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Review

Geochemical and equilibrium trends in mine pit lakes

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Abstract

Chemical composition and equilibrium trends in mine pit lakes were examined to provide guidance for the application of geochemical models in predicting future lake water quality at prospective open pit mines. Composition trends show that elevated solute levels generally occur only at the extremes of acidic and alkaline pH conditions. Concentrations of cationic metals (Al, Cd, Cu, Fe, Mn, Pb, and Zn) are elevated only in acidic pit lakes, whereas anionic metalloids (As and Se) are generally elevated only in alkaline pit lakes. These trends are indicative of sulfide mineral oxidation and evapoconcentration for acidic and alkaline conditions, respectively.

For nearly all pit lakes, SO_4 is the dominant solute, but is limited by gypsum solubility. Fluorite, calcite, and barite are also important solubility controls. Well-defined solubility controls exist for the major metals (Al, Fe, Mn), including jurbanite and alunite for Al, ferrihydrite for Fe, and manganite, birnessite, and, possibly, rhodochrosite for Mn. Determinations of definite controls for the minor metals are less distinct, but may include otavite for Cd, brochantite and malachite for Cu, cerrusite and pyromorphite for Pb, and hydrozincite and Zn silicates for Zn. Concentrations of As and Se appear to be limited only by adsorption, but this control is sharply diminished by increased pH and SO_4 concentration. In general, the concentrations of minor metals in pit lakes are not well represented by the theoretical solubilities of pure-phase minerals contained in the thermodynamic databases. Hence, modeling efforts will generally have to rely on empirical data on the leaching characteristics of pit wall-rocks to predict the concentrations of minor metals (Cd, Cu, Pb, Zn) in mine pit lakes.

Methodologies for predicting pit lake water chemistry are still evolving. Geochemical and equilibrium trends in existing pit lakes can provide valuable information for guiding the development and application of predictive models. However, mineralogical studies of pit lake sediments, suspended particles, and alteration assemblages and studies of redox transformations are still needed to validate and refine the representations of geochemical processes in water quality models of mine pit lakes.

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1. Introduction

In recent years, significant technological and operational improvements in the extraction of Au from low grade ores by heap-leaching methods have been achieved. As a result, mining of low grade deposits has increased substantially in the western USA, particularly in the Au belts of Nevada. In most cases, the efficient extraction of Au requires the excavation of huge tonnages of low grade ores by surface mining methods. Besides Au, Cu is also generally mined by surface mining methods from low grade porphyry deposits in the western USA and throughout the world. The huge amounts of rock excavated in surface mining operations for Au and Cu leave behind large open pits, where mineralized rocks are exposed to weathering.

At surface mines where open pits intersect the water table, dewatering systems are used to remove water from surrounding aquifers to allow mining to proceed. At mine closure, the dewatering systems are shut down. Subsequently, a lake may form in the mine pit as the local groundwater rebounds. The rate of filling is dependent on the local hydrologic and climatic conditions. Because mining operations expose subsurface mineralized rocks directly to atmospheric weathering, the potential exists for the release of metals to the nascent pit lake. Consequently, the prediction of the quality of the water in the pit lake is an important part of the environmental permitting process for both the startup of new surface mines and the expansion of existing surface mines.

The methods for predicting water quality in future mine pit lakes are technically complex. They are also generally hypothetical because, in nearly all cases, the pit lake does not exist at the time of mine permitting, hence there is no monitoring record to guide or calibrate the predictions. Methodologies for predicting pit lake chemistry most commonly involve the construction of a series of linked mechanistic and empirical models to represent the major processes that add or remove chemicals to the lake (Bird et al., 1994; Davis and Eary, 1996; Eary, 1998; Havis and Worthington, 1997; Kempton et al., 1997; Miller et al., 1996). These major processes may include groundwater inflow, precipitation, evaporation, pit wall runoff, wall-rock leaching, biological processes, lake hydrodynamics, and geochemical equilibria.

In general, modeling methods for representing chemical dynamics and processes in pit lakes are still undergoing extensive development. It is the contention of this paper that existing mine pit lakes can provide some of the most relevant information for conceptualizing how geochemical equilibrium processes affect the chemical compositions of pit lakes. Geochemical equilibrium processes are among the many processes that affect pit lake chemistry, but are important for bounding the concentrations of specific solutes through solid-phase solubilities, aqueous speciation, redox, and adsorption reactions.

The application of geochemical models to represent chemical equilibria in pit lakes is the focus of this paper. Geochemical modeling is not necessarily a

Table 1
Reactions used in equilibrium calculations with PHREEQC

Mineral	Reaction	log $K_{25^\circ C}$
Alunite	$KAl_3(SO_4)_2(OH)_6 + 6\ H^+ = K^+ + 3\ Al3^+ + 2\ SO_4^{-2} + 6\ H_2O$	−1.35
$Al(OH)_3$(am)	$Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O$	10.38
Anglesite	$PbSO_4 = Pb^{2+} + SO_4^{2-}$	−7.79
Barite	$BaSO_4 = Ba^{2+} + SO_4^{2-}$	−9.98
Birnessite	$\delta\text{-}MnO_2 + 4\ H^+ + e^- = Mn^{3+} + 2\ H_2O$	18.09
Brochantite	$Cu_4(OH)_6SO_4 + 6\ H^+ = 4\ Cu^{2+} + 6\ H_2O + SO_4^{2-}$	15.34
Calcite	$CaCO_3 + 2\ H^+ = Ca^{2+} + CO_2(g) + H_2O$	9.69
$Cd(OH)_2$(c)	$Cd(OH)_2(c) + 2\ H^+ = Cd^{2+} + 2\ H_2O$	13.65
$Cd_4(OH)_6SO_4$	$Cd_4(OH)_6SO_4 + 6\ H^+ = 4\ Cd^{2+} + 6\ H_2O + SO_4^{2-}$	28.4
Celestite	$SrSO_4 = Sr^{2+} + SO_4^{2-}$	−6.47
Cerrusite	$PbCO_3 = Pb^{2+} + CO_3^{2-}$	−13.13
Chloropyromorphite	$Pb_5(PO_4)_3Cl = 5\ Pb^{2+} + 3\ PO_4^{3-} + Cl^-$	−84.43
Dioptase	$CuSiO_3{:}H_2O + 2\ H^+ = Cu^{2+} + H_4SiO_4^0$	6.5
Ferrihydrite	$Fe(OH)_3 + 3\ H^+ = Fe^{3+} + 3\ H_2O$	4.89
Fluorite	$CaF_2 = Ca^{2+} + 2\ F^-$	−10.96
Gibbsite(c)	$Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O$	8.77
Gibbsite(μc)	$Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O$	9.35
Goethite	$FeOOH + 3H^+ = Fe^{3+} + 2\ H_2O$	0.5
Gypsum	$CaSO_4{:}2\ H_2O = Ca^{2+} + SO_4^{2-} + 2\ H_2O$	−4.58
Hydroxypyromorphite	$Pb_5(PO_4)_3OH + H^+ = 5\ Pb^{2+} + 3\ PO_4^{3-} + H_2O$	−62.79
Hydrozincite	$Zn_5(OH)_6(CO_3)_2 + 2\ H^+ = 5\ Zn^{2+} + 6\ H_2O + 2\ CO_3^{2-}$	−12.68
Jurbanite	$AlOHSO_4 + H^+ = Al^{3+} + SO_4^{2-} + H_2O$	−3.23
K-Jarosite	$KFe_3(SO_4)_2(OH)_6 + 6\ H^+ = K^+ + 3\ Fe^{3+} + 2SO_4^{2-} + 6\ H_2O$	−14.8
Larnakite	$PbO{:}PbSO_4 + 2\ H^+ = 2\ Pb^{2+} + SO_4^{2-} + H_2O$	−0.28
Malachite	$Cu_2(OH)_2CO_3 + 2\ H^+ = 2\ Cu^{2+} + 2\ H_2O + CO_3^{2-}$	−5.18
Manganite	$\gamma\text{-}MnOOH + 3\ H^+ = Mn^{3+} + 2\ H_2O$	0.24
$MnHPO_4$(c)	$MnHPO_4(c) = Mn^{2+} + PO_4^{3-} + H^+$	−25.4
Na-Jarosite	$NaFe_3(SO_4)_2(OH)_6 + 6\ H^+ = Na^+ + 3\ Fe^{3+} + 2\ SO_4^{2-} + 6\ H_2O$	−11.2
Otavite	$CdCO_3 = Cd^{2+} + CO_3^{2-}$	−13.74
Rhodochrosite	$MnCO_3 = Mn^{2+} + CO_3^{2-}$	−10.41
Smithsonite	$ZnCO_3 = Zn2^+ + CO_3^{2-}$	−10.0
Strontianite	$SrCO_3 = Sr^{2+} + CO_3^{2-}$	−9.25
Tenorite	$CuO + 2\ H^+ = Cu^{2+} + H_2O$	7.62
Witherite	$BaCO_3 = Ba^{2+} + CO_3^{2-}$	−8.59
$Zn(OH)_2$(c)	$Zn(OH)_2(c) + 2\ H^+ = Zn^{2+} + 2\ H_2O$	12.2
Zincite	$ZnO + 2\ H^+ = Zn^{2+} + H_2O$	11.14
Zn_2SiO_4	$Zn_2SiO_4 + 4\ H^+ = 2\ Zn^{2+} + H_4SiO_4^0$	15.33
$ZnSiO_3$	$ZnSiO_3 + H_2O + 2\ H^+ = Zn^{2+} + H_4SiO_4$	2.93

straightforward operation. Generally, there is substantial room to control model results through the judicious selection of the specific chemical equilibria used to set up the model. Consequently, it is critical to identify the chemical reactions expected to be at equilibrium versus those at disequilibrium to guide the setup of geochemical models and interpret the results. The purpose of this paper is to provide this conceptual information by examining trends of chemical compositions and determining states of equilibria for specific geochemical reactions for existing pit lakes. These trends should allow investigators attempting to predict future pit lake water quality to determine whether their model results are consistent with known trends or deviate for one reason or another; information that is critical for assessing the reasonableness of predictions.

2. Methods

2.1. Water quality data

Data on water quality for existing pit lakes were obtained from a number of sources. The largest single source was Price et al. (1995), which contains data for 18 pit lakes located at former hard rock mines (Cu and Au) in Nevada. Water quality data for 6 other pit lakes at hard rock mines (Cu, Au, and U) in the USA and Canada were obtained from individual journal

Table 2
Surface protonation reactions for ferrihydrite used in geochemical modeling

Site	Reaction	Concentration (mol/g)	log $K_{25°C}$
Weak	$Hfo\_wOH^0 = Hfo\_w0^- + H^+$	$Hfo\_wOH^0 = 2 \times 10^{-4}$	−8.93
	$Hfo\_wOH^0 + H^+ = Hfo\_wOH_2^+$;		7.29
Strong	$Hfo\_sOH^0 = Hfo\_sO^- + H^+$	$Hfo\_sOH^0 = 5 \times 10^{-6}$	−8.93
	$Hfo\_sOH^0 + H^+ = Hfo\_sOH_2^+$		7.29

articles and permit-related reports (Davis and Ashenberg, 1989; Davis and Eary, 1996; Levy et al., 1997; Mcdonald, 1993; Miller et al., 1996; Pillard et al., 1995; SEPC, 1990; Tones, 1982; Vandersluis et al., 1995). For these 24 hard rock pit lakes, a total of 107 water quality analyses were compiled. The data for the hard rock pit lakes were supplemented by data on metal concentrations (Al, Cd, Fe, Mn, Pb, and Zn) in 29 to 66 (number dependent on the metal) coal pit lakes in Germany reported by Klapper and Schultze (1997). Although coal mines and hard rock mines may have substantially different wall-rock characteristics, the processes leading to acid mine drainage in coal mines, that is the oxidation of Fe sulfides, is the same as for hard rock mines. Consequently, the concentration trends and equilibria in the two types of environments are expected to be comparable, particularly for acidic pH conditions.

The water quality data were obtained from a wide variety of sources and complete information on sampling procedures was not always available. The vast majority of the data appear to represent samples that were collected according to standard procedures. However, complete information on filter pore size and preservation was not always available, making it difficult to determine whether analytical results truly represent dissolved concentrations as opposed to dissolved plus some portion of suspended particles. This problem is most important for evaluating equilibria trends for the metals because of the tendencies of many metals to be associated with colloidal-size Fe and Al hydroxide particles, especially at pH above about 3–4. The solubility calculations and comparisons to trends of metal concentration discussed below should be viewed with the caveat that some of the instances of oversaturation with metal oxides and hydroxides may reflect analytical results for unfiltered samples.

2.2. Modeling procedures

Geochemical equilibria in pit lakes were evaluated with the PHREEQC model (Parkhurst, 1995). PHREEQC is often used for pit lake predictive studies because of the ease with which it can be used to mix waters and specify equilibrium controls. The MINTEQ.DAT thermodynamic database that is supplied with the PHREEQC package was used for the calculations discussed here (Table 1). Because of the common use of PHREEQC for pit lake modeling, this database was used unchanged to provide baseline comparisons of the results that can be obtained from the standard version. The exception was that the solubility product for gypsum was corrected from its erroneous value of log $K = -4.85$ in the MINTEQ.DAT database

Table 3
Surface complexation reactions for metal adsorption used in geochemical modeling

Reaction	log $K_{25°C}$
$Hfo\_wOH^0 + Cd^{2+} = Hfo\_wOCd^+ + H^+$	−2.9
$Hfo\_sOH^0 + Cd^{2+} = Hfo\_sOCd^+ + H^+$	0.43
$Hfo\_wOH^0 + Cu^{2+} = Hfo\_wOCu^+ + H^+$	0.6
$Hfo\_sOH^0 + Cu^{2+} = Hfo\_sOCu^+ + H^+$	2.85
$Hfo\_wOH^0 + Pb^{2+} = Hfo\_wOPb^+ + H^+$	0.3
$Hfo\_sOH^0 + Pb^{2+} = Hfo\_sOPb^+ + H^+$	4.71
$Hfo\_wOH^0 + Zn^{2+} = Hfo\_wOZn^+ + H^+$	−1.99
$Hfo\_sOH^0 + Zn^{2+} = Hfo\_sOZn^+ + H^+$	0.97
$Hfo\_wOH^0 + AsO_4^{3-} + 3\ H^+ = Hfo\_wH_2AsO_4^0 + H_2O$	29.31
$Hfo\_wOH^0 + HAsO_4^{2-} + 2\ H^+ = Hfo\_wHAsO_4^- + H_2O + H^+$	23.51
$Hfo\_wOH^0 + AsO_4^{3-} = Hfo\_wAsO_4^{3-}$	10.58
$Hfo\_wOH^0 + SeO_4^{2-} + H^+ = Hfo\_wSeO_4^- + H_2O$	7.73
$Hfo\_wOH^0 + SeO_4^{2-} = Hfo\_wOHSeO_4^{2-}$	0.80

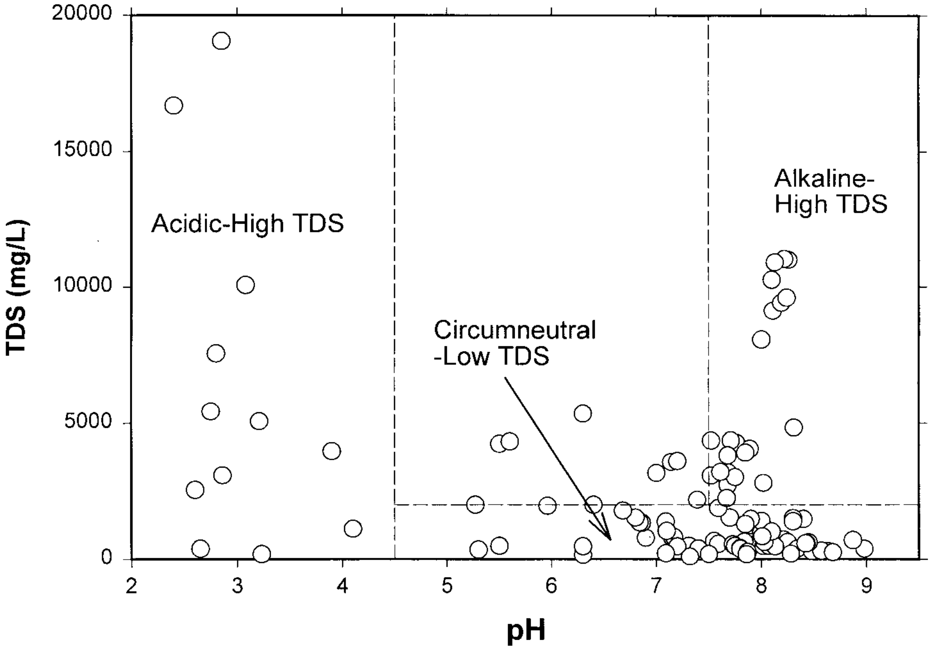

Fig. 1. Trends in total dissolved solids in hard rock pit lakes. Dashed lines indicate boundaries for categorizing pit lakes according to chemical composition characteristics.

to a value of log $K=-4.58$ (25°) (Nordstrom et al., 1990). The water quality data for the pit lakes were input to the PHREEQC model without modification, except that nondetect data were entered at one-half the detection level.

The water quality data generally did not include information on redox conditions. Thus, the pit lakes were modeled as if they were aerobic, in equilibrium with an atmosphere containing 20% O_2. This approach caused all multivalent solutes, that were reported as total concentrations, to be present completely in their highest stable oxidation states in the calculations [i.e., As(V), Cu(II), Fe(III), and Se(VI)]. A few of the water quality data represent samples that were taken at depth in pit lakes, and the assumption of aerobic conditions may not be completely representative for those samples. Most of the data analyzed represent near-surface grab-samples of lake water, for which the assumption of aerobic conditions is reasonable.

Additionally, the alkalinity values reported for the pit lakes were converted to consistent units of mg $CaCO_3$/L. If the water temperature was recorded at the time of sampling, then it was used as input to PHREEQC. Otherwise, the water temperature was arbitrarily set at 25°C.

The results from the PHREEQC modeling are presented in two different ways in this paper. In the first, the results of calculations of saturation indices (SI) are presented. The SI for a solid is defined by $SI=\log(IAP/K_{sp})$, where IAP is the ion activity product of the constituents involved in a solubility reaction and K_{sp} is the solubility product for that reaction (Langmuir, 1997). The saturation index is a convenient parameter for evaluating the proximity to equilibrium for various solubility reactions for aqueous systems that show a range of solution compositions, such as mine pit lakes.

In the second application of the PHREEQC model, metal concentrations calculated from the solubilities of specific mineral assemblages were directly compared to concentrations observed in pit lakes. Solubility calculations for oxides and hydroxides were done for a theoretical 0.021 M Na_2SO_4(~2000 mg/L SO_4) solution at 25°C. Solubility calculations for minerals containing an anionic constituent, such as K-jarosite, which contains a SO_4 component, were performed for an equilibrium assemblage that included gypsum as a solubility-controlling phase for SO_4. Solubility calculations for phosphate minerals were made for equilibrium with hydroxyapatite to fix phosphate concentrations and gypsum to fix Ca concentrations. Solubility calculations for silicates were made for equilibrium with chalcedony. Solubility calculations for carbonates were made for the range of CO_2(g) partial pressures calculated for pit lake overall (i.e., $10^{-2.0}$ to $10^{-3.5}$ atm).

The concentrations of metals calculated for specific adsorption reactions were also compared to those observed in pit lakes. For the adsorption calculations, the adsorbing substrate was a model ferrihydrite solid [$Fe(OH)_3$] at 1 mg/L and specific surface area of

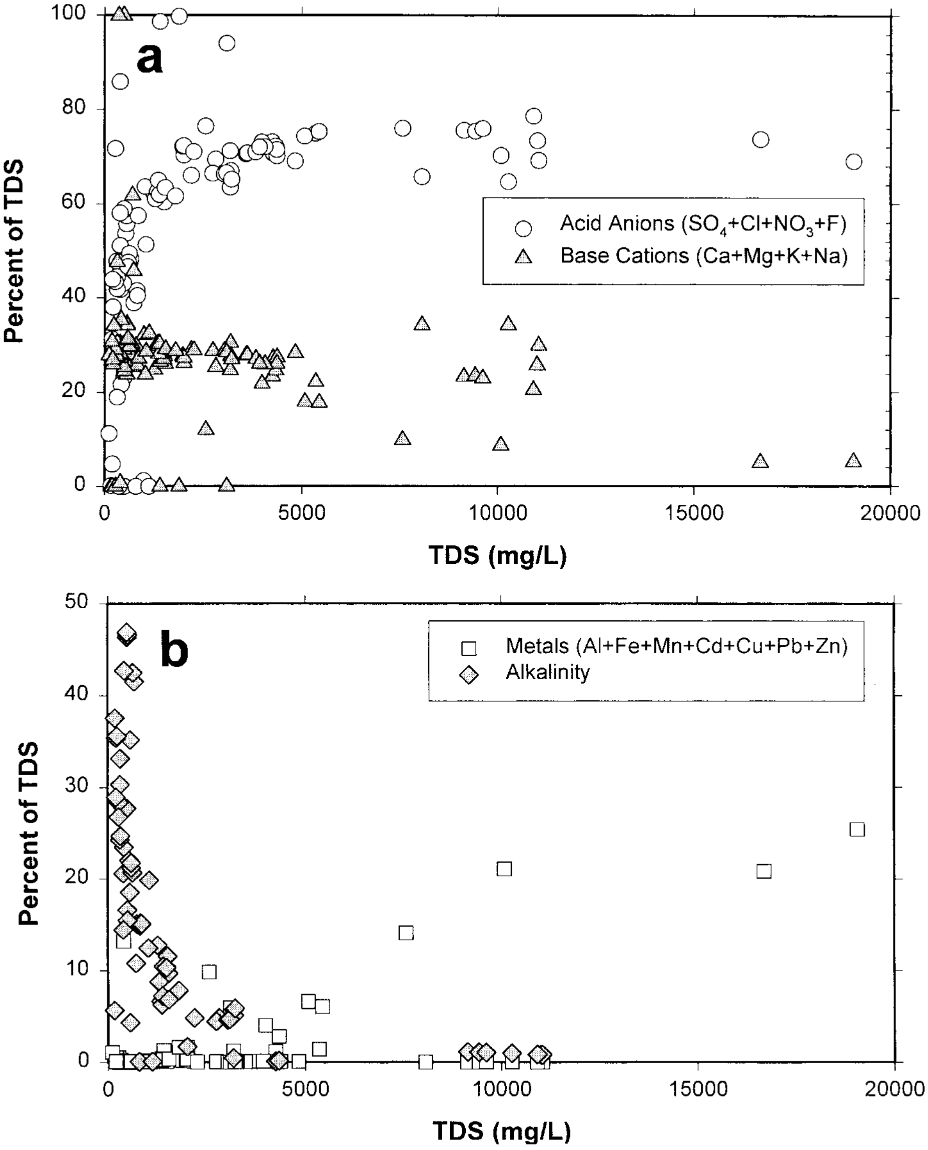

Fig. 2. Major components of TDS in hard rock pit lakes expressed as percentages of TDS as (a) acid anions and base cations and (b) metals and alkalinity.

600 m^2/g (Dzombak and Morel, 1990). The default values in the PHREEQC database (Parkhurst, 1995) were used to define the surface properties of the ferrihydrite in terms of strong and weak binding sites (Table 2). These default surface properties are from Dzombak and Morel (1990). The surface protonation reactions and related constants for ferrihydrite for the weak and strong sites are also those provided in the PHREEQC databases and are derived from the compendium by Dzombak and Morel (1990) (Table 2). The constants for adsorption reactions involving weak and strong-site binding for specific metals are given in Table 3.

3. Discussion

3.1. Major solutes

The total dissolved solids (TDS) concentration is an important parameter in the evaluation of water quality permit requirements. A general depiction of water quality in hard rock pit lakes can be obtained from a

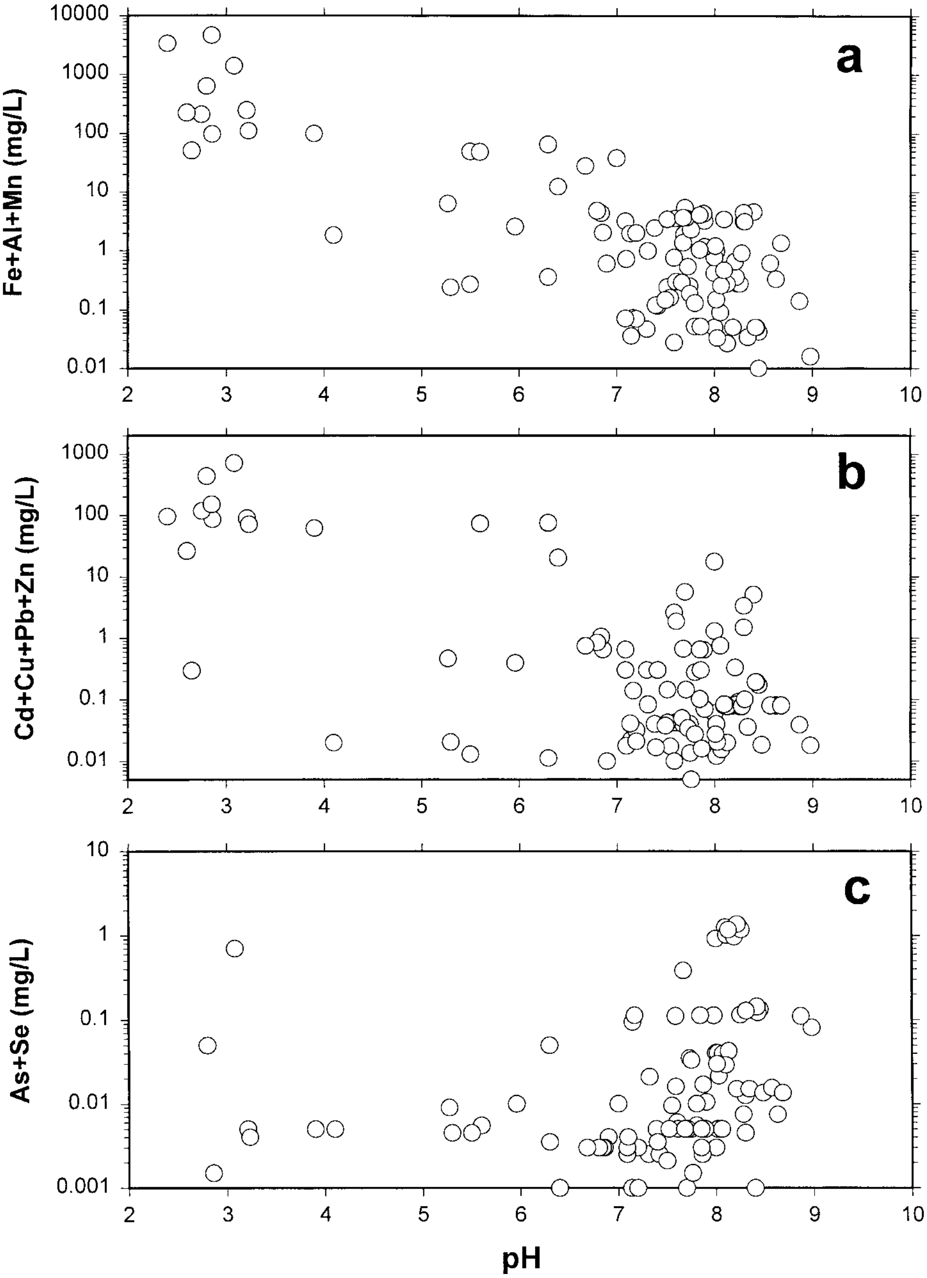

Fig. 3. Trends in metals in hard rock pit lakes with pH for (a) major metals (Al + Fe + Mn), (b) cationic base metals (Cd + Cu + Pb + Zn), and (c) anionic metalloids (As + Se).

simple plot of TDS against pH (Fig. 1). The TDS data indicate that the greatest tendency towards elevated TDS concentrations occurs at either $pH < 4.5$ or $pH > 7.5$. Lakes with pH between pH 4.5 and 7.5 generally have low TDS concentrations, although there is a population of lakes with $pH > 7.5$ that also have low TDS concentrations.

A closer examination of the major components of TDS indicates that the proportion comprised of acid anions ($SO_4 + Cl + NO_3 + F$) increases as TDS increases (Fig. 2a). Sulfate is, by far, the dominant solute in nearly all pit lakes with elevated TDS. The proportion of TDS as base cations ($Ca + Mg + K + Na$) decreases somewhat as TDS increases, but, overall, the base cations comprise a relatively constant proportion of the solute load over much of the pH range of pit lakes (Fig. 2a).

The proportion of TDS as alkalinity shows a decrease as TDS is increased (Fig. 2b) as it is increasingly supplanted by SO_4. The proportion of TDS comprised of metals (Al + Fe + Mn + Cd + Cu + Pb + Zn) increases as TDS is increased, but reaches high levels only in the most acidic pit lakes (Fig. 2b).

3.2. Dissolved metals

For convenience of discussion, the metal solutes can be grouped based on similarities in geochemical characteristics. The more common metals, Al, Fe, and Mn, that form cations in solution, comprise one such group. At $pH > 4.5$, the summed concentrations of these common metals are low, but show wide variability, especially for near-neutral to alkaline pH conditions (Fig. 3a). Some of this variability may reflect redox disequilibria for Fe; a possibility that cannot be fully evaluated because the available analytical data do not distinguish between Fe(II) and Fe(III) iron but only report total Fe. Variable concentrations of these metals for near-neutral pH conditions may also be artifacts related to inconsistent methods of sample filtration and preservation or lack thereof for the diverse set of data collected for this paper.

Overall, the concentrations of (Al + Fe + Mn) show a distinct increase at $pH < 4.5$, and reach levels of 10s to 100s of mg/L in the most acidic pit lakes (Fig. 3a). The acidic hard rock pit lakes examined include the Berkeley Pit in Montana, the Spenceville Pit in California, and Liberty and Ruth Pits in Nevada. The solubilities of the oxyhydroxide and sulfate solids that incorporate Al, Fe, and Mn generally increase markedly at low pH, resulting in higher metal concentrations in solution. Overall, the trends in concentrations of (Al + Fe + Mn) for hard rock pit lakes are the same as those observed in coal pit lakes (Klapper and Schultze, 1997).

The divalent base metals (Cd + Cu + Pb + Zn) comprise a second metal solute group with similar chemical characteristics. The concentrations of the sums of these metals are lowest in pit lakes with $pH > 4.5$, although there is a fair amount of scatter in the data (Fig. 3b). At $pH < 4.5$, the summed concentrations of these metals increase sharply, reaching levels of 10s to 100s of mg/L in the most acidic pit lakes. Similar to (Al + Fe + Mn), the solubilities of the oxide, carbonate, silicate, and sulfate solids that incorporate Cd, Cu, Pb, and Zn generally increase markedly with a decrease in pH, allowing higher concentrations in solution. Additionally, the adsorption of these base metals, which form divalent cationic solutes (i.e., Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}), is markedly decreased under acidic conditions as the surfaces of adsorption substrates, such as Fe hydroxides, Al hydroxides, and silicates, become increasingly positively charged (Dzombak and Morel, 1990). The combination of increased solubilities and decreased adsorption tends to allow these metals to accumulate in solution under acidic pH conditions.

A final group of solutes is the anionic metalloids, As and Se. The concentrations of (As + Se) show the approximate opposite trend to that observed for the cationic metals (Fig. 3c). In the case of (As + Se), concentrations are lowest at $pH < 7.5$, generally ranging from 0.0015 to 0.01 mg/L, although two relatively high concentrations of As of 0.05 and 0.7 mg/L have been reported for the acidic Berkeley Pit lake. At $pH > 7.5$, the concentrations of (As + Se) range to higher concentrations of 0.1–3 mg/L for many of the pit lakes examined.

The adsorption of As and Se anions is minimized under alkaline pH conditions, under which surfaces tend to become negatively charged. 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 phenomena is seen for natural evaporative lakes of the 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).

3.3. Pit lake categorization

Based on the observed concentration trends in TDS, major solutes, and metals in hard rock pit lakes can be roughly grouped into 3 main categories: (1) acidic-high TDS, (2) alkaline-high TDS, and (3) circumneutral-low TDS (Fig. 1).

The acidic-high TDS pit lakes are indicated by the coincident increases in the proportions of TDS made up of SO_4, and metals for the small population of lakes that have $pH < 4.5$. Acidic pH values, elevated SO_4, and elevated metal concentrations in mineralized terrains are nearly always a result of the oxidation of Fe sulfide minerals (e.g., pyrite, marcasite, pyrrhotite). The decrease in pH that results from Fe sulfide oxidation typically leads to elevated cationic metal concentrations (Figs. 3a and b).

Alkaline-high TDS pit lakes may be defined as those with $pH > 7.5$ and TDS concentrations in excess of 2000 mg/L (Fig. 1). The bulk of the TDS concentrations in these lakes is comprised of acid anions, base cations, and, in some cases, HCO_3. These conditions may be indicative of a combination of geochemical processes, including the presence of soluble minerals in the pit wall-rocks, such as gypsum, oxidation of Fe sulfides with neutralization of the pro-

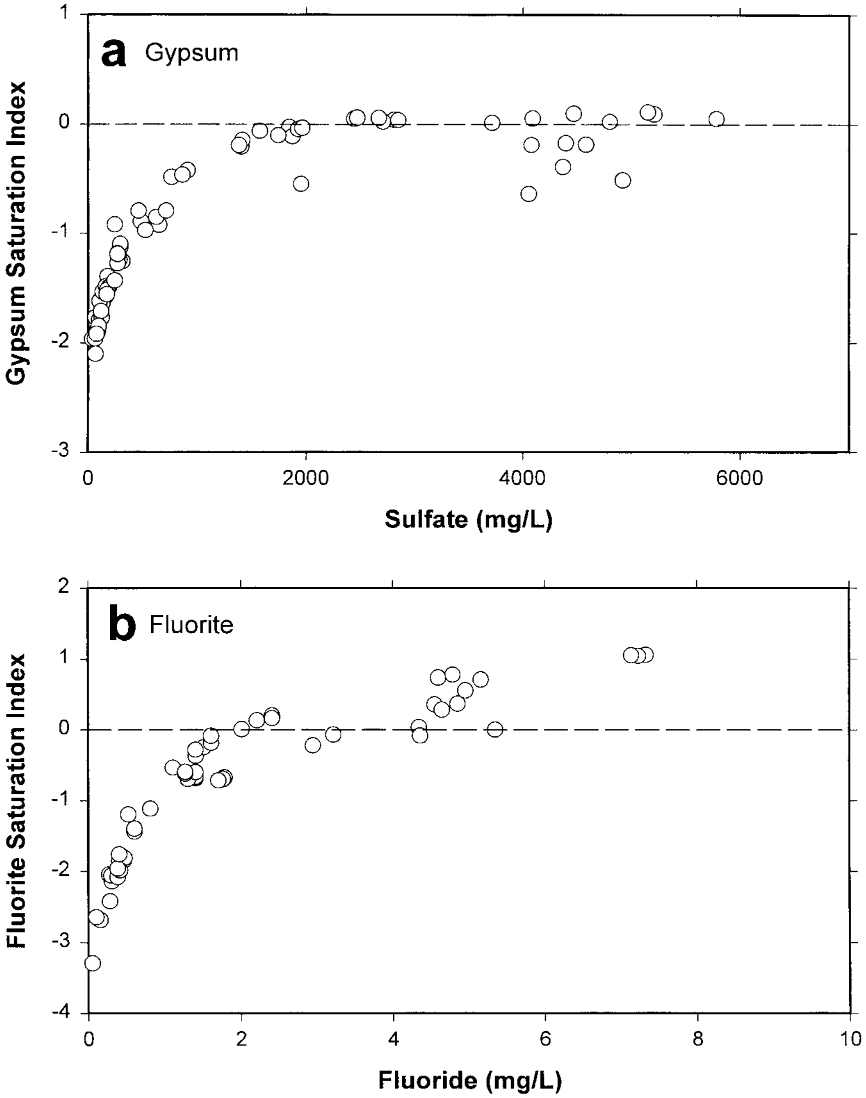

Fig. 4. Saturation indices in hard rock pit lakes for (a) gypsum and (b) fluorite.

duced acidity by reactions with carbonates, and/or evapoconcentration. Which of these processes is dominant is impossible to distinguish based on these general data trends, but it is important to recognize that high TDS levels can be reached in alkaline, as well as, acidic pit lakes.

Circumneutral-low TDS pit lakes are best described as those having near-neutral pH (4.5–8.5) and low TDS concentrations (Fig. 1). These lakes must have minimally reactive wall-rocks in the remnant mining surfaces of the pits and low solute loads in inflows. They may also reflect hydrologic flow-through conditions in which water in the pits is continuously refreshed by incoming groundwater, hence extensive evapoconcentration does not occur. The proportions of TDS comprised of base cations (Fig. 2a) and alkalinity (Fig. 2b) are high in these pit lakes compared to others. Metal concentrations in these pit lakes are low, consistent with their near-neutral pH conditions (Figs. 3a–c).

3.4. Equilibrium trends for sulfate, fluoride, calcium, and alkalinity

The common occurrence of Fe sulfides at hard rock mines and their subsequent oxidation after exposure to the atmosphere can produce elevated SO_4 concentrations in pit lakes. Evapoconcentration can also cause elevated SO_4 concentrations. As a result, SO_4 is typically the major solute in most pit lakes, especially

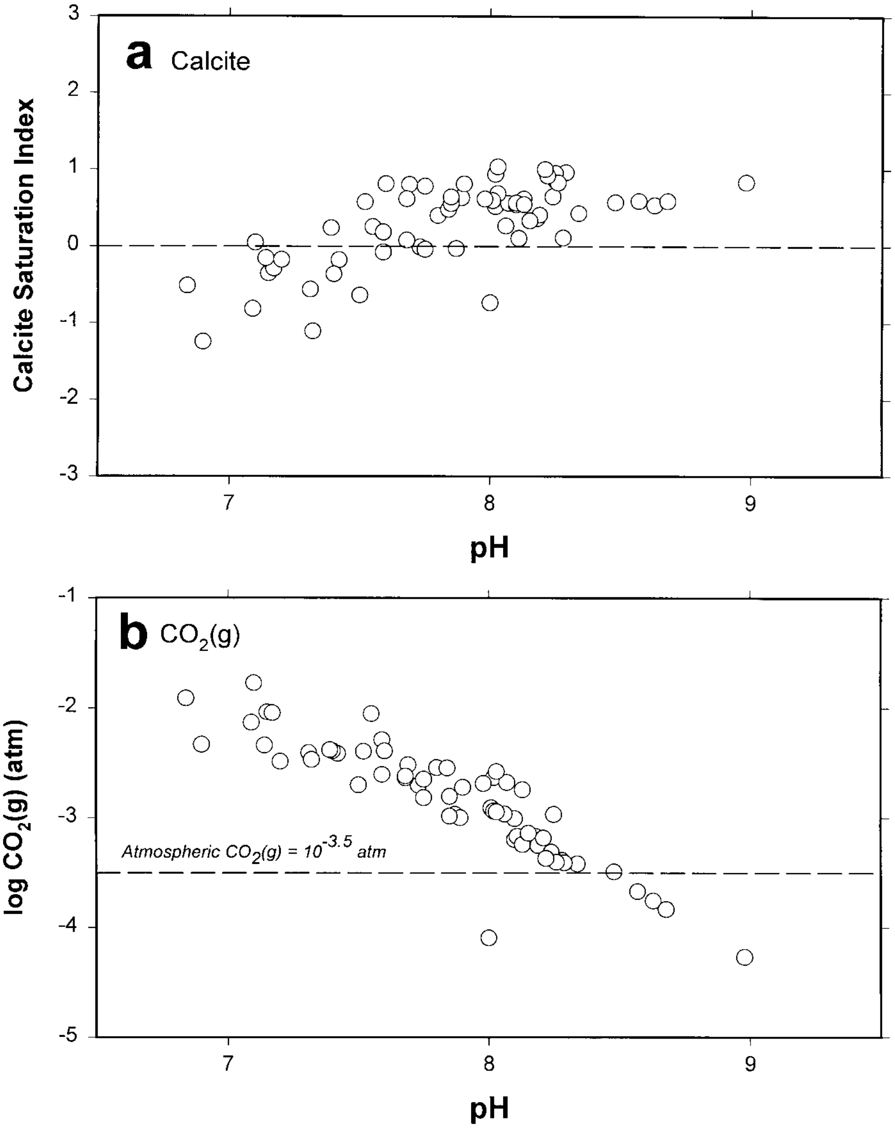

Fig. 5. Saturation indices in hard rock pit lakes for (a) calcite and (b) equilibrium partial pressures of CO_2(g).

those with high TDS concentrations, under both acidic and alkaline pH conditions.

In many aqueous systems, gypsum solubility may be the only limiting factor for SO_4 concentration (Drever, 1988; Langmuir, 1997). This generalization is also true for pit lakes in that values of SI for gypsum increase from negative values at low SO_4 concentrations to values that approximate zero with increasing SO_4 concentration (Fig. 4a). This result combined with the flattening of the SI curve with increasing SO_4 concentration indicates that gypsum solubility limits SO_4 concentrations in pit lakes. However, gypsum is a relatively soluble mineral, hence SO_4 concentrations can become high before its solubility limit is reached. For example, conditions of gypsum saturation in pit lakes are not reached until SO_4 concentrations exceed about 2000 mg/L (Fig. 4a).

Fluorite [CaF_2] is a common accessory mineral in many hydrothermal ore deposits, and its dissolution can release F. The dissolution of some layered silicates, such as biotite, can also release F. Fluorite is the least soluble F-containing mineral that might be expected to form and limit F concentrations in low temperature systems. Consistent with this hypothesis, values of SI for fluorite in pit lakes show a pattern that is similar to that observed for gypsum, with an increase from negative values at low F concentrations to values near or above zero at F concentrations greater than about

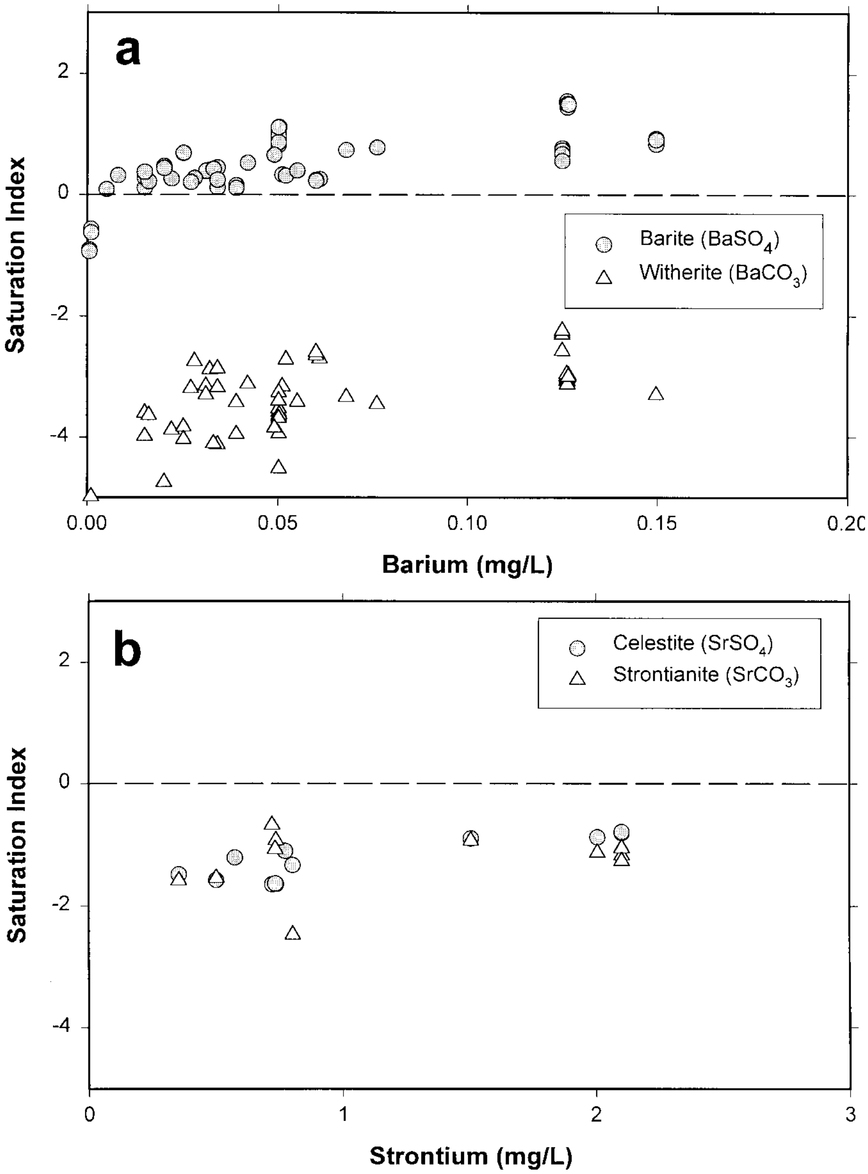

Fig. 6. Saturation indices in hard rock pit lakes for (a) Ba minerals and (b) Sr minerals.

2 mg/L (Fig. 4b). This pattern indicates that fluorite solubility is a reasonably effective control for F concentrations in pit lakes, although conditions of slight oversaturation typically occur.

Calcium and carbonate alkalinity are typically major solutes in alkaline pit lakes. In most natural waters with near-neutral to alkaline pH, Ca and carbonate alkalinity concentrations are affected by the solubility of calcite [$CaCO_3$]. In pit lakes, the values of SI for calcite show an increase over the pH range of 6.8–9 and slight flattening (Fig. 5a). Pit lakes with a pH > 7 generally have calcite SI values > 0, indicating that conditions of oversaturation are typical. The apparent oversaturation with calcite is common in natural aqueous systems and is often attributed to slow precipitation kinetics (Herman and Lorah, 1988; Inskeep and Bloom, 1986; Suarez, 1983).

The degree of calcite oversaturation is also related to the solubility of CO_2(g) in solution and the rate of CO_2(g) loss or gain by the solution (Langmuir, 1997). Calculations based on measured pH and alkalinity values, show that most pit lakes are oversaturated with CO_2(g) compared to the atmospheric level of $10^{-3.5}$ atm, ranging up to levels of $10^{-2.0}$ atm. The degree of

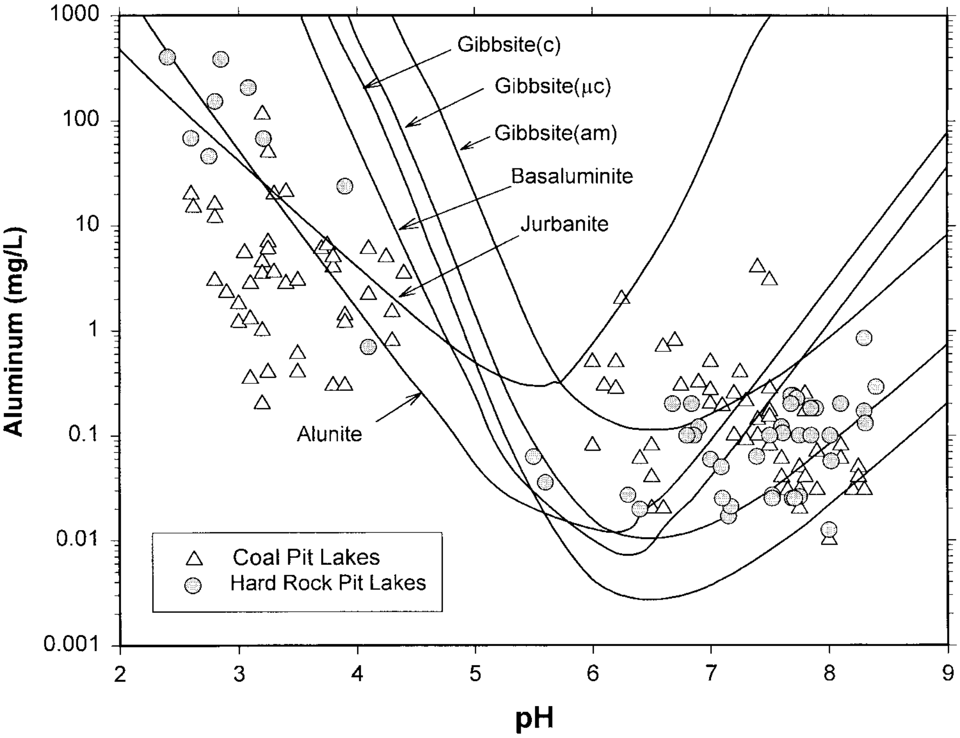

Fig. 7. Concentrations of Al in pit lakes compared to solubilities of Al hydroxide phases for 25°C in 0.021 M Na_2SO_4 (2000 mg/L SO_4). Solubility curves for alunite, basaluminite, and jurbanite shown for 25°C in equilibrium with gypsum.

oversaturation decreases with increasing pH (Fig. 5b). This decrease is probably related to the increase in solubility of CO_2(g) in water with increase in pH.

Overall, the SI values for calcite and CO_2(g) indicate that there is a tendency for oversaturation in most pit lakes, but the levels of oversaturation are not excessive compared to most natural systems (Drever, 1988). In general, values of SI for calcite are within a log unit of saturation and CO_2(g) levels approach 30 times atmospheric.

3.5. Equilibrium trends for barium and strontium

Barium and Sr are typically present in low concentrations in pit lakes. Saturation indices show that most pit lakes are slightly oversaturated with barite [$BaSO_4$] and undersaturated with witherite [$BaCO_3$] (Fig. 6a). The tendency for oversaturation with barite increases slightly with increased Ba concentration, but SI values generally remain between 0 and 1. The flattened trend in SI values for barite with Ba concentrations indicates that barite may be a reasonable solubility control for representing Ba concentrations in pit lakes with excess SO_4 relative to alkalinity. Barite is generally thought to be a primary control for Ba concentrations in low temperature systems (Hem, 1985; Jenne et al., 1980). In strongly alkaline pit lakes, conditions of saturation with witherite may be reached eventually as a result of extensive evapoconcentration, although the existing pit lakes are clearly undersaturated.

Strontium concentrations in pit lakes range from 0.35 to 2.1 mg/L, although analytical data were available for only a small portion of the pit lakes (Fig. 6b). Values of SI for probable solubility controls, including celestite [$SrSO_4$] and strontianite [$SrCO_3$], indicate that conditions of undersaturation prevail. Most natural water are undersaturated with celestite and strontianite (Hem, 1985). By analogy with Ca and Ba, however, the designation of either celestite, for SO_4-dominant pit lakes, or strontianite, for alkaline-carbonate pit lakes, should provide realistic bounds for Sr concentrations in predictive models of pit lake composition.

3.6. Equilibrium trends for aluminum

In many low temperature aqueous systems, some form of gibbsite [$Al(OH)_3$] is often considered to be the most probable solubility-limiting solid for Al (Driscoll et al., 1984; Hsu, 1977; Nordstrom and Ball, 1986; Sullivan et al., 1986). In the MINTEQ.DAT thermodynamic database, 3 forms of gibbsite are listed, including crystalline [gibbsite(c)], microcrystalline [gibbsite(μc)], and amorphous [$Al(OH)_3$(am)] (Table 1). The wide range in equilibrium constants for these

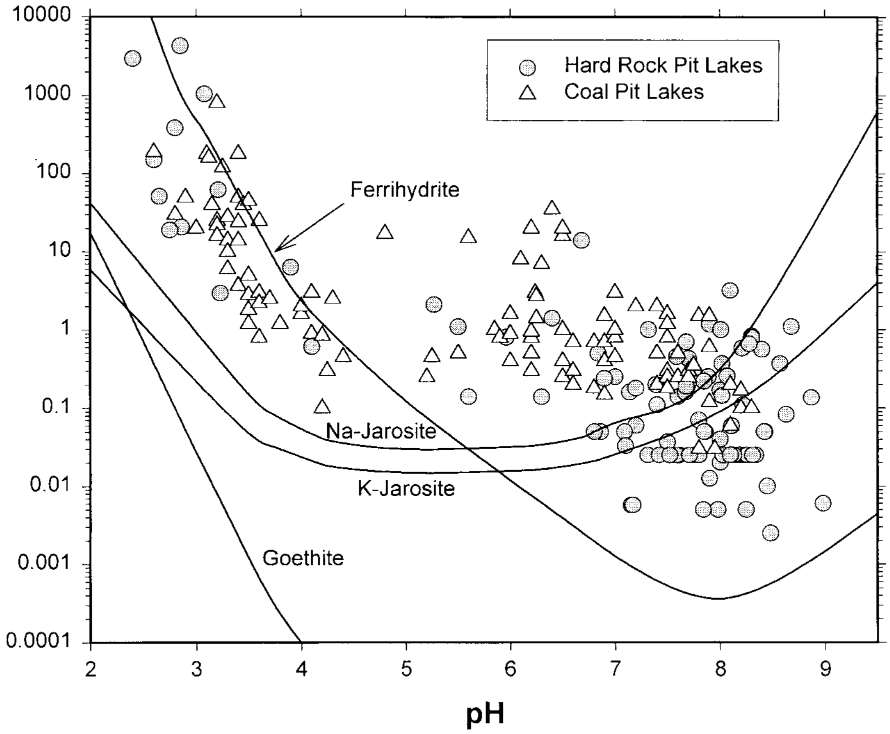

Fig. 8. Concentrations of Fe [as Fe(III)] in pit lakes compared to solubilities of ferrihydrite and goethite for 25°C in 0.021 M Na_2SO_4. Solubility curves for K-jarosite and Na-jarosite shown for 25°C in equilibrium with gypsum.

forms of gibbsite makes selecting one to represent a solubility control for Al in pit lakes an important consideration for predictive modeling.

The concentrations of Al measured in pit lakes are compared to the solubilities of a number of Al-containing solids in Fig. 7. This comparison shows that the selection of the gibbsite(c) as a solubility control for Al concentrations in pit lakes would overpredict the observed concentrations at $pH < 6$ and underpredict them at $pH > 6$. Gibbsite(μc) and $Al(OH)_3$(am) solubilities show the same pattern, overpredicting observed Al concentrations for $pH < 6$ and underpredicting them at $pH > 6$.

Instead of gibbsite, Al sulfate minerals appear to provide a better representation of observed Al concentrations in pit lakes with $pH < 6$ (Fig. 7). The solubilities of 3 possible Al sulfate minerals, basaluminite [$Al_4(OH)_{10}SO_4$], jurbanite [$AlOHSO_4$] and alunite [$KAl_3(SO_4)_2(OH)_6$], are shown in Fig. 7 for conditions under which SO_4 concentrations are controlled by gypsum solubility. Based on these comparisons, alunite or jurbanite are the best solids to use in pit lake predictive models to represent Al concentrations in pit lakes that are expected to have a $pH < 6$. Basaluminite solubility also provides a reasonable upper bound for observed Al concentrations. Consistent with this observation, Al sulfate minerals have been previously assumed or found to be solubility controls for Al in acid mine drainage environments (Karathanasis et al., 1988; Nordstrom, 1982; Sullivan et al., 1988; Van Breeman, 1973).

For conditions of $pH > 6$, the solubility of amorphous gibbsite [$Al(OH)_3$(am)] bounds most of the observed data for the pit lakes. In contrast to an acidic system, for neutral to alkaline pit lakes, the selection of $Al(OH)_3$(am) in predictive models as the solubility control for Al should provide a reasonable upper bound for Al concentrations.

3.7. Equilibrium trends for iron

Concentrations of Fe in pit lakes are compared to the solubilities of potential solubility controls in Fig. 8. This comparison shows that ferrihydrite solubility provides an excellent representation of Fe concentrations in pit lakes with $pH < 5$. Ferrihydrite is generally considered to be the primary solubility control for Fe in acidic systems (Langmuir, 1997; Karathanasis et al., 1988; Nordstrom et al., 1979; Sullivan et al., 1988), although a range of solubilities have been reported for it, depending on solution conditions and crystallinity (Hsu and Marion, 1985; Langmuir and Whittemore, 1971; Norvell and Lindsay, 1982).

Other potential solubility controls for Fe include

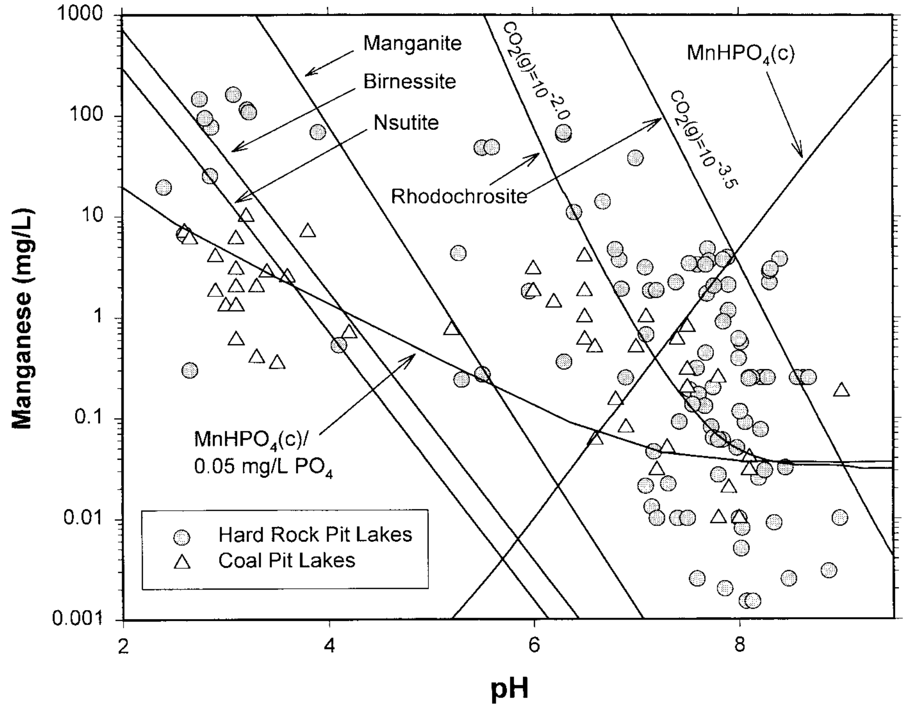

Fig. 9. Concentrations of Mn in pit lakes compared to solubilities of Mn-bearing solids for 25°C in 0.021 M Na_2SO_4. Solubility curves for $MnHPO_4(c)$ are shown for equilibrium with 0.05 mg/L PO_4 and with hydroxyapatite and gypsum. Solubility curves for rhodochrosite shown for $CO_2(g) = 10^{-3.5}$ and $10^{-2.0}$ atm.

goethite and the jarosites. However, Fe concentrations calculated for goethite [FeOOH] solubility underpredict the observed Fe concentrations by 4–5 orders of magnitude for acidic conditions (Fig. 8). Also, the solubilities of K-jarosite [$KFe_3(SO_4)(OH)_6$] and Na-jarosite [$NaFe_3(SO_4)(OH)_6$], tend to underpredict the observed concentrations of Fe in acidic pit lakes. This result is different from that obtained for Al for which alunite, which is the Al analogue of the jarosites, appears to provide a good representation of Al concentrations in acidic pit lakes.

In contrast to the acidic pit lakes, none of the solubility relationships tested appear to provide a bound for Fe concentrations for pit lakes with $pH > 5$ (Fig. 8). The lack of a clear solubility control under these conditions may reflect a lack of analytical information on the redox speciation of Fe in pit lakes. Ferrous iron is rapidly oxidized by dissolved O_2 to Fe(III) at $pH > 5$ (Eary and Schramke, 1990), but photocatalytic reactions, interactions with organic compounds, and microbial processes, can cause redox cycling of Fe and result in redox disequilibria (McKnight et al., 1988; Waite, 1986; Wehrli et al., 1989). Another possibility for the apparent disequilibria of Fe is the possible inclusion of unfiltered samples in the data presented here or the passage of colloidal-sized Fe hydroxide particles through the standard 0.45-μm filters generally used in water sampling.

While none of the probable solubility controls for Fe provide an accurate representation of Fe concentrations in neutral to alkaline pit lakes, total Fe concentrations in these pit lakes are generally very low. The majority have Fe concentrations between 0.002 and 5 mg/L (Fig. 8), making the predictions of Fe concentrations under such circumstances less important to overall predictions of water quality than for acidic pit lakes in which Fe concentrations can exceed 100 mg/L.

3.8. *Equilibrium trends for manganese*

Manganese concentrations in pit lakes show a trend with pH that is similar to those observed for Al and Fe (Fig. 9). The highest Mn concentrations exceed 100 mg/L at $pH < 4.5$, but decrease at $pH > 4.5$ to levels as low as 0.002 mg/L, although there is considerable scatter in the data for the higher pH pit lakes.

For acidic pit lakes with $pH < 6$, observed Mn concentrations are bounded by the solubility of manganite [γ-MnOOH] (Fig. 9). Also, for the most acidic pit lakes ($pH < 3.5$), birnessite [δ-MnO_2] solubility provides a reasonable representation of the measured Mn concentrations. Birnessite is slightly more soluble than nsutite [γ-MnO_2], another possible Mn oxide.

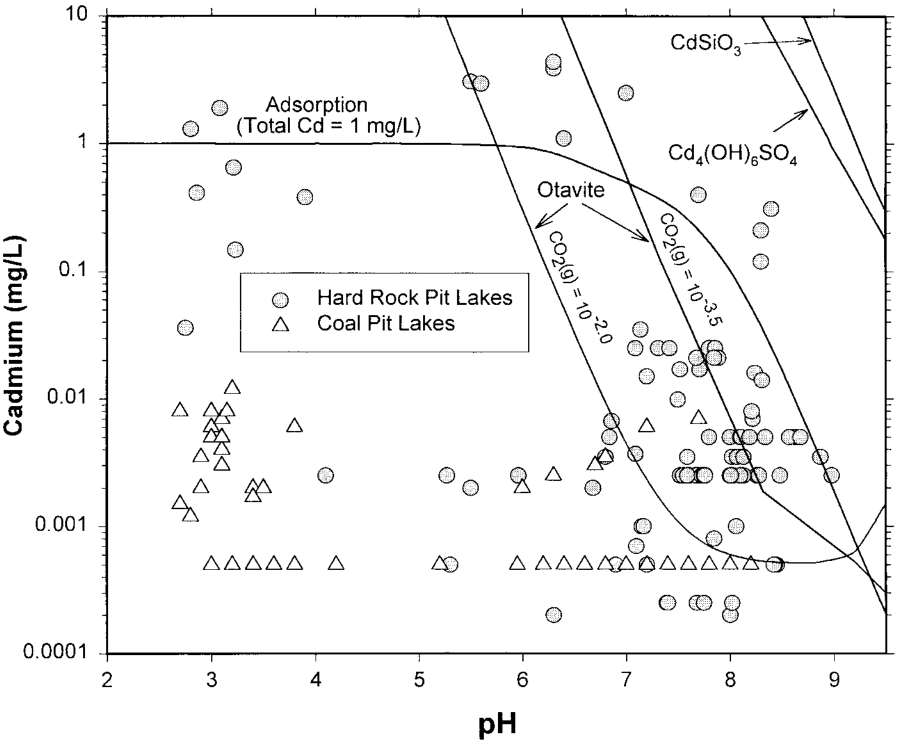

Fig. 10. Concentrations of Cd in pit lakes compared to solubilities of Cd-bearing solids for 25°C and 0.021 M Na_2SO_4. Solubility curves for Cd-SO_4 [$Cd_4(OH)_6SO_4$] shown for equilibrium with gypsum. Solubility curves for otavite shown for $CO_2(g) = 10^{-3.5}$ and $10^{-2.0}$ atm. Adsorption curves shown for 1 mg/L ferrihydrite.

Laboratory studies of Mn precipitation from SO_4-solutions under alkaline conditions have found that the initial precipitates generally have a composition that approximates MnOOH (manganite or feitnechtite) or Mn_3O_4 (hausmannite) (Hem, 1978; Hem and Lind, 1983; Lind, 1988). After aging, these initial precipitates convert to a composition that approximates birnessite [δ-MnO_2] (Cornell and Giovanoli, 1988; Hem and Lind, 1983). Consistent with these laboratory results on the instability of manganite, the weathering of primary Mn carbonates and silicates in laterite soils has been shown to result in the formation of birnessite, nsutite, and lithiophorite [$Al_2Mn_3O_9{:}3H_2O$] as secondary solids (Parc et al., 1989). In sum, these studies imply that birnessite may be the most representative control for Mn in acidic pit lakes over the long term.

The selection of a realistic solubility control for Mn in pit lakes with pH between 6 and 7.5 is problematical because of the wide scatter in the measured Mn concentrations (Fig. 9). One possibility is $MnHPO_4$(c), whose solubility is shown in Fig. 9 for equilibrium with hydroxyapatite [$Ca_5(PO_4)_3OH$] and gypsum [$CaSO_4{:}2H_2O$]. Under these conditions, the solubility of $MnHPO_4$(c) approximates the average of the measured Mn concentrations. However, it does not provide a convincing upper bound for the observed Mn concentrations. Manganese phosphates of various compositions are known to precipitate from solution at low temperature and have been suggested as solubility controls in soils (Boyle and Lindsay, 1985a,b), but their presence in pit lakes is speculative and dependent on some source of phosphate, such as hydroxyapatite.

For conditions of $pH > 7.5$, rhodochrosite solubility, may provide a reasonable upper bound for the observed Mn concentrations. Its solubility over the range of $CO_2(g)$ partial pressures observed in pit lakes brackets much of the observed data.

3.9. Equilibrium trends for cadmium

Cadmium concentrations observed in pit lakes are generally highest under acidic conditions, reaching concentrations from 0.01 to 1 mg/L at $pH < 4$ (Fig. 10). Under pH conditions of 4–7, observed Cd concentrations are very low and range from analytical detection limits at 0.0005 mg/L to about 0.002 mg/L. A few higher Cd concentrations, up to 0.04 mg/L, have been measured in pit lakes with $pH > 7$.

Potential solubility controls do not reproduce the observed trends in Cd concentrations in pit lakes over

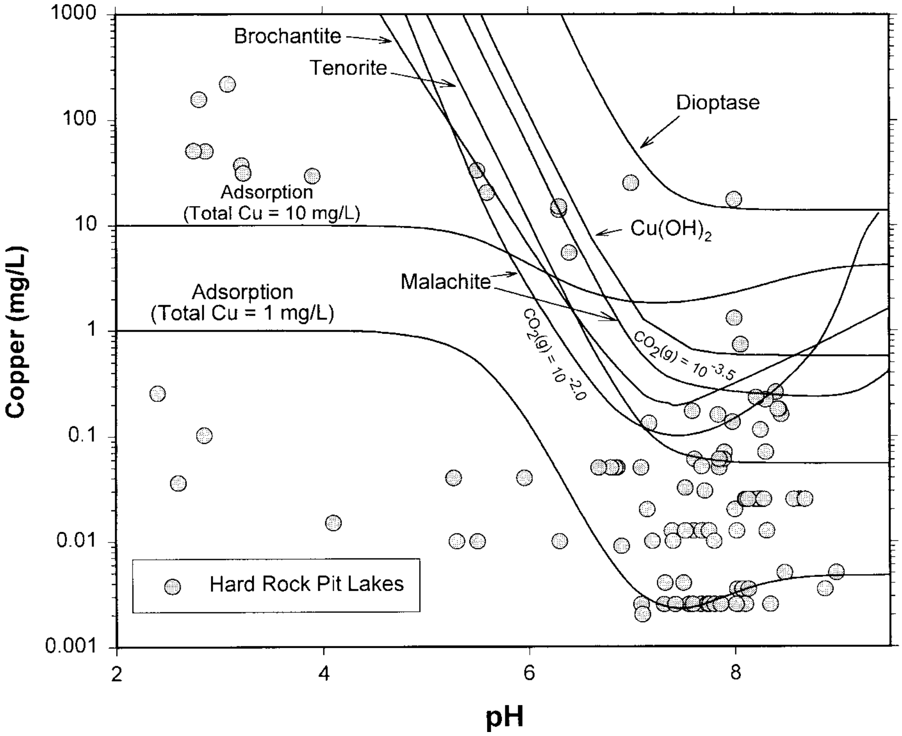

Fig. 11. Concentrations of Cu [as (Cu(II)] in pit lakes compared to solubilities of Cu-bearing solids for 25°C and 0.021 M Na_2SO_4. Solubility curves for brochantite shown at equilibrium with gypsum, for malachite at equilibrium with $CO_2(g) = 10^{-3.5}$ and $10^{-2.0}$ atm, and for dioptase at equilibrium with chalcedony. Adsorption curves shown for 1 mg/L ferrihydrite.

the entire pH range (Fig. 10). Solids, such as $CdSiO_3$ and $Cd_4(OH)_6SO_4$, are clearly too soluble to represent the observed Cd concentrations. The solubility of otavite [$CdCO_3$] bounds most of the observed Cd concentrations in pit lakes for pH from 7.5 to 8.5, depending on the $CO_2(g)$ partial pressure, but substantially overpredicts concentrations for $pH < 7.5$.

The adsorption of Cd^{2+} on ferrihydrite could be used to bound nearly all of the observed data as shown in Fig. 10, given a total Cd concentration of 1 mg/L. However, the Cd^{2+} adsorption reactions do not reproduce the low observed concentrations for pH 4–7.5.

In situations such as described here for Cd, in which no specific equilibria appears to provide a reasonable representation of concentration trends, predictions of future concentrations in hypothetical pit lakes must rely on determinations of the inventory of soluble metal species present in influent sources and in the pit wall-rocks. Influent sources include Cd concentrations in groundwater entering the pit. Leaching reactions that occur as meteoric water intermittently runs down pit walls into the lake and at the interface between the lake surface and pit wall-rock can also release metals from the weathering of sulfides and associated ore and gangue minerals. Generally, the mass of readily leached Cd (and other metals) is determined by laboratory tests as part of a pit lake modeling effort. The laboratory methods may include humidity cell tests, meteoric water mobility tests, or customized tests, that are designed to measure the metal leaching characteristics of the rock types that make up the wall-rock of a prospective pit lake.

3.10. Equilibrium trends for copper

Copper concentrations in pit lakes range as high as 180 mg/L at the low pH of the Spenceville Pit (Levy et al., 1997) to analytical detection levels of 0.0025 mg/L in pit lakes with $pH > 7$ (Fig. 11). A fair amount of scatter in the concentration data exists for pit lakes with $pH > 7$ that smears the concentrations trends. The scatter may be indicative of disequilibria with solubility controls or redox cycling between Cu(I) and Cu(II), possibly from photocatalytic reactions (Gray, 1969; Moffett and Zika, 1983, 1987).

Comparisons of the solubilities of different Cu(II) solids with the Cu concentrations in pit lakes indicate that dioptase [$CuSiO_3{:}H_2O$] and $Cu(OH)_2$ are too soluble to be probable controls for Cu (Fig. 11). Empirical studies have shown that the coprecipitation of $Cu(OH)_2$ with Fe and Al hydroxides is an efficient

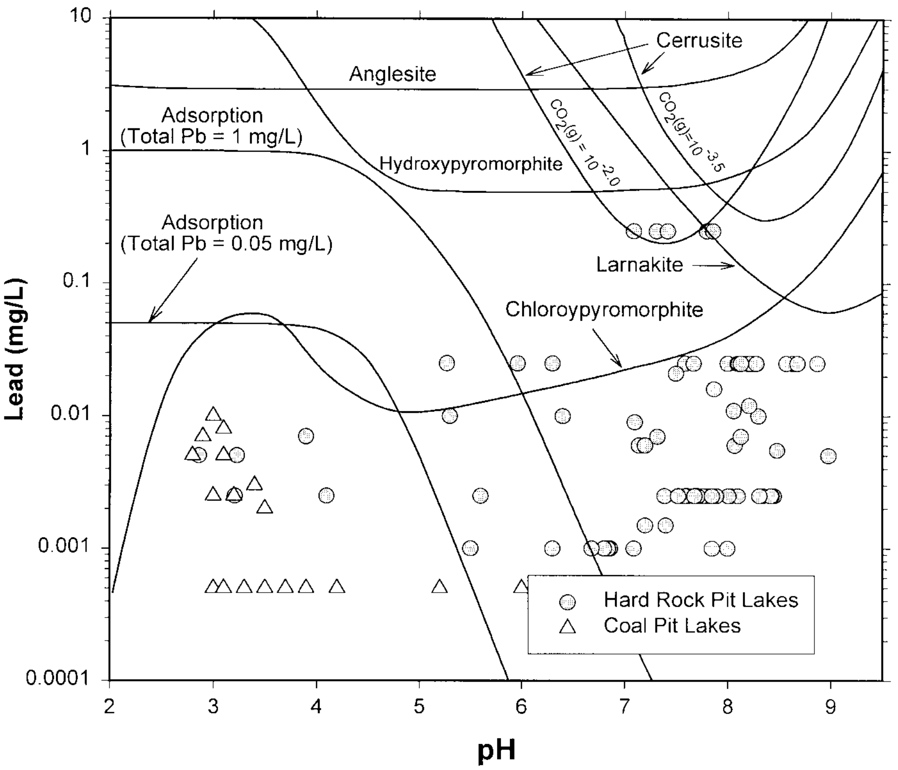

Fig. 12. Concentrations of Pb in pit lakes compared to solubilities of Pb-bearing solids for 25°C and 0.021 M Na_2SO_4. Solubility curves for anglesite and larnakite shown for equilibrium with gypsum. Solubility curves for cerrusite shown for equilibrium with $CO_2(g) = 10^{-3.5}$ and $10^{-2.0}$ atm. Solubility curves for hydroxypyromorphite and chloropyromorphite shown for equilibrium with hydroxyapatite and gypsum. Adsorption curves shown for 1 mg/L ferrihydrite.

mechanism for removing Cu from solution at pH values from 5 to 9 (Karthikeyan et al., 1997; Martiínez and McBride, 1998). However, the importance of co-precipitation reactions with Fe hydroxides for affecting the concentrations of metals, such as Cu, in pit lakes has not been established, making it difficult to extrapolate the empirical results to predictions of pit lake chemical composition.

For neutral to alkaline pH conditions, more probable solubility controls for Cu include tenorite [CuO], brochantite [$Cu_4(OH)_6SO_4$], and malachite [$Cu_2(OH)_2CO_3$] (Fig. 11). The Cu concentrations calculated for the solubilities of these minerals bound most of the measured Cu concentrations for pit lakes with $pH > 7$. Consistent with this observation, tenorite has been inferred to be a solubility control for Cu in fly ash leachates (Fruchter et al., 1988).

A number of other possible Cu(II) sulfates exist that could be potential solubility controls, such as antlerite [$Cu_3(OH)_4SO_4$], chalcanthite [$CuSO_4{:}5H_2O$], and langite [$Cu_4(OH)_6SO_4{:}H_2O$], but brochantite is the least soluble over the entire pH range for the conditions used in the calculations. Brochantite and antlerite are common secondary alteration products of the weathering of Cu sulfide minerals under oxidizing conditions (Alpers et al., 1994). Malachite [$Cu_2(OH)_2CO_3$] is also a common alteration product of the weathering of primary Cu minerals under alkaline conditions (Alpers et al., 1994; Hudson-Edwards et al., 1996).

The solubilities of tenorite, brochantite, and malachite increase to levels that are much higher than any of the measured concentrations for $pH < 7$ for the conditions used in the solubility calculations (Fig. 11), hence are probably not representative solubility controls for acidic pit lakes. In fact, no solids in the PHREEQC database that would be expected to form under low temperature conditions give a reasonable approximation of the Cu concentrations measured in acidic pit lakes.

Also shown on Fig. 11 are computed concentrations of Cu(II) in equilibrium with adsorption on ferrihydrite. The adsorption curves for Cu(II) are typical of divalent metals with little or no adsorption at low pH and increasing adsorption and removal from solution at $pH > 5.5$. The curves also indicate that although adsorption can be expected to occur at $pH > 5.5$, adsorption is probably not the only mechanism that limits Cu concentrations in solution. In fact, compari-

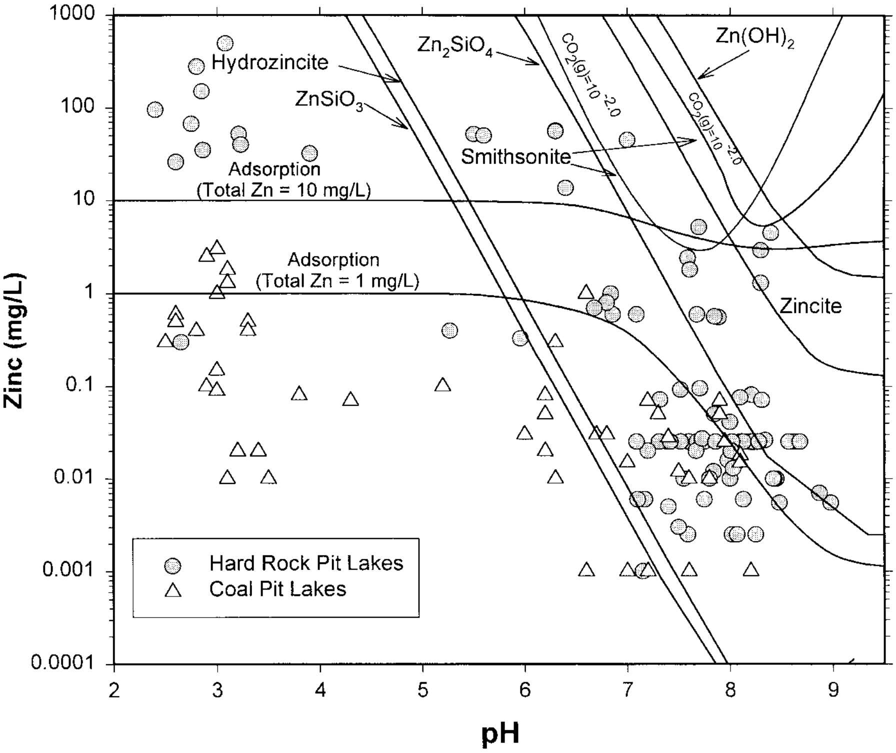

Fig. 13. Concentrations of Zn in pit lakes compared to solubilities of Zn-bearing solids for 25°C and 0.021 M Na_2SO_4. Solubility curves for Zn silicates ($ZnSiO_3$ and $ZnSi_2O_4$) shown for equilibrium with chalcedony and for smithsonite shown with $CO_2(g) = 10^{-3.5}$ and $10^{-2.0}$ atm. Adsorption curves shown for 1 mg/L ferrihydrite.

sons of calculated Cu concentrations based on solubility or adsorption to measured concentrations indicate that no single geochemical process can be specified that fully describes the variability in Cu levels in alkaline pit lakes.

In summary, for the purposes of predictive pit lake modeling, brochantite solubility provides a reasonable upper bound for Cu concentrations in systems that are gypsum-saturated and have $pH > 7.5$. In carbonate-rich systems with $pH > 7.5$, the selection of malachite as a solubility control would be a better choice. A third alternative for pit lakes with $pH > 7.5$, that are neither gypsum or carbonate saturated, would be the specification of tenorite as a solubility control.

For acidic pit lakes, one of the Cu sulfates, such as brochantite, would provide a conservative overprediction of probable Cu concentrations in that its formation requires much higher Cu concentrations than have been measured in existing pit lakes. For predictive purposes, methods involving empirical measurements of soluble Cu in pit wall-rocks combined with data on Cu concentrations in influent groundwater sources may provide more reasonable alternatives for estimating Cu concentrations in future pit lakes than what can be expected from equilibrium modeling.

3.11. Equilibrium trends for lead

Lead concentrations measured in pit lakes are low over the entire pH range (Fig. 12). Many of the measured concentrations are exactly the same and are indicative only of the analytical detection levels (multiple detection limits exist in the data). These factors make it difficult to define trends that might be related to specific solubility controls or adsorption reactions. However, a few general observations can be made that may be helpful for bounding Pb concentrations for predictive modeling of pit lakes.

The most common Pb minerals, that have been inferred to be solubility controls for acid–sulfate and alkaline–carbonate environments, include anglesite [$PbSO_4$] and cerrusite [$PbCO_3$], respectively (Jenne et al., 1980). However, their solubilities clearly predict higher concentration than those observed in pit lakes (Fig. 12). The solubility of another Pb sulfate mineral, larnakite [$PbO{:}PbSO_4$] appears to predict Pb concentrations consistent with measured concentrations for pit lakes with $pH > 7.5$, but trends to much higher than measured concentrations at lower pH. Other Pb sulfate minerals, such as plumbojarosite [$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$] may be important controls for

Pb under acidic conditions (Alpers et al., 1994), but solubility data for such minerals are not available for making direct comparisons.

Lead also forms phosphate minerals that are much less soluble than the sulfates and carbonates. Two possible phosphates that may control Pb concentrations in pit lakes include hydroxypyromorphite [$Pb_5(PO_4)_3OH$] and chloropyromorphite [$Pb_5(PO_4)_3Cl$]. The solubility of chloropyromorphite, in particular, appears to provide a reasonable bound for the majority of the Pb concentrations measured in pit lakes (Fig. 12). Hydroxypyromorphite is shown to have a higher solubility than chloropyromorphite in Fig. 12, although in nature some intermediate composition between these two end-members may be the actual Pb phosphate that forms.

While the formation of Pb phosphates in pit lakes may be speculative, because no reports of their existence in pit lakes have been found in the literature, Pb phosphates can precipitate readily from solution (Nriagu, 1974). Additionally, Pb phosphates have been identified as probable solubility controls for Pb in waste rocks, soils, and solutions in mining areas (Davies, 1990; Davis et al., 1993; Hudson-Edwards et al., 1996; Jenne et al., 1980; Santillan-Medrano and Jurinak, 1975). Laboratory experiments have also indicated that chloropyromorphite forms readily by the oxidation of galena and alteration of cerrusite in the presence of hydroxyapatite (Zhang and Ryan, 1999a,b). The results of these various studies make it reasonable to expect that Pb phosphates may form in pit lake environments as well and limit Pb concentrations in solution.

Adsorption curves for Pb are also shown in Fig. 12, and they show sharp decreases in Pb concentrations for $pH > 4$ to levels that are well below those measured in pit lakes, although the extent of this decrease is dependent on the total Pb concentration. While some adsorption of Pb undoubtedly occurs in pit lakes, calculations of the effects of Pb adsorption do not, by themselves, provide concentration trends that are consistent with measured concentrations.

3.12. Equilibrium trends for zinc

Zinc concentrations in pit lakes follow the same trend with pH as those observed for the other divalent base metals, with the highest concentrations occurring at $pH < 4$ and decreasing concentrations at higher pH (Fig. 13). However, no single reaction appears to be representative of Zn concentrations over the entire pH range. Zinc hydroxide [$Zn(OH)_2$] is too soluble to be a reasonable solubility control for Zn. Zincite [ZnO] solubility bounds most of the measured Zn concentrations for pit lakes with $pH > 7.5$, although it yields much higher than measured concentrations at lower pH.

Zinc silicate [Zn_2SiO_4] provides an upper bound for Zn concentrations in pit lakes with $pH > 7.5$, when calculated for equilibrium with chalcedony [SiO_2] solubility. Zinc silicates, such as Zn_2SiO_4, $ZnSiO_3$, and hemimorphite [$Zn_4Si_2O_7(OH){:}2H_2O$] have been inferred to be solubility controls in mining districts where Zn-bearing solutions migrate through and react with silicate rocks by equilibrium modeling (Jenne et al., 1980), experimental studies (White et al., 1998), and mineralogical characterization (Hudson-Edwards et al., 1996).

However, Zn_2SiO_4 is too soluble to represent the observed Zn concentrations at lower pH. Other possible Zn solids, including $ZnSiO_3$, and hydrozincite [$Zn_5(OH)_6(CO_3)_2$], have solubilities that also appear to be too high at $pH < 4.5$ and too low at $pH > 7.5$) to represent the Zn concentration trend observed in pit lakes, although they may be adequate for the intermediate pH range of 4.5 to 7.5 (Fig. 13).

Another possible process that may control Zn concentrations in pit lakes is coprecipitation with Fe hydroxides. Martiínez and McBride, (1998) report that coprecipitation results in substantially lower Zn concentrations than would be predicted purely from the solubilities of Zn oxides and hydroxides. However, thermodynamic data for coprecipitation reactions are not available for incorporation into geochemical models, making it difficult to provide direct comparisons of coprecipitate equilibria to observed Zn concentrations.

The adsorption of Zn^{2+} on ferrihydrite is a potential limiting reaction in pit lakes. However, ferrihydrite has a limited capacity to adsorb Zn (Fig. 13). For example, in a system with a high Zn concentration, such as 10 mg/L, limited adsorption under low pH conditions results in high solution concentrations. At higher pH, a decrease in Zn concentrations is predicted because of adsorption on ferrihydrite, but not to the extent that levels as low as those in pit lakes are reached. For a system with a total Zn concentration of 1 mg/L, a decrease in concentration from adsorption on ferrihydrite can be predicted for $pH > 7$, which is consistent with the observed data in pit lakes. However, consideration of only adsorption reactions would result in underprediction of Zn concentrations for conditions of $pH < 3.5$.

For the purposes of predictive pit lake modeling, no specific solid phase appears to provide a complete description of Zn concentration trends in existing pit lakes, although some solids may provide reasonable bounds for different pH ranges. For instance, the selection of Zn_2SiO_4 or zincite as a solubility control for Zn may provide a reasonable approximation of maximum Zn concentrations in pit lakes expected to have a

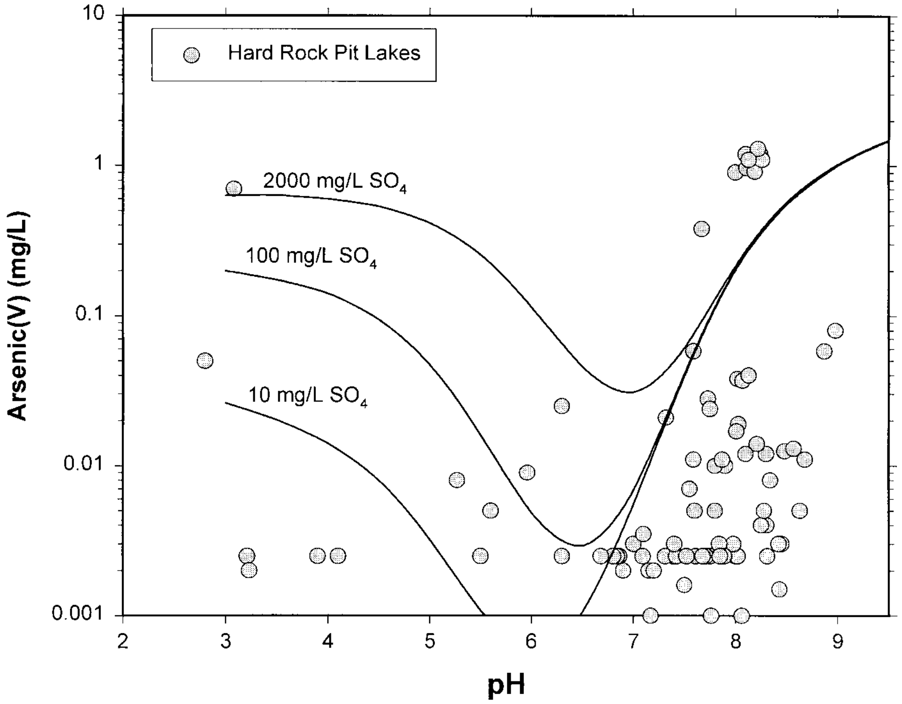

Fig. 14. Concentrations of As(V) in pit lakes compared to those predicted for adsorption on ferrihydrite for 25°C and a range of SO_4 concentrations. Adsorption curves shown for 1 mg/L ferrihydrite.

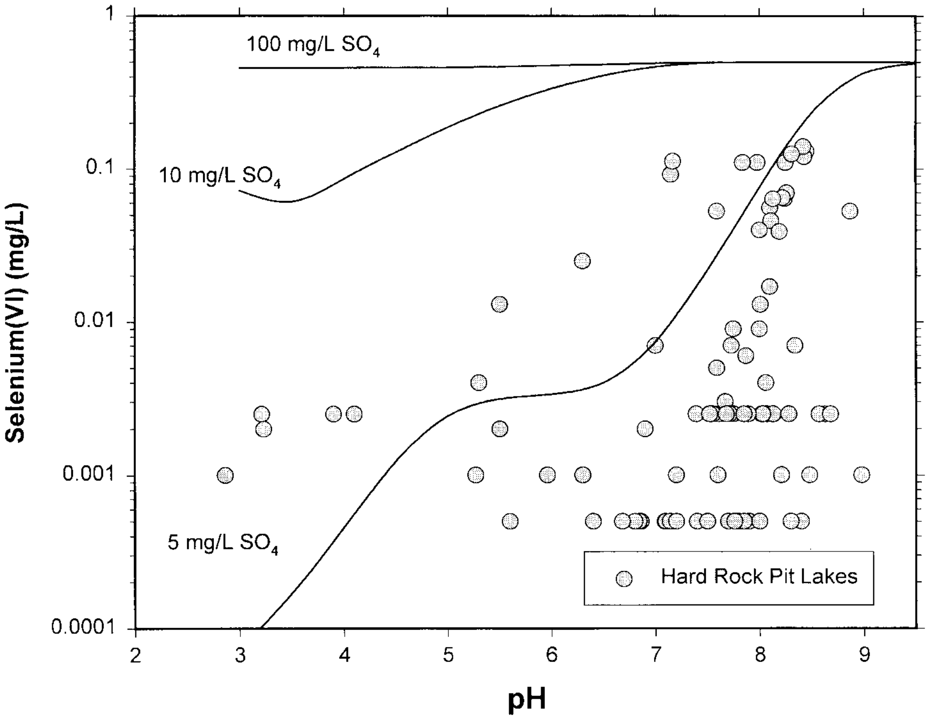

Fig. 15. Concentrations of Se(VI) in pit lakes compared to those predicted for adsorption on ferrihydrite for 25°C and a range of SO_4 concentrations. Adsorption curves shown for 1 mg/L ferrihydrite.

Table 4
Summary of probable geochemical controls for specific solutes in pit lakes

Solute	Pit lake acid–base characteristics		
	Acidic (pH $<$ 4.5)	Circumneutral (pH 4.5–7.5)	Alkaline (pH $>$ 7.5)
Aluminum	Alunite, Basaluminute, or Jurbanite	Gibbsite(am)	Gibbsite(am)
Alkalinity	Not applicable	Calcite[b]	Calcite[b]
Arsenic	Adsorption on Ferrihydrite[h]	Adsorption on Ferrihydrite[h]	None identified
Barium	Barite	Barite/Witherite	Barite/Witherite
Cadmium	None identified	Adsorption on Ferrihydrite	Otavite
Calcium	Gypsum	Gypsum	Gypsum/Calcite[a]
Cu	None identified	Brochantite[g]	Malachitee or Brochantite[g]
Fluoride	Fluorite	Fluorite	Fluorite
Iron[c]	Ferrihydrite	None identified	None identified
Lead	Anglesite[f] or Chloropyromorphite[d]	Anglesite[f], Chloropyromorphite[d], and/or adsorption on Ferrihydrite	Cerrusite[e] or Chloropyromorphite[d]
Manganese	Manganite or Birnessite	$MnHPO_4$[d]	Rhodochrosite
Selenium	Adsorption on Ferrihydrite[i]	Adsorption on ferrihydrite[i]	None identified
Strontium	Celestite	Celestite/Strontianite	Celestite/Strontianite
Sulfate	Gypsum	Gypsum	Gypsum
Zinc	None identified	Hydrozincite[e] or $ZnSiO_3$[g]	Zn_2SiO_4[g] or zincite

[a] Oversaturation with calcite is typical in most pit lakes (see Fig. 5a).

[b] Oversaturation with atmospheric $CO_2(g)$ at $10^{-3.5}$ atm typically occurs for conditions of $pH < 8.5$ and undersaturation for $pH > 8.5$ (see Fig. 5b).

[c] Assumed to be ferric iron [Fe(III)].

[d] Dependent on the presence of phosphate.

[e] Requires the presence of carbonate alkalinity.

[f] Requires relatively high SO_4 concentrations such as those reached at gypsum saturation.

[g] Requires the presence of dissolved silica near or approaching conditions of chalcedony saturation.

[h] Decreases in efficiency with increases in SO_4 concentration.

[i] Negligible for SO_4 concentrations > 100 mg/L.

$pH > 7.5$. For pit lakes expected to have a pH between 4.5 and 7.5, the solubilities of either $ZnSiO_3$ or hydrozincite may provide reasonable bounds for Zn concentrations, depending on silica and alkalinity levels. For pit lakes with $pH < 4.5$, no specific equilibria are sufficiently insoluble to represent the observed concentrations.

3.13. Equilibrium trends for arsenic

Arsenic concentrations are comparatively low in neutral to acidic pit lakes, generally ranging from detection levels at 0.002 mg/L up to 0.01 mg/L (Fig. 14). In contrast, higher As concentrations, ranging up to 3 mg/L, tend to occur most commonly in pit lakes with $pH > 8$, although there is a fair amount of scatter in the data. Minerals that contain As(III) and As(V) are very soluble and even the highest As concentrations observed in the alkaline pit lakes are well below what would be predicted for any potential solubility controls in the PHREEQC database. Thus, the trends in As concentrations with pH cannot be ascribed to the solubility of a specific mineral.

However, the trends in As concentrations in pit lakes are reflective of the adsorptive characteristics of As(V) species on ferrihydrite, and by analogy, on other oxide and oxyhydroxide sorbents, as shown by the curves for As(V) adsorption onto ferrihydrite in Fig. 14. In general, anionic As(V) species are increasingly adsorbed onto ferrihydrite at $pH < 7.5$ because of the increase in positively charged sites that occurs under acidic conditions from surface protonation (Dzombak and Morel, 1990). Consequently, there is an increasing tendency for the removal of As from solution under acidic pH conditions compared to alkaline pH conditions. Adsorption onto ferrihydrite is known to be an effective mechanism for removing As from solution as evidenced by its implementation in water treatment applications (De Carlo and Thomas, 1985; Merrill et al., 1986).

However, the effectiveness of adsorption reactions for removing As(V) from solution is decreased by other negatively charged solutes, such as SO_4, that compete for positively charged adsorption sites. Sulfate is the most common anionic solute in pit lakes, and as shown in Fig. 14, is predicted to cause a significant decrease in As adsorption at $pH < 7.5$, depending on its concentration. At $pH > 7.5$, the effect of SO_4 on As(V) adsorption is diminished as the abundance of positively charged adsorption sites on ferrihydrite is decreased. As a result, both As(V) and other anionic species can accumulate in solution under alkaline conditions, as is observed for pit lakes. A similar observation of elevated As concentrations is seen for some alkaline–carbonate lakes of the western USA that have undergone extensive evapoconcentration (Davis and Eary, 1996).

3.14. Equilibrium trends for selenium

The observed trend for the concentration of Se with pH in pit lakes is similar to that for As (Fig. 15). Under aerobic conditions, Se(VI) should be the dominant oxidation state. Similar to As(V), pure mineral forms that incorporate Se(VI) are too soluble to be expected to limit Se concentrations in pit lakes.

Selenium(VI) forms anionic solutes that are less strongly adsorbed under alkaline pH conditions compared to acidic conditions. This characteristic is consistent with the tendency for the highest Se concentrations to occur in alkaline pit lakes. Additionally, calculations of adsorption equilibria indicate that SO_4 effectively prevents Se(VI) adsorption even at concentrations as low as 10 mg/L, according to model calculations (Fig. 15). At SO_4 concentrations > 100 mg/L, the calculations indicate no adsorption of Se(VI) should occur over the entire pH range. Because SO_4 can generally be expected to be present in much higher concentrations than Se, its presence in solution limits Se(VI) adsorption.

For the purposes of pit lake modeling, the inclusion of Se adsorption is unlikely to serve as a limiting factor for Se concentration. For making accurate predictions of Se concentrations in pit lakes, site-specific information on the inventory of soluble Se in the pit wall-rocks and influent sources is needed through analytical determinations of groundwater concentrations and measurements of Se release from pit wall-rocks by laboratory leaching tests.

4. Conclusions

The concentrations of solutes measured in mine pit lakes show distinct trends that are related primarily to the pH. Major solute concentrations (i.e., Ca, Mg, Na, K, and SO_4) are highest under low pH conditions because of the oxidation of sulfides, and, in some pit lakes with alkaline pH values, because of reactive wall-rocks and/or evapoconcentration. Cationic metal concentrations (i.e., Al, Fe, Mn, Cd, Cu, Pb, and Zn) are generally high only in pit lakes with $pH < 4.5$ because of the increase in the solubilities of various oxide, hydroxide, sulfate, silicate, and carbonate minerals that occurs under acidic conditions. The concentrations of anionic metalloids (i.e., As and Se) reach the highest levels in the most alkaline pit lakes ($pH > 7.5$) because of a lack of geochemical controls for these solutes under such conditions combined with the concentrating effects of evaporation.

The results of the equilibrium modeling and comparisons of mineral solubilities to measured metal concentrations in pit lakes are summarized in Table 4. These results identify a number of specific minerals that can be used in predictive modeling of pit lake water quality to set upper bounds for the concentrations of various major solutes and metals. In the absence of site-specific information on geochemical processes, which is usually the case for pit lakes, the identification of specific geochemical controls should provide useful guidance in the setup and application of equilibrium geochemical models used to predict future water quality in pit lakes. However, it is also important to recognize that geochemical equilibrium is only one of a number of processes that can affect water quality in pit lakes. Other hydrogeochemical processes are also important and may have to be taken into account in making predictions of the chemical compositions of future pit lakes.

Importantly, the type of analysis presented here begs the question of whether the specific minerals inferred to be solubility controls for various dissolved constituents actually exist in pit lake environments. At the current time, detailed mineralogical studies of pit lake sediments, suspended particles, and wall-rock alteration products have not been conducted and presented in the literature. Additionally, information on redox transformations in the water columns of pit lakes is lacking. Clearly, there is a need for these types of studies, particularly those focused on the fate of environmentally important metals (e.g., As, Cd, Cu, Hg, Pb, Se, Zn) to provide some level of validation to the equilibrium geochemical modeling approach described here. Research in these areas would provide valuable information for refining conceptualizations of the important geochemical processes that need to be represented in models used to make predictions of future water quality in mine pit lakes.

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References

Alpers, C.N., Blowes, D.W., Nordstrom, D.K., Jambor, J.L., 1994. Secondary minerals and acid mine-water chemistry. In: Blowes, D.W., Jambor, J.L. (Eds.), The Environmental Geochemistry of Sulfide Mine-Wastes, Short Course Handbook, vol. 22. Mineral. Assoc. Canada, Waterloo, Ontario, pp. 247–270.

Bird, D.A., Lyons, W.B., Miller, G.C., 1994. An assessment of hydrogeochemical computer codes applied to modeling post-mining pit water geochemistry. In: Proceedings of Tailings & Mine Waste '94. Balkema, Rotterdam, pp. 31–40.

Boyle, F.W., Lindsay, W.L., 1985a. Preparation, x-ray diffraction pattern, and solubility product of manganese(II) phosphate hydrate. Soil. Sci. Soc. J 49, 758–760.

Boyle, F.W., Lindsay, W.L., 1985b. Diffraction patterns and solubility products of several divalent manganese phosphate compounds. Soil. Sci. Soc. J 49, 761–766.

Cornell, R.M., Giovanoli, R., 1988. Transformation of hausmannite into birnessite in alkaline media. Clays and Clay Minerals 36, 249–257.

Davies, B.E., 1990. Lead. In: Alloway, B.J. (Ed.), Heavy Metals in Soils. Halsted Press, New York, pp. 177–196.

Davis, A., Ashenberg, D., 1989. The aqueous geochemistry of the Berkeley Pit, Butte, Montana, U.S.A. Appl. Geochem 4, 23–36.

Davis, A., Eary, L.E., 1996. In: Pit lake water quality in the western U.S.: Unifying concepts, 1996 SME Annual Meeting, Phoenix. Soc. Min. Metall. Expl, Littleton, CO Preprint 96-136,.

Davis, A., Drexler, J.W., Ruby, M.V., Nicholson, A., 1993. Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. Environ. Sci. Technol. 27, 1415–1425.

De Carlo, E.H., Thomas, D.M., 1985. Removal of arsenic from geothermal fluids by adsorptive bubble flotation with colloidal ferric hydroxide. Environ. Sci. Technol. 19, 538–544.

Drever, J.I., 1988. The Geochemistry of Natural Waters, 2nd ed. Prentice-Hall, Englewood Cliffs, New Jersey.

Driscoll, C.T., Baker, J.P., Bisogni, J.J., Schofield, C.L., 1984. Aluminum speciation and equilibria in dilute acidic surface waters of the Adirondack Region of New York State. In: Bricker, O.P. (Ed.), Geological Aspects of Acid Deposition. Butterworth, Boston, pp. 55–75.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complex Modeling, Hydrous Ferric Oxide. Wiley, New York.

Eary, L.E., 1998. Predicting the effects of evapoconcentration on water quality in mine pit lakes. J. Geochem. Expl 64, 223–236.

Eary, L.E., Schramke, J.A., 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. In: Melchior, D.C., Bassett, R.L. (Eds.), Chemical Modeling of Aqueous Systems II, Am. Chem. Soc. Symp. Ser. 416. Am. Chem. Society, Washington, DC, pp. 379–396.

Fruchter, J.S., Rai, D., Zachara, J.M., Schmidt, R.L., 1988. Leachate Chemistry at the Montour Fly Ash Test Cell, Rep. EA-5922. Electric Power Research Institute, Palo Alto, California.

Gray, R.D., 1969. The kinetics of oxidation of Cu(I) by molecular oxygen in perchloric acid-acetronitrile solutions. J. Am. Chem. Soc. 91, 56–62.

Havis, R.N., Worthington, S.J., 1997. A simple model for the management of mine pit-lake filling and dewatering. In: Proceedings of Tailings & Mine Waste '97. Balkema, Rotterdam, pp. 478–549.

Hem, J.D., 1978. Reactions of metal ions at surfaces of hydrous iron oxide. Geochim. Cosmochim. Acta 41, 527–538.

Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Surv., Gov. Printing Office, Washington, DC.

Hem, J.D., Lind, C.J., 1983. Non-equilibrium models for predicting forms of precipitated manganese oxides. Geochim. Cosmochim. Acta 47, 2037–2046.

Herman, J.S., Lorah, M.M., 1988. Calcite precipitation rates in the field: Measurement and prediction for a travertine-depositing stream. Geochim. Cosmochim. Acta 52, 2347–2355.

Hudson-Edwards, K.A., Macklin, M.G., Curtis, C.D., Vaughan, D.J., 1996. Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne Basin, Northeast England: Implications for metal-contaminated river systems. Environ. Sci. Technol. 30, 72–80.

Hsu, P.H., 1977. Aluminum hydroxides and oxyhydroxides. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. Soil Sci. Soc. Am., Madison, Wisconsin, pp. 99–143.

Hsu, P.H., Marion, G., 1985. The solubility product of goethite. Soil. Sci. 140, 344–351.

Inskeep, W.P., Bloom, P.R., 1986. Calcium carbonate supersaturation in soil solutions of Calciaquolls. Soil. Sci. Soc. Am. J. 50, 1431–1437.

Jenne, E.A., Ball, J.W., Burchard, J.M., Vivit, D.V., Barks, J.M., 1980. Geochemical modeling: Apparent solubility controls of Ba, Zn, Cd, Pb, and F in waters of the Missouri Tri-State mining area. In: Hemphill, D.D. (Ed.), Trace Substances in Environmental Health-XIV. Univ. Missouri, Columbia, Missouri, pp. 353–361.

Karathanasis, A.D., Evangelou, V.P., Thompson, Y.L., 1988. Aluminum and iron equilibria in soil solutions and surface waters of acid mine watersheds. J. Environ. Qual. 17, 534–543.

Karthikeyan, K.G., Elliot, H.A., Cannon, F.S., 1997. Adsorption and coprecipitation of Cu with the hydrous oxides of iron and aluminum. Environ. Sci. Technol. 31, 2721–2725.

Kempton, J.H., Locke, W.L., Nicholson, A.D., Bennett, M., Bliss, L., Maley, P., 1997. Probabalistic prediction of water quality in the Twin Creeks Mine pit lake, Golcanda, Nevada. In: Fourth Int. Conf. on Acid Rock Drainage Proc., Vancouver, B.C., May 31–June 6, 1997, pp. 891–904.

Klapper, H., Schultze, M., 1997. Sulfur acidic mining lakes in Germany—Ways of controlling geogenic acidification. In: Fourth Int. Conf. on Acid Rock Drainage Proc., Vancouver, BC, pp. 1729–1744.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice-Hall, Upper Saddle River, New Jersey.

Langmuir, D., Whittemore, D.O. 1971 Variations in the stability of precipitated ferric oxyhydroxides. Nonequilibrium Systems in Natural Water Chemistry. Am. Chem. Soc. Advances in Chemistry Series 106, Am. Chem. Soc., Washington, DC. p. 209–234.

Levy, D.B., Custis, K.H., Casey, W.H., Rock, P.A., 1997. The aqueous geochemistry of the abandoned Spenceville Cu Pit, Nevada, County, California. J. Environ. Qual. 26, 233–243.

Lind, C.J., 1988. Hausmannite (Mn_3O_4) conversion to manganite (γ-MnOOH) in dilute oxalate solution. Environ. Sci. Technol. 22, 62–70.

Maest, A.S., Pasilis, S.P., Miller, L.G., Nordstrom, D.K., 1992. Redox chemistry of arsenic and iron in Mono Lake, California, USA. In: Proceedings of Tailings & Mine Waste '92. Balkema, Rotterdam, pp. 507–511.

Martiínez, C.E., McBride, M.B., 1998. Solubility of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} in aged coprecipitates with amorphous iron hydroxides. Environ. Sci. Technol. 32, 743–748.

Mcdonald, M.S. 1993 Water Quality in Open Pit Precious Metal Mines. M.S. Thesis, University of Nevada, Reno, Nevada, 75pp.

McKnight, D.M., Kimball, B.A., Bencala, K.E., 1988. Iron photoreduction and oxidation in an acidic mountain stream. Science 240, 637–640.

Merrill, D.T., Manzione, M.A., Peterson, J.J., Parker, D.S., Hobbs, A.O., 1986. Field evaluation of arsenic and selenium removal by iron coprecipitation. J. Water. Pollut. Control Fed. 58, 18–26.

Miller, G.C., Lyons, W.B., Davis, A., 1996. Understanding the water quality of pit lakes. Env. Sci. Technol. 30, 118A–123A.

Moffett, J.W., Zika, R.G., 1983. Oxidation kinetics of Cu(I) in seawater: Implications for its existence in the marine environment. Marine Chem. 13, 239–251.

Moffett, J.W., Zika, R.G., 1987. Reaction kinetics of hydrogen peroxide with copper and iron in seawater. Environ. Sci. Technol. 21, 804–810.

Nordstrom, D.K., 1982. The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K. Geochim. Cosmochim. Acta 46, 681–692.

Nordstrom, D.K., Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters. Science 232, 54–56.

Nordstrom, D.K., Jenne, E.A., Ball, J.W., 1979. Redox equilibria of iron in acid mine waters. In: Jenne, E.A. (Ed.), Chemical Modeling in Aqueous Systems, Am. Chem. Soc. Symp. Ser. 93. Am. Chem. Society, Washington, DC, pp. 51–79.

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, E., May, H.M., Jones, B.F., Parkhurst, D.L., 1990. Revised chemical equilibrium data for major water-mineral reactions and their limitations. In: Melchior, D.C., Bassett, R.L. (Eds.), Chemical Modeling of Aqueous Systems II, Am. Chem. Soc. Symp. Ser. 416. Am. Chem. Society, Washington, DC, pp. 398–413.

Norvell, W.A., Lindsay, W.L., 1982. Estimation of the concentration of Fe^{3+} and the $(Fe^{3+})(OH^{-})^3$ ion product from equilibria of EDTA in soil. Soil Sci. Soc. Am. J. 46, 710–715.

Nriagu, J.O., 1974. Lead orthophosphates—IV. Formation and stability in the environment. Geochim. Cosmochim. Acta 38, 887–895.

Parc, S., Nahon, D., Tardy, Y., Viellard, P., 1989. Estimated solubility products and fields of stability for cryptomelane, nsutite, birnessite, and lithiophorite based on lateritic weathering sequences. Am. Mineral 74, 466–475.

Parkhurst, D.L., 1995. User's Guide to PHREEQC—A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations, Water-Resources Investigations Report 95-4227. U.S. Geological Survey, Lakewood, Colorado.

Pillard, D.A., Runnells, D.D., Doyle, T.A., Young, J., 1995. Post-mining pit lakes: Predicting lake chemistry and assessing ecological risks. In: Tailings & Mine Waste '96. Balkema, Rotterdam, pp. 469–478.

Price, J.G., Shevenell, L., Henry, C.D., Rigby, J.G., Christensen, L.G., Lechler, P.J., Desilets, M.O., 1995. Water Quality at Inactive and Abandoned Mines in Nevada, Open-File Rep. 95-4. Nevada Bureau of Mines and Geology, University of Nevada, Reno, Nevada.

Santillan-Medrano, J., Jurinak, J.J., 1975. The chemistry of lead and cadmium in soil. Soil Sci. Soc. Am. Proc. 39, 851–856.

SEPC, 1990. Environmental Monitoring Investigation of the Flooded "D" Pit at Cluff Lake. Saskatchewan Environment and Public Safety, Saskatchewan, April, 1990.

Seiler, R.L., Ekechukwu, G.A., Hallock, R.J., 1993. Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in and near Humboldt Wildlife Management Area, Churchill and Pershing Counties, Nevada, 1990-91, Water Res. Invest. Rep. 93-4071. U.S. Geol. Surv., Carson City, Nevada.

Suarez, D.L., 1983. Calcite supersaturation and precipitation kinetics in the Lower Colorado River, All-American Canal and East Highline Canal. Water Resource Res. 19, 653–661.

Sullivan, P.J., Yelton, J.L., Reddy, K.J., 1988. Solubility relationships of aluminum and iron minerals associated with acid mine drainage. Environ. Geol. Water Sci. 11, 83–287.

Sullivan, T.J., Christophersen, N., Muniz, I.P., Seip, H.M., Sullivan, P.D., 1986. Aqueous aluminum chemistry response to episodic increases in discharge. Nature 323, 324–327.

Tones, P.I., 1982. Limnological and Fisheries Investigations of the Flooded Open Pit at the Gunnar Uranium Mine. Saskatchewan Research Council.

Van Breeman, N., 1973. Dissolved aluminum in acid sulfate soils and in acid mine water. Soil Sci. Soc. Am. Proc. 37, 694–697.

Vandersluis, G.D., Straskraba, V., Effner, S.A., 1995. Hydrogeological and geochemical aspects of lakes forming in abandoned open pit mines. In: Proc. Water Resources at Risk, May 14-18. Am. Inst. Hydrology, Denver, Colorado, pp. 162–177.

Waite, T.D., 1986. Photoredox chemistry of colloidal metal oxides. In: Davis, J.A., Hayes, K.F. (Eds.), Geochemical Processes at Mineral Surfaces, Am. Chem. Soc. Symp. Ser. 323. Am. Chem. Society, Washington, DC, pp. 426–445.

Wehrli, B., Sulzberger, B., Stumm, W., 1989. Redox processes catalyzed by hydrous oxide surfaces. Chem. Geol. 78, 167–179.

White, W.B., Scheetz, B.E., Silsbee, M.R., 1998. Interactions of aqueous metal silicates with mine water. In: Proc. 5th Int. Conf. Tailings and Mine Waste '98. Balkema, Rotterdam, pp. 589–598.

Whitehead, H.C., Feth, J.H., 1961. Recent chemical analyses of waters from several closed-basin lakes and their tributaries in the western United States. Geol. Soc. Am. Bull. 72, 1421–1425.

Zhang, P., Ryan, J.A., 1999a. Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite. Environ. Sci. Technol. 33, 618–624.

Zhang, P., Ryan, J.A., 1999b. Transformation of Pb(II) from cerrusite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH. Environ. Sci. Technol. 33, 625–630.