, Al, and Mn as functions of pH (Figs. 3.43, 3.44 and 3.45 respectively). Iron concentrations may exceed 1,000 mg/L in the most acidic pit lakes formed in massive sulfide, polymetallic high sulfidation, and porphyry deposits (Fig. 3.43). Only total Fe concentrations are shown in Fig. 3.43, but both ferrous and ferric iron are usually present when pH values are less than about 4.5 due to slow oxidation kinetics and absence of dissolved oxygen in the lower layers of acidic pit lakes. Iron concentrations tend to be low in pit lakes formed in Carlin type, quartz adularia, and low sulfidation deposits due to circumneutral to slightly alkaline pH conditions resulting from low sulfide content in the host rocks of many of the pit lakes included in this dataset. The secondary minerals reported to best explain iron concentrations in acidic pit lakes are schwertmannite and ferrihydrite, whereas siderite may be a reasonable solubility control for neutral to alkaline pit lakes (Table 3.8), depending on redox conditions. Trends in Al and Mn concentrations with pH (Figs. 3.44 and 3.45) are similar to Fe, although there are fewer data for Al, and Mn shows much more variability through the mid-pH range. Most secondary oxyhydroxide and sulfate minerals containing Fe, Al, and Mn have amphoteric solubilities, and hence show similar trends in concentrations with pH. Secondary solids such as gibbsite and various Al-sulfates, such as jurbanite, alunite, and basaluminite, are important solubility controls for dissolved Al in acidic pit lakes. For slightly acidic to alkaline pit lakes, poorly crystalline clay-type minerals, such as kaolinite and allophane, may be the most common secondary minerals incorporating dissolved Al.

Concentration data for divalent cationic metals are shown in a Ficklin-type plot in Fig. 3.46. These metals show the expected trend of greatly increased



Fig. 3.42 Major components of TDS in metal-mine pit lakes expressed as percentages of TDS

concentrations in acidic pit lakes formed in massive sulfide, polymetallic high sulfidation, and porphyry deposits. A number of circumneutral lakes (pH >  $\approx$ 4.5 and <  $\approx$ 8) formed in massive sulfide and porphyry deposits also show relatively high metal concentrations due primarily to Cu and Zn (Fig. 3.46). Secondary minerals incorporating Cu and Zn are relatively soluble in the slightly acidic to neutral pH range. High solubilities allow high concentrations of these metals to occur in pit lakes due to the combined effects of sulfide oxidation and evapo-concentration, although adsorption to iron oxides may partially moderate cationic metal concentrations under these conditions (Fig. 3.39).

A final group of solutes is the anionic metalloids of As and Se. The trends for As concentrations in metal-mine pit lakes show a more complex relationship to pH than the cationic metals. Arsenic concentrations are highest at low pH, decrease to their lowest values in the pH range from about 4.5-7, and then tend to be higher at pH > 7 (Fig. 3.47). On the acidic end, pit lakes formed in massive sulfide deposits have the highest As concentrations due in part to the mineral arsenopyrite, whereas pit lakes formed in quartz adularia deposits tend to have the highest As concentrations. Selenium concentrations show a different pattern: the lowest concentrations (generally below detection limits) occur in acidic pit lakes formed in quartz adularia and porphyry deposits tend to have the highest Se concentrations (Fig. 3.48).

The tendency for elevated As and Se concentrations to occur in quartz adularia and porphyry pit lakes has been previously recognized by Shevenell et al. (1999), who examined water quality trends for 16 pit lakes in Nevada. Neither As or Se form low solubility secondary minerals under most pH conditions and the adsorption of As and Se anions is minimized under alkaline pH conditions. Because of these adsorption characteristics, the highest concentrations of As and Se tend to occur in alkaline pit lakes that have or are expected to evapoconcentrate (Eary 1998). A similar phenomenon is seen in natural evaporative lakes of the



Fig. 3.43 Trends in total Fe concentrations with pH in metal-mine pit lakes



Fig. 3.44 Trends in Al concentrations with pH in metal-mine pit lakes

western USA that also contain elevated alkalinities and As concentrations, such as Mono Lake, California (Maest et al. 1992), Toulon and Upper Humboldt Lake, Nevada (Seiler et al. 1993), and Abert Lake, Oregon (Whitehead and Feth 1961).

#### 3.2.2.12 Conclusions

The concentrations of solutes in metal-mine pit lakes show distinct trends that are primarily related to pH. The pH, in turn, is a complex function of the geoenvironmental characteristics, sulfide mineral content and oxidation rates, water



Fig. 3.45 Trends in Mn concentrations with pH in metal-mine pit lakes



Fig. 3.46 Ficklin plot of divalent cationic metal concentrations with pH in metal-mine pit lakes

balance, solubilities of secondary mineral phases, water column dynamics, sediment biogeochemical processes, and remediation efforts. Thus, geoenvironmental characteristics can provide a useful framework for interpreting the hydrochemistry of existing pit lakes, making predictions of water quality for future pit lakes, and designing remedial strategies. However, there are still many areas where research could greatly improve our understanding of metal-mine pit lakes. A regularly



Fig. 3.47 Trends in As concentrations with pH in metal-mine pit lakes



Fig. 3.48 Trends in Se concentrations with pH in metal-mine pit lakes

updated, international database on water quality from existing pit lakes in different types of mining regions, deposit types, metal resource, climate, and hydrologic environment could be valuable for identifying important factors affecting water quality, testing numerical models, and tracking remediation effectiveness. In addition, detailed studies on metal and nutrient cycling in the water column and sediments of pit lakes are needed to better understand the role of biogeochemical processes on water quality. 3.3 The Biology and Ecosystems of Acidic Pit Lakes

## 3.3 The Biology and Ecosystems of Acidic Pit Lakes

#### Katrin Wendt-Potthoff

#### Acid Pit Lakes as Special Habitats

Compared to typical acid mine drainage and chemically-similar hydrothermal solutions, the ionic composition of acid pit lakes is generally less concentrated, due to dilution of acid-generating oxidation products with groundwater or rainwater. The dissolved metal concentrations are typically elevated compared to natural lakes, but not necessarily at levels considered toxic for freshwater biota-this depends largely on the origin of the pit (lignite/coal versus metal ore mining, Sects. 2.2 and 3.2). As in natural lakes, stratification and mixis depend on the ambient climate, but also on the chemical influence of catchment and in-lake processes (Sects. 3.1 and 3.2.2). Iron and sulfur cycling determine the biogeochemistry, especially in the anoxic zones, in contrast to natural freshwater lakes, where the main anaerobic process is typically methanogenesis. The high iron concentrations of pit lakes also bring about significant photochemical reduction of Fe(III) near the lake surface, which is coupled with photochemical oxidation of dissolved organic carbon, a process that further diminishes the available organic carbon for organisms. The food webs of acidic pit lakes have much fewer levels and species than those of natural freshwater lakes. This makes them interesting locations for studying fundamental ecological processes. Therefore, the trophic interactions and flow of energy have been comprehensively investigated (Sect. 3.3.1.4). Much less is known about the taxonomy and physiology of bacterioplankton components and fungi in the water column, since microbiological studies have mainly focused on the sediments, where anaerobic, alkalinity-generating processes are common. Besides their extreme chemistry, many pit lakes are quite young (decades or years), which might also explain deficits in their colonization.

# 3.3.1 Plankton

## 3.3.1.1 Phytoplankton

#### **Dieter Lessmann and Brigitte Nixdorf**

Phytoplankton plays a key role in the biocoenotic structure of lakes—in acidic lakes just as in pH neutral lakes, although the importance of biotic factors decreases with increasing acidity, in contrast to abiotic conditions (Arnott and Vanni 1993). Phytoplankton species composition, in terms of species-related characteristics such as size, edibility, preferred nutrient sources, together with species abundance and biomass, profoundly influence other trophic levels (see also Sect. 3.3.1.4).