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Predicting the effects of evapoconcentration on water quality in mine pit lakes

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Abstract

For mine pit lakes that are hydrologic sinks, evapoconcentration can be an important process affecting long-term water quality. Based on the concept of chemical divides, pit lakes may be categorized according to the ratio of Ca to alkalinity. Lakes with $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$ can be expected to evolve to alkaline pH, Na–HCO_3–CO_3–($\pm SO_4$)–($\pm$Cl)-dominated solutions. Most predictions of long-term chemistry for pit lakes fall into this first category. Lakes with $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$ will to evolve to near-neutral pH, Ca–Na–($\pm SO_4$)–($\pm$Cl)-dominated solutions. Most existing pit lakes fall into the second category. This comparison suggests that the models used for predicting long-term pit lake chemistry may overestimate rates of alkalinity-generating processes. The distinction between the two evapoconcentration pathways is important for predicting the concentrations of trace constituents, such as As and Se, that are often chemicals of concern for eco-risk assessments. Pit lakes falling into the first category can reach pH > 9, at which anionic As and Se species are not adsorbed, hence accumulate in solution over time. Pit lakes falling into the second category remain at near-neutral pH, under which most of the anionic As and Se species are adsorbed, hence do not accumulate in solution. Observations of solute compositions in existing pit lakes combined with consideration of evapoconcentration pathways in natural lakes can provide useful analogies for understanding the long-term chemical evolution of pit lakes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: geochemistry; mining; water; model; prediction

1. Introduction

A boom in gold mining in the United States in recent years has been driven by improvements in hydrometallurgical technologies for extracting gold from low-grade ores. Depending on various factors that affect the economics of mining, gold can be economically recovered from ore grades as low as 0.01 ounces/ton by heap leaching methods (NBMG, 1989). In most cases, excavation of the huge tonnages required for the extraction of gold from low-grade ores is done by open-pit mining methods. Additionally, the mining of low-grade copper ores from porphyry deposits has often required the excavation of open pits.

To mine ore deposits located beneath the water table, pumping wells or sumps must be used to dewater the rocks located around the pit. After mining is completed and the dewatering systems are shut down, the water table will eventually recover to a level near its pre-mining elevation. As a result, the open pits will become lakes. In Nevada alone, there are over 30 gold and copper mines where pit lakes have formed or will form sometime in the future af-

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ter mine closures (Miller et al., 1996). Lakes formed by infilling of open-pit mines also exist in other mining districts throughout the world, where large, low-grade ore have been mined.

Generally, if a pit lake is expected to form after mine closure, then a prediction of its future water quality must be conducted as part of an Environmental Impact Statement (EIS) associated with new mine permitting, expansion, and closure. The period for predictions may vary according to the time required for infilling of the pit lake, but can range up to hundreds of years. However, few pit lakes have been in existence long enough to allow a valid comparison of geochemical predictions to monitoring data over extended periods of time. Additionally, although the types of different geochemical processes that potentially affect water quality are generally known (e.g., sulfide mineral oxidation, acid buffering by carbonate minerals, ground water composition, secondary mineral solubility, ionic adsorption, evapoconcentration, etc.), the relative importance of each process during the evolution of the pit lake is not well understood and modeling procedures for making long-term predictions are still being developed (Bird et al., 1994; Pillard et al., 1995; Davis and Eary, 1996; Miller et al., 1996).

The purpose of this paper is twofold: (1) to describe the effects of evapoconcentration on water quality in alkaline pit lakes using the concepts developed to explain the geochemical evolution of natural lakes of the western United States, and (2) to develop procedures for modeling the effects of evapoconcentration in predictions of pit lake chemical compositions. Evapoconcentration is an important process that affects the chemical compositions of lakes located in hydrologically closed basins, where the primary means for water loss is evaporation. Many natural lakes of the western United States have undergone evapoconcentration for thousands of years, and may provide reasonable analogues for the long-term chemical evolution of mining pit lakes that are located in hydrologically closed basins.

2. Pit-lake water-quality characteristics

At many mines, the primary environmental concern is the generation of acid rock drainage. Acid rock drainage results from the oxidation of exposures of sulfide minerals, primarily pyrite and marcasite, located in mine pit walls and waste rock. At mines with an absence or paucity of acid-buffering capacity, the generation of acid mine drainage can produce elevated metal concentrations in ground water and surface water. At most mines, carbonates (calcite and dolomite) are the most effective acid-buffering agents, although the hydrolysis of mafic silicates may also partially mitigate acid generation

The environmental concern of acid rock drainage in pit lakes is exemplified by the Berkeley Pit in Montana (Davis and Ashenberg, 1989) and Spenceville Pit in California (Levy et al., 1997), which show elevated concentrations of most cationic metals compared to neutral to alkaline pit lakes (Fig. 1). This trend is predictable from solubility and adsorption characteristics of most cationic metals. The major metals, such as Al, Fe, and Mn, show nearly linear relationships between logarithmic concentrations and pH reflective of the amphoteric solubilities of their respective oxyhydroxide solids (Fig. 1a). The concentrations of minor cationic metals, such as Cd, Cu, and Zn, also show general trends of increased concentrations in the pit lakes with acidic pH values (Fig. 1b). The pH dependence for these metal solutes is in part a function of increased solubilities of oxyhydroxide solids under acidic conditions and in part a reflection of the decreasing tendency of cationic metals to adsorb to oxyhydroxide surfaces in solutions with pH less than about 6 to 7 (Dzomback and Morel, 1990).

In Nevada, where much of the current mining activity is located, acid rock drainage and potential creation of acidic pit lakes are environmental problems at only a small fraction of known mining locales (Price et al., 1995). Many of the low-grade gold deposits actively being mined, such as those in the Carlin Trend, are hosted in predominantly sedimentary rocks including carbonate units and carbonate-cemented clastic units (Bagby and Berger, 1985; Sillitoe and Bonham, 1990). The acid-buffering capacities of the carbonates in the wallrocks in many of these deposits effectively limit the degree of acidification potentially generated by sulfide mineral oxidation, resulting in neutral to alkaline pit lakes. Because of the common occurrence of carbonate rocks, the majority of existing pit lakes in Nevada are alkaline (Fig. 2).

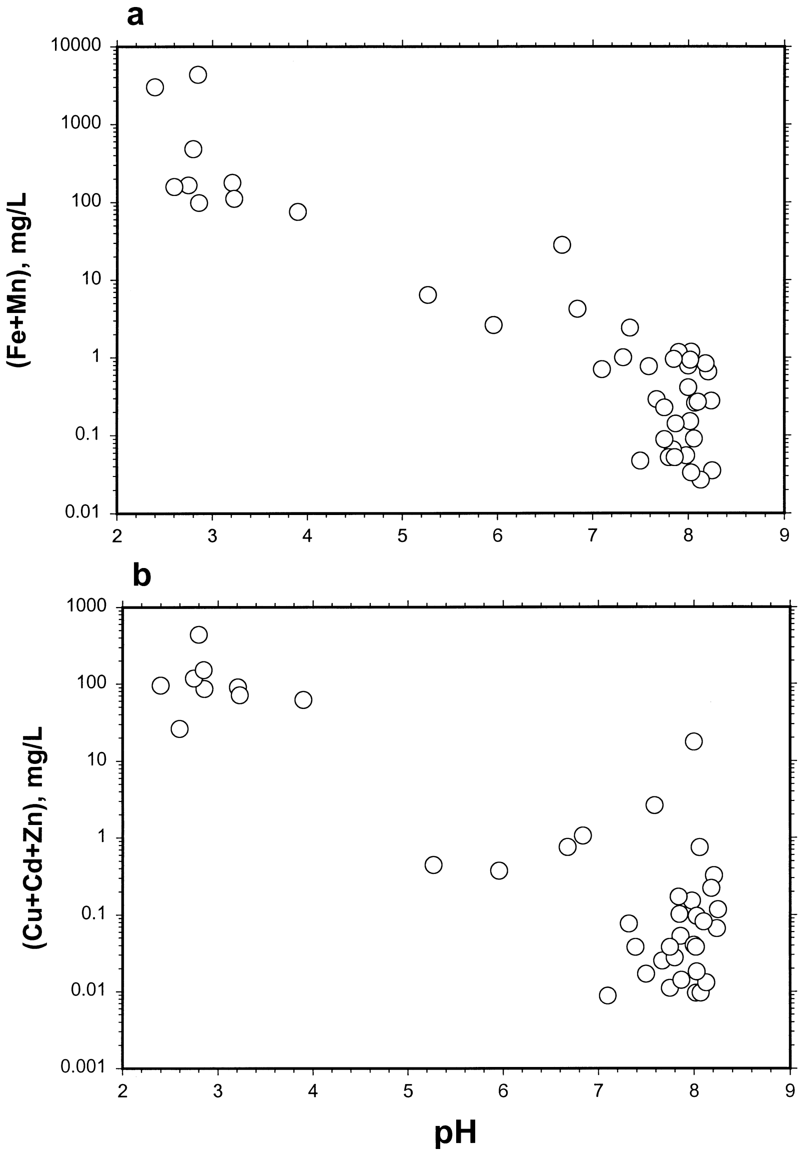

Fig. 1. Summed concentrations of metals observed for existing pit lakes, including: (a) Fe + Mn, and (b) Cd + Cu + Zn. A total of 42 analyses from 18 pit lakes. Sources: Davis and Ashenberg (1989), McDonald (1993), Bird et al. (1994), Price et al. (1995), Miller et al. (1996), Levy et al. (1997).

Under alkaline pH conditions, the concentrations of cationic metals are generally very low because of solubility and adsorption controls (Fig. 1). However, a different set of solutes, primarily As and Se, can potentially become an environmental concern under alkaline pH conditions when combined with the effects of evapoconcentration. Arsenic is commonly present in disseminated gold deposits as arsenopyrite associated with iron sulfides or as limited solid–solution substitutes in the iron sulfides (Arehart et al., 1993). Small amounts of As sulfides, realgar and orpiment, may also exist in some deposits in association with other sulfides. Selenium may also exist as impurities in Fe sulfides or as Fe selenides in sulfide ore deposits (Howard, 1977), although it is generally less abundant than in As in disseminated gold deposits in Nevada.

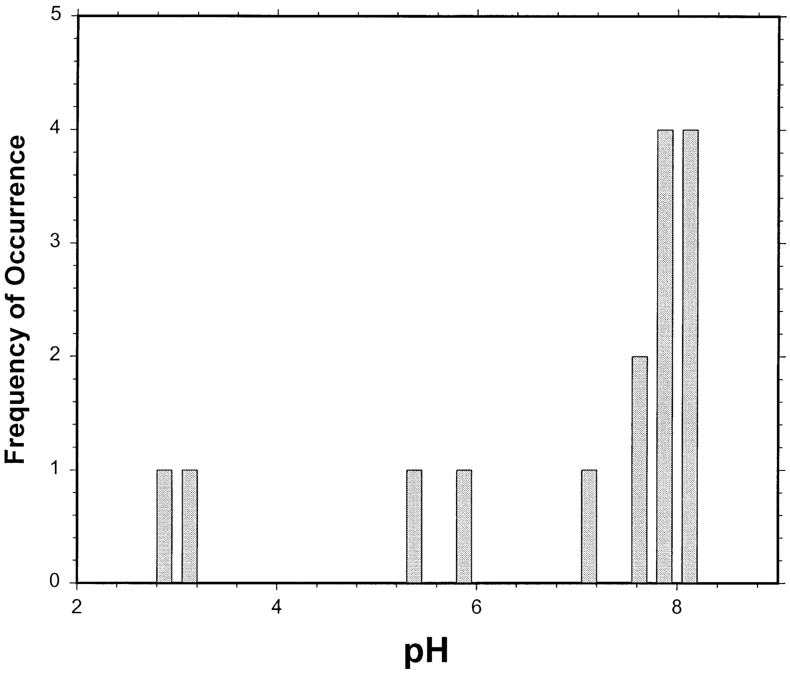

Fig. 2. Frequency of occurrence of pH reported for pit lakes in Nevada. Source: Price et al. (1995).

Under alkaline and oxidizing conditions, the As and Se released from the dissolution of iron sulfides will exist predominantly as anionic species (e.g., $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}, $HSeO_4^-$, and SeO_4^{2-}). These anions do not form any sparingly soluble solids. Also, they are generally not strongly adsorbed to mineral surfaces under alkaline pH conditions (Dzomback and Morel, 1990). As a result, dissolved As and Se may accumulate in pit lakes from continued oxidative dissolution of iron sulfides present in the wallrocks of the pits and evaporation.

The lack of attenuation processes for As and Se can be seen in a number lakes of the western United States that are located in hydrologically closed basins (Fig. 3). Continuous evapoconcentration of these lakes over long periods has produced alkaline pH conditions and elevated As and Se concentrations. Alkaline pit lakes generally show a trend that is consistent with the naturally alkaline lakes with increasingly elevated concentrations of As and Se for $pH > 7.5$. In both natural and pit lakes, Se is greatly subordinate to As in concentration, probably reflecting their relative abundance in the sulfide minerals in the pit wallrocks. In general, pit lakes have not been in existence long enough to become as alkaline or as high in total solute concentration as natural lakes through evapoconcentration processes (Fig. 3). However, pit lakes probably receive higher influx rates of As and Se from the oxidation of sulfidic rocks exposed in the pit wallrocks than natural lakes, which receive solutes primarily from the weathering of surficial deposits.

3. Evapoconcentration paths for pit lakes

The trends reported for metal concentrations in existing pit lakes (Figs. 1 and 3) underscore the importance of correctly representing the processes that affect the solution pH in making predictions of the chemical compositions of future pit lake. In pit lakes situated in sulfide-poor rocks, evapoconcentration processes can be expected to exert a major influence on the pH.

The effects of evapoconcentration for controlling water compositions have been well developed by Garrels and MacKenzie (1967) and Eugster and Hardie (1978). These effects are based on the concept of ‘chemical divides’ which describes how a solution composition changes as a result of the pre-

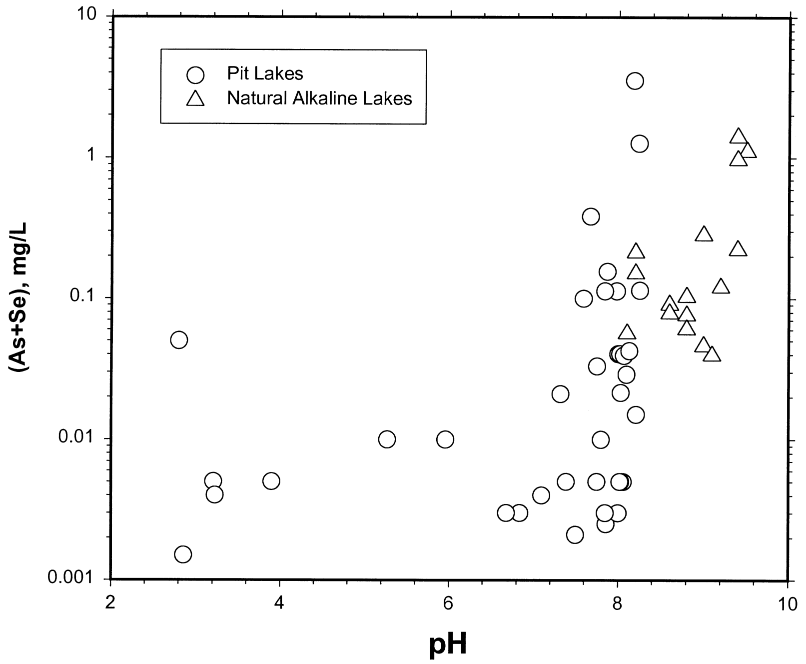

Fig. 3. Summed concentrations of As and Se observed for existing pit lakes and in naturally alkaline lakes of the western United States. Total of 38 analyses from 18 pit lakes and 19 analyses from 10 natural lakes. Pit lake sources: Davis and Ashenberg (1989), McDonald (1993), Bird et al. (1994), Price et al. (1995), Miller et al. (1996), Levy et al. (1997). Natural lake sources: Maest et al. (1992), Seiler et al. (1993), Davis and Eary (1996).

cipitation of binary salts. The concept is nicely stated by Drever (1982) as follows: "... whenever a binary salt is precipitated during evaporation, and the effective ratio of the two ions in the salt is different from the ratio of the concentrations of these ions in solution, further evaporation will result in an increase in the concentration of the ion present in greater relative concentration in solution and a decrease in the concentration of the ion present in lower relative concentration." The concept of chemical divides has provided a fundamental framework for describing how evapoconcentration processes control the chemical evolution of natural lakes located in hydrologically closed basins (Eugster and Hardie, 1978). Some pit lakes can be expected to be hydrologic sinks and will evapoconcentrate over time. Hence, the concept of chemical divides is relevant for conceptualizing the major geochemical processes that may affect the long-term evolution of pit lakes.

For most neutral to alkaline solutions that have predominantly carbonate alkalinity, evaporation initially increases the concentrations of all solutes. This increase will continue until the solubility of calcite is reached. In a system at equilibrium with atmospheric $CO_2(g)$, calcite precipitation is generally the first chemical divide that is encountered during evapoconcentration (Drever, 1982), i.e.:

$$Ca_{2+} + 2HCO_3^- = CaCO_3 + CO_2(g) + H_2O \qquad (1)$$

In an evaporating solution at calcite saturation, the concentrations of Ca and carbonate alkalinity and pH will remain approximately constant as the rate of calcite precipitation keeps up with the rate of evapoconcentration. Under the same conditions, Mg may act similarly to Ca and be removed from solution by coprecipitation with calcite or precipitation of hydrated Mg-carbonates or Mg-silicates (Garrels and MacKenzie, 1967).

Following the above axiom from Drever (1982), if the solution had the original condition of $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$, where $m_{\mathrm{alkalinity}}$ refers to carbonate alkalinity in equivalents $(m_{\mathrm{HCO_3}} + 2m_{\mathrm{CO_3}})$, then with continued evaporation, calcite precipitation will effectively remove nearly all Ca from solution, leaving behind excess carbonate alkalinity. After the Ca concentration has been reduced to the extent that calcite formation ceases, the concentrations of carbonate alkalinity will continue to increase in concentration with more evaporation. Other soluble ions (e.g., Na, Cl, SO_4) will also increase as direct functions of evapoconcentration until very high ionic strengths are reached. The end result is a highly alkaline, Na–HCO_3–CO_3–(±SO_4)–(±Cl) solution. These types of solutions are represented by a number of alkaline lakes in the western U.S. that have undergone evapoconcentration for thousands of years (e.g., Mono Lake, California; Pyramid Lake, Nevada; Abert Lake, Oregon; Winnemucca Lake, Nevada; Eugster and Hardie, 1978; Drever, 1982).

For the case of $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$, calcite precipitation will continue until the carbonate alkalinity is reduced to the point that calcite precipitation stops. After that, Ca will continue to increase in concentration along with other soluble ions with continued evaporation until the solubility limit of another Ca mineral is reached. Most commonly, the next Ca mineral that reaches saturation is gypsum. The end result of this evaporation pathway is a near-neutral, Na–Ca–SO_4–(±Cl) solution (Eugster and Hardie, 1978; Drever, 1982).

There are numerous other possible chemical subdivides that can occur, depending on the original chemical composition (Eugster and Hardie, 1978). Yet, based on the preceding discussion, it is clear that the effect of evapoconcentration on the long-term pH of a pit lake can be categorized most simply according to the following criteria:

if $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}} \rightarrow$ alkaline pH conditions are predicted;
if $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}} \rightarrow$ near-neutral pH conditions are predicted.

An examination of the concentrations of Ca and carbonate alkalinity in existing pit lakes indicates that the majority fall into the second category with $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$ (Fig. 4). A notable exception is the Cortez Pit lake which falls below the line for $2m_{\mathrm{Ca}} = m_{\mathrm{alkalinity}}$ shown in Fig. 4. According to these data and the concept of chemical divides, most of the existing pit lakes would be expected to evolve to near-neutral (pH = 7 to 8) solutions with major solute concentrations dominated by Ca, Na, SO_4, (±Cl), eventually reaching saturation with gypsum after some period of evapoconcentration. This hypothesis is consistent with the fact that most ore deposits contain sulfide minerals whose dissolution upon exposure to air produces Ca–SO_4-dominated solutions after neutralization by reactions with carbonate host rocks.

In contrast to the above observations for existing pit lakes, most of the chemical compositions that have been predicted for future pit lakes indicate that they have been modeled to follow the first category evapoconcentration pathway of $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$ (Fig. 4). These predictions have been conducted as part of recent EIS studies directed at issues related to the permitting of open-pit mines, where pit lakes are expected to form after closure. The evapoconcentration pathway selected for these future pit lakes has yielded predictions of alkaline (up to pH = 9.5), Na–HCO_3–CO_3–(±SO_4)–(±Cl) solutions. These predictions are inconsistent with the chemical compositions of most existing pit lakes (Fig. 4), and expected weathering reactions of sulfide minerals in carbonate host rocks. It is possible that some future pit lakes will be similar in hydrogeochemical characteristics to the Cortez Pit, which has a composition consistent with $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$. Alternatively, the models that have been used to predict future pit lake chemistry prospective pit lake may overestimate the amount of alkalinity generation in their representations of acid/base reactions at the expense of sulfate release. Another possibility is that constraints of proton balance in geochemical models may not have been fully implemented. In any case, evidence from most existing pit lakes in Nevada suggests that most would be expected to evolve to near-neutral, Ca–Na–SO_4–(±Cl)-dominated solutions rather than the alkaline Na–HCO_3–CO_3–(±SO_4)–(±Cl) solutions that have been predicted in recent studies.

4. Predicting long-term pit lake compositions: two examples

The above discussion of chemical divides and evapoconcentration paths has important implications for predictions of water quality in future pit lakes. This importance arises primarily from the differences in major solute composition and extent of

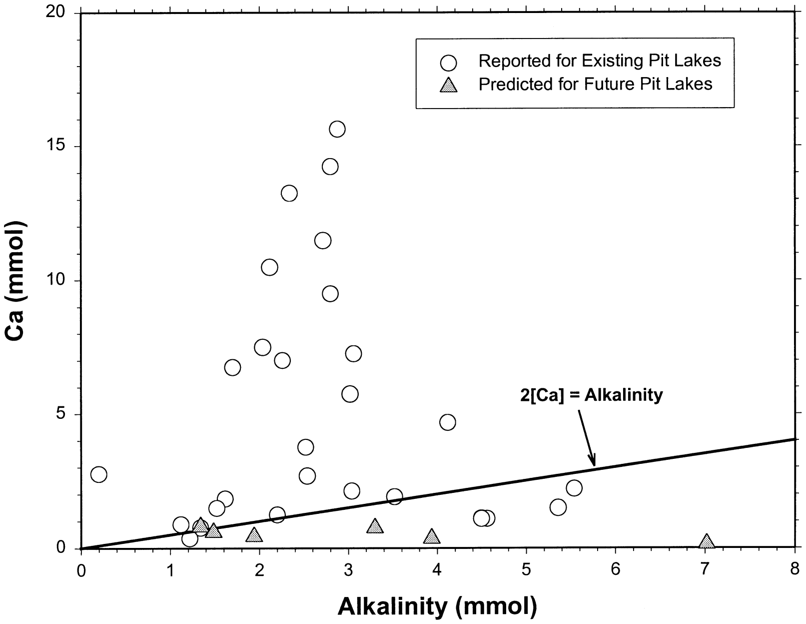

Fig. 4. Categorization of pit lakes according to the criteria of $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$ or $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$. Total of 38 analyses from 18 pit lakes and 8 predictions for 5 future pit lakes. Existing pit lake sources: Davis and Ashenberg (1989), McDonald (1993), Bird et al. (1994), Price et al. (1995), Miller et al. (1996), Levy et al. (1997). Prediction sources: PTI (1992, 1994, 1995, 1996), Cortez FEIS (1995), Kirk et al. (1996).

adsorption of As and Se (and other metals) that can result depending on which evapoconcentration path is followed. Arsenic and Se are emphasized in this discussion because they are often solutes of potential environmental concern with respect to risk assessment issues.

To illustrate the importance of the starting composition on the future chemical composition of a pit lake that would be predicted with a numerical model, the effects of evapoconcentration of two pit lakes were modeled with the PHREEQC geochemical model (Parkhurst, 1995). The two pit lakes that were examined include the Cortez Pit lake and Yerington Pit lake, both located in Nevada.

4.1. Pit lake compositions

The Cortez Pit lake is located in north-central Nevada. It was a Carlin-type gold deposit that was mined from 1968 to 1982. The pit walls of the Cortez Pit lake are comprised primarily of the Roberts Mountain Limestone and the ore was mostly oxide. The pit lake has very good water quality (Table 1) and supports a population of fish. The solute balance of the Cortez Pit lake places it in the category of $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$ (Table 1), indicating that it would be expected to evolve to an alkaline, Na–HCO_3–CO_3–($\pm SO_4$)–($\pm$Cl)-dominated solution with evapoconcentration.

The Yerington Pit lake is located in western Nevada. It was a porphyry copper deposit that was mined from 1950s to 1978. The Yerington Pit lake also has good water quality (Table 1). Its major solute composition places it in the category of $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$, indicating that it would be expected to evolve to a near-neutral Ca–Na–SO_4–($\pm$Cl)-dominated solution with evapoconcentration.

4.2. Modeling procedures

The water compositions for the two pit lakes shown in Table 1 were used as starting points for modeling the effects of evapoconcentration with PHREEQC. PHREEQC can be used to simulate the effects of evapoconcentration by the stepwise removal of water from a hypothetical 1-kg starting solution (Parkhurst, 1995). After each step, the composition of the solution is recalculated given

Table 1
Initial concentration for the Cortez and Yerington Pit lakes and modeling constraints included in the evapoconcentration simulations

	Cortez Pit lake	Yerington Pit lake
pH	8.07	8.02
Ca (mg/l)	43.5 (2.17 mmol)	86.9 (4.34 mmol)
Mg (mg/l)	17.8	15
K (mg/l)	11.3	5.3
Na (mg/l)	72.2	71.8
SO_4 (mg/l)	84.7	272
Cl (mg/l)	26.5	33.2
F (mg/l)	1.76	1.3
Alkalinity (mg/l as $CaCO_3$)	226 (3.52 mmol HCO_3)	193 (3.86 mmol HCO_3)
Fe (mg/l)	0.1	0.1
As (mg/l)	0.060 (0.050 [a])	0.004 (0.050 [a])
Se (mg/l)	<0.005 (0.050 [a])	0.11 (0.050 [a])
log CO_2(g), atm	−2.64 (−2.65 [a])	−2.67 (−2.65 [a])
log O_2(g), atm	−0.7 [a]	−0.7 [a]
Initial calcite SI [b]	0.63 (0.0 [a])	0.77 (0.0 [a])
Solubility controls	calcite, sepiolite, chalcedony, gypsum, ferric hydroxide, hydromagnesite	

Source: Price et al. (1995)

[a] Concentration used in evapoconcentration simulations.

[b] Saturation index (SI) = $\log([Ca^{+2}][CO_3^{-2}]/K_{eq})$ where K_{eq} is the solubility product for calcite.

the amount of water removed, which represents a concentration factor.

Equilibrium modeling of the initial compositions of the lake water indicated that both were oversaturated with calcite and CO_2(g) relative to the atmospheric level at $10^{-3.5}$ atm (Table 1). In the first step of the simulations of evapoconcentration, the solutions were forced to be in exact equilibrium with calcite solubility. Because the solutions were oversaturated with calcite, this constraint produced a small decrease in the pH. The partial pressure of CO_2(g) was fixed at $10^{-2.65}$ atm, similar to that determined for the initial solution compositions. The O_2(g) partial pressure was fixed at the atmosphere level so that aerobic conditions were maintained throughout the model runs.

Analytical data for silica were not available for the pit lakes, hence the initial solutions were assumed to be in equilibrium with chalcedony. Solubility-controlling phases that were used in the simulations included calcite, sepiolite, gypsum, ferric hydroxide, and hydromagnesite. If the solutions became saturated with any of these minerals as a result of simulated evapoconcentration, then the solutions were forced to be in equilibrium with the appropriate solubility product. The same constraints were used in simulating the effects of evapoconcentration for both pit lakes so that each was conducted under similar states of equilibrium with respect to the carbonate–water system, making differences in resulting chemical compositions easier to discern and interpret.

Additionally, the lakes were assumed to be oxygenated. Hence, As was specified to be arsenate [As(+5)], Se to be selenate [Se(+6)], and all dissolved sulfur to be sulfate. For purposes of illustrating the modeling, the initial concentrations of arsenate and selenate for both lakes were arbitrarily set at 0.05 mg/l, which is the drinking water standard for both solutes, so that the effects of evapoconcentration on these solutes could be directly compared.

The adsorption of solutes was also included in the modeling using ferric hydroxide as the primary substrate with a concentration of 5 mg/l. This concentration is an estimate of the amount of suspended ferric hydroxide that may be present in the pit lakes. Standard surface properties, defined by Dzomback and Morel (1990) (i.e., surface area = 600 m^2/g, strong binding sites = 5×10^{-3} mol/mol $Fe(OH)_3$, weak binding sites = 2×10^{-1} mol/mol $Fe(OH)_3$), were used to represent the surface properties of the ferric hydroxide. Ferric hydroxide is a common alteration product of the oxidation of iron sulfides exposed in the wall rocks of pit lakes, and is often the most important adsorption substrate in many aqueous systems (Dzomback and Morel, 1990; McLean and Bledsoe, 1992). Also, the adsorption characteristics of ferric hydroxide have been studied for a variety of solutes, and surface complexation constants that are descriptive of solute adsorption to ferric hydroxide have been parameterized by Dzomback and Morel (1990), allowing them to be incorporated into geochemical models, such as PHREEQC. These factors make ferric hydroxide a reasonable choice for representing the extent to which solutes may be removed from solution by adsorption reactions, although other minerals, such as clays, carbonates, and silicates, may also serve as substrates for solute adsorption in pit lakes.

4.3. Modeling results

Results of the evapoconcentration modeling of the Cortez Pit lake composition show approximately linear increases in SO_4 and Cl with the concentration factor (Fig. 5a). Sodium and K are not shown but are similar to Cl. These solutes are not predicted to be incorporated into any solid phases for the range of concentration factors simulated, hence they increase as direct functions of the concentration factor. The simulated Ca concentrations show a decrease with evapoconcentration, whereas HCO_3 increases. The initial solution was saturated with calcite, hence for each incremental increase in the concentration factor, calcite is precipitated, removing Ca from solution. The solution, however, contains an excess of carbonate alkalinity (mostly HCO_3) over Ca, resulting in a net increase in alkalinity with each incremental increase in the concentration factor. Magnesium concentrations initially increase until states of saturation with sepiolite and hydromagnesite are reached, and thereafter decreases slightly. The pH increases fairly steadily from about 8.0 to 9.3 over the range in concentration factors used in the simulation. These observations are consistent with that expected for an initial solution with $2m_{\text{Ca}} < m_{\text{alkalinity}}$. The net result of evapoconcentration of the Cortez Pit lake is an alkaline, Na–HCO_3–CO_3–SO_4–Cl-dominated solution (Fig. 5a).

For the Yerington Pit lake, the simulated results show continual increases in SO_4 and Cl with concentration factor (Fig. 5b). Sodium and K are not shown but are similar to Cl. The Mg concentration is also predicted to increase, although saturation with sepiolite is eventually reached at the highest concentration factors. The simulations also show a moderate increase in the Ca concentration until saturation with gypsum is reached. Thereafter, the predicted Ca concentration is approximately constant. The concentration of carbonate alkalinity is predicted to remain constant while calcite saturation is maintained up to a concentration factor of about 20. At higher factors, the simulated carbonate alkalinity increases gradually because saturation with gypsum is reached. The removal of SO_4 by gypsum formation requires that more CO_2(g) must be dissolved to form HCO_3 and maintain charge balance. The predicted pH remains approximately constant at about 7.6 to 7.8 throughout the simulation in contrast to the increase to 9.4 predicted for the Cortez Pit lake water. The net result of the evapoconcentration of the Yerington Pit lake is a near-neutral pH, Ca–Na–SO_4–Cl-dominated solution, consistent with its categorization as having $2m_{\text{Ca}} > m_{\text{alkalinity}}$ (Fig. 5b).

For the Cortez Pit lake, the concentrations of As(+5) and Se(+6) are predicted to increase as direct functions of the evapoconcentration factor (Fig. 6a) because neither of these components is precipitated or adsorbed. However, for the Yerington Pit lake, selenate increases with evapoconcentration whereas arsenate remains approximately constant (Fig. 6b). The difference in the behavior of As(+5) between the two lakes is a reflection of the adsorption characteristics of As(+5) to ferric hydroxide as a function of pH. The predicted adsorption of As(+5) to ferric hydroxide reaches a maximum at pH = 7.0 and decreases sharply over the pH range of 7.5 to 8.5, reaching near zero percent adsorption at pH = 9.0 (Fig. 7a), so that As(+5) is not adsorbed from the Cortez Pit water.

In contrast, for the Yerington Pit water, the pH is predicted to remain relatively constant at 7.6 to 7.8 with evapoconcentration. Under these conditions, As(+5) is continually removed from solution by adsorption and remains near the initial concentration of 0.05 mg/l even at high evapoconcentration factors (Fig. 6b). Although not considered in the model simulations for the pit lakes, which were run for oxidizing conditions, the adsorption of arsenite [As(+3)] shows a behavior similar to As(+5) but the decrease

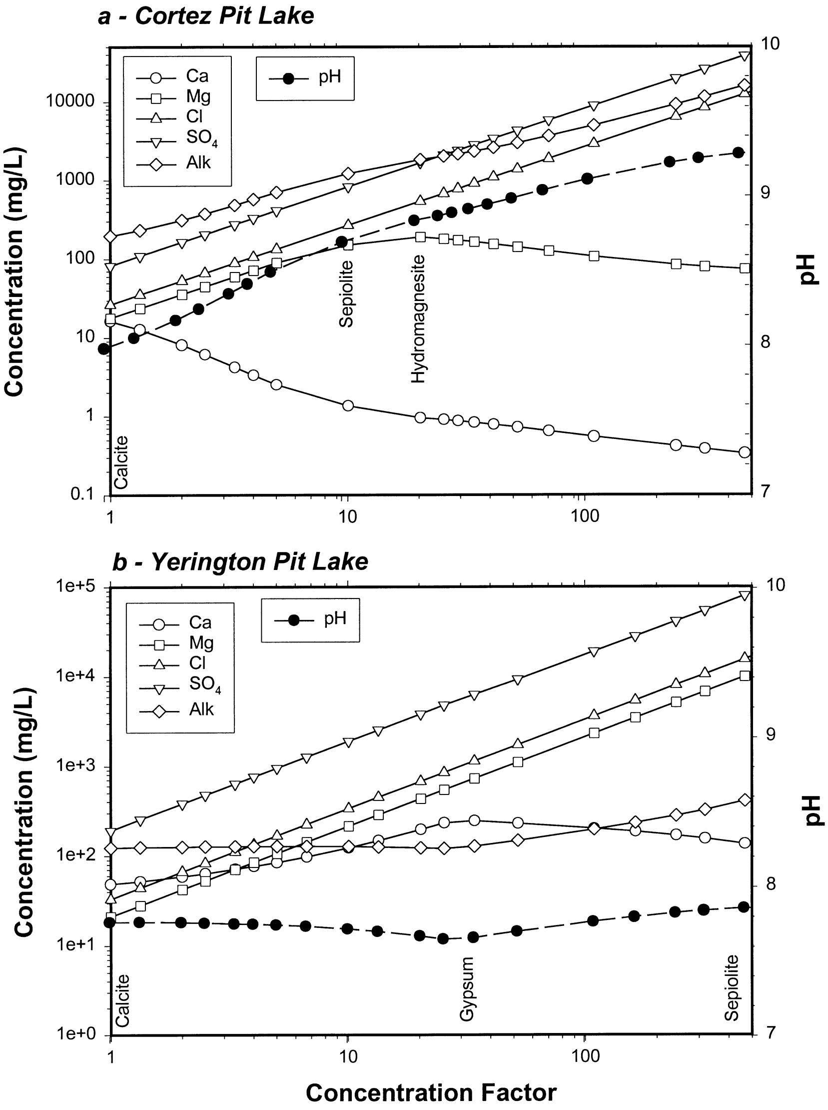

Fig. 5. Effects of evapoconcentration on major solutes predicted with PHREEQC for: (a) the Cortez Pit Lake ($2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$); (b) the Yerington Pit Lake ($2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$).

in adsorption is displaced to higher pH (Fig. 7a). Consequently, if As were present as As(+3), then it would also be expected to be removed from solution by adsorption even in the evapoconcentrated Cortez Pit water.

Selenate [Se(+6)] also shows a decreasing degree of adsorption to ferric hydroxide with increasing pH, and is generally not adsorbed over the pH range expected for alkaline pit lakes (Fig. 7b). Selenate adsorption is also strongly dependent on the competing sulfate concentrations and is substantially decreased when sulfate concentrations are greater than about 85 mg/l. Because of these adsorption characteristics, Se(+6) concentrations in alkaline pit lakes can be expected to increase as a function of evapoconcentration as was predicted for the Cortez and Yerington Pit lakes. In contrast to selenate, selenite [Se(+4)] adsorption shows similarities to As(+3) and is maximized at pH 7 to 9, decreasing sharply at higher pH (Fig. 7b). The pit lake simulations were run

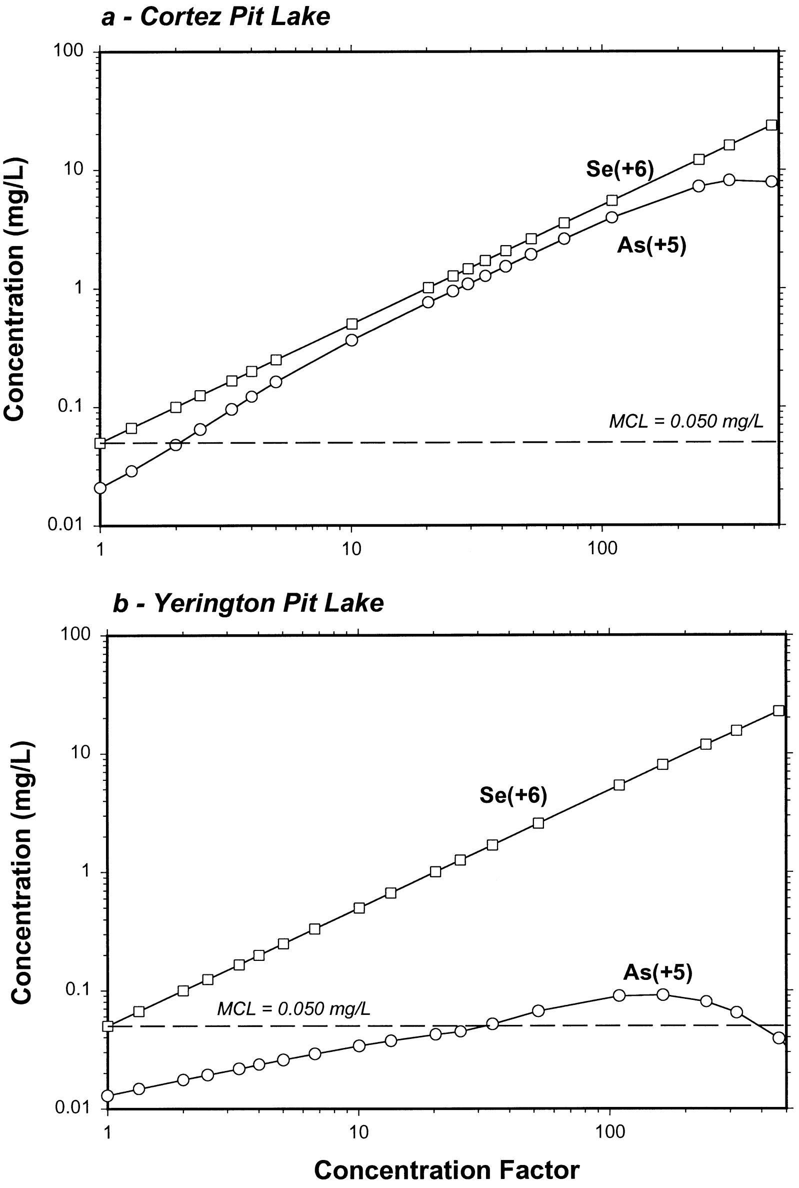

Fig. 6. Effects of evapoconcentration on As and Se predicted with PHREEQC for: (a) the Cortez Pit Lake ($2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$); (b) the Yerington Pit Lake ($2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$).

for oxidizing conditions with Se present as Se(+6). However, the adsorption characteristics indicate that if Se is present as Se(+4) in pit lakes, then it is likely to be adsorbed, analogous to the As species. The adsorption characteristics in combination with the simulation results indicate that analytical information on the oxidation states of As and Se can provide critical information for correctly predicting their tendency to accumulate in solution with evapoconcentration or be removed from solution by adsorption processes.

5. Conclusions

Metal concentrations in existing pit lakes show trends that are consistent with their known solubility

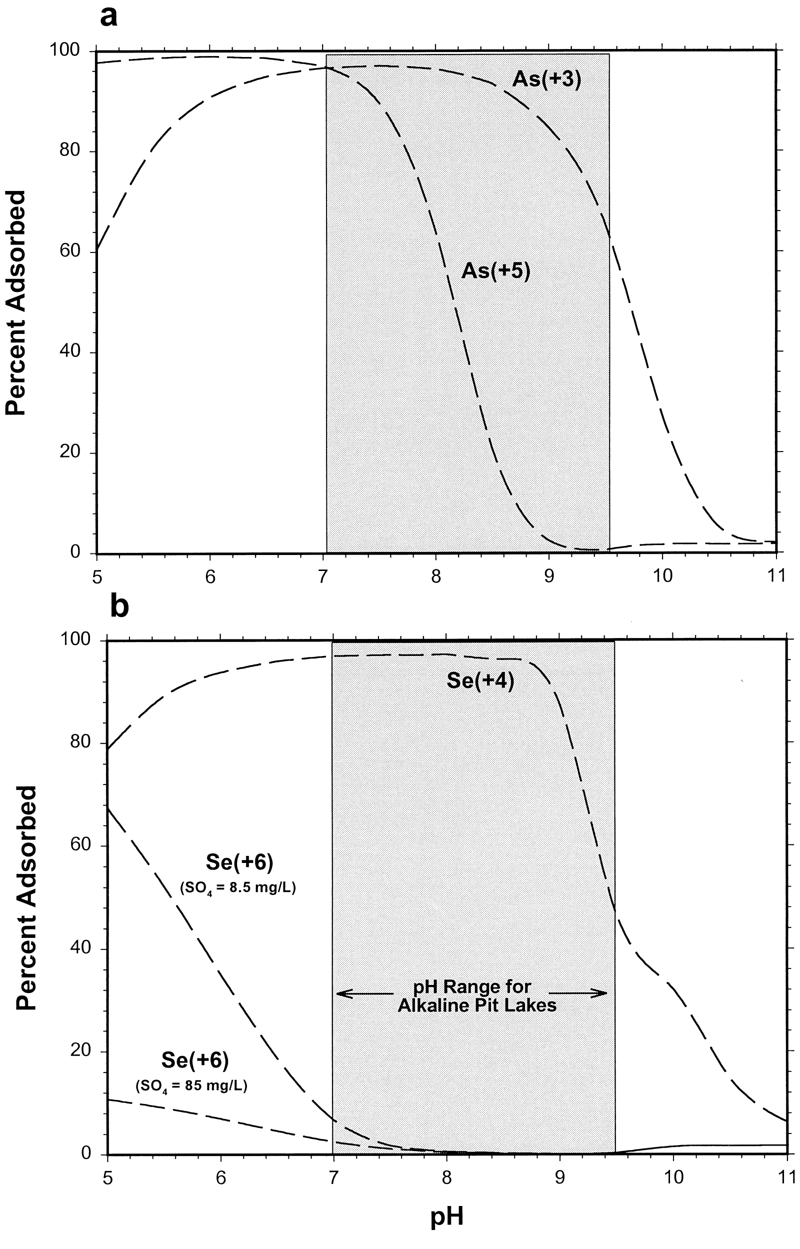

Fig. 7. Adsorption curves for: (a) As species; (b) Se species calculated with the PHREEQC model for 5 mg/l $Fe(OH)_3$, standard surface properties (Dzomback and Morel, 1990), 0.050 mg/l As and Se, and Cortez Pit lake water composition (see Table 1).

and adsorption characteristics. Cationic heavy metals generally reach higher concentrations in acidic pit lakes and decrease to near-analytical detection levels in most neutral to alkaline pit lakes. Conversely, concentrations of anionic metals are generally most elevated in alkaline pit lakes; a trend that is consistent with that observed for natural alkaline lakes of the western United States that have undergone evapoconcentration.

The concept of chemical divides that has been developed to explain the chemical evolution of natural lakes provides a useful means to categorize pit lakes. Lakes with $2m_{\mathrm{Ca}} < m_{\mathrm{alkalinity}}$ can be expected to evolve to alkaline pH, Na–HCO_3–CO_3–($\pm SO_4$)–($\pm$Cl)-dominated solutions with evaporation. The Cortez Pit lake and many natural lakes fall in this category. Alternatively, lakes with $2m_{\mathrm{Ca}} > m_{\mathrm{alkalinity}}$ can be expected to evolve to near-neutral pH, Ca–Na–SO_4–($\pm$Cl)-dominated solutions with evaporation. The Yerington Pit lake and most other existing pit lakes fall into this second category. However, most predictions of water quality for future pit lakes that have been conducted as part of recent EIS studies for permitting of mines in Nevada indicate evapoconcentration paths consistent with the first category.

The distinction between the two different evapoconcentration paths is important for making predictions of future pit lake quality because it defines which geochemical processes will be used to model the effects of evapoconcentration. Each of the two evapoconcentration pathways described in this paper leads to different trends in major solute concentrations and pH, which in turn, determines the extent to which As and Se (and other metals) are adsorbed. These factors make the correct depiction of evapoconcentration processes critical for predicting the future water quality of pit lakes from the perspective of obtaining realistic results and providing fundamental data to the risk assessment process.

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