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Geochemistry of Concentrated Waters at Mine Waste Sites

By:

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Abstract:

The oxidation of sulfide minerals at mine sites leads to the release of high concentrations of dissolved SO_4, H^+ and metals to drainage waters. At some sites, the concentrations of these constituents can reach very high levels, beyond the range of accuracy of conventional geochemical modelling approaches. Over the past four decades geochemical speciation/mass transfer models have been widely used for delineation of geochemical processes in natural systems and at waste sites. These models have been continually expanded and refined and now cover a variety of geochemical reactions, including precipitation-dissolution, oxidation-reduction, adsorption-desorption, cation exchange, and metal complexation. The majority of geochemical models use relatively simple methods to calculate activity coefficients and rely on the use of ion-pairs to account for deviations from ideality. These models are generally limited to calculating geochemical relations for relatively fresh waters. Introduction of the Pitzer ion-interaction method of estimating activity coefficients allowed the extension of geochemical models to a much broader range of concentrations and compositions. There is a need to calculate mineral solubility relations and ion activities for concentrated mine drainage waters. The Pitzer theory is well suited to these problems. A summary of recent developments of the Pitzer ion interaction model for application to mine waste sites is provided.

NWRI RESEARCH SUMMARY

Plain language title

Predicting metal release from highly contaminated mine waste sites

What is the problem and what do sicentists already know about it?

The weathering of sulfide minerals contained in mine wastes leads to the release of acid and metals to the environment. In some cases, these releases can continue for many decades to centuries. Computer models have been applied widely over the last several decades to predict contaminant releases from mine waste sites. At a subset of sites, exceedingly high concentrations of dissolved metals can develop in porewaters and groundwater associated with the waste piles. At these sites, conventional computer models fail because of the very high concentrations, and predictions of metal release can be erroneous.

Why did NWRI do this study?

Sites that have highly concentrated porewaters have the greatest potential to leach elevated concentrations of metals to the environment. Yet modelling tools for these sites are in the least evolved state of development. This study provides a summary of current modelling tools, and provides several example applications of applying specialized models to these highly contaminated sites.

What were the results?

For the major contaminants at mine sites, including iron, sulfate and acid, model predictions are in good agreement with field observations. For trace contaminants the predictions are either not available or are in poor agreement. Trace contaminants, however, can be highly toxic. Model improvements to include the trace contaminants are therefore recommended.

How will these results be used?

The results can be used to improve predictions of acid and metal release from highly contaminated mine sites over the long-term. The results can also be used to assist in the design of remedial systems for these sites.

Who were our main partners in the study?

University of Waterloo.

Géochimie des eaux d'exhaure concentrées aux sites d'entreposage de déchets miniers

Carol J. Ptacek et David W. Blowes

Résumé

Dans les mines, l'oxydation de minéraux sulfurés entraîne la libération de concentrations élevées de SO_4, de H^+ et de métaux dissous dans les eaux de drainage. Sur certains sites, la concentration de ces éléments peut atteindre des valeurs très élevées dépassant l'intervalle d'exactitude des méthodes conventionnelles de modélisation géochimique. Depuis quatre décennies, des modèles de spéciation géochimique-transfert de masse ont été souvent utilisés pour mettre en évidence les processus géochimiques à l'œuvre dans les systèmes naturels et sur les sites d'entreposage de déchets miniers. Ces modèles sont sans cesse développés et perfectionnés et portent maintenant sur une variété de réactions géochimiques, notamment la précipitation-dissolution, l'oxydo-réduction, l'adsorption-désorption, l'échange cationique et la formation de complexes métalliques. La plupart des modèles géochimiques font intervenir des méthodes relativement simples pour le calcul des coefficients d'activité et reposent sur l'utilisation de paires d'ions pour expliquer les écarts par rapport aux valeurs idéales. Ces modèles sont généralement limités au calcul des relations géochimiques pour les eaux relativement douces. L'introduction de la méthode d'interactions ioniques de Pitzer pour l'estimation des coefficients d'activité permet d'étendre les modèles géochimiques à un plus grand intervalle de concentrations et à une plus grande variété de compositions. Le calcul des relations de solubilité des minéraux et des activités ioniques pour les eaux d'exhaure concentrées est nécessaire. La théorie de Pitzer s'applique bien à ces problèmes. Nous résumons les récents progrès de l'application du modèle d'interaction ionique de Pitzer aux sites de déchets miniers.

Sommaire des recherches de l'INRE

Titre en langage clair

Prédiction de la libération de métaux par les sites de résidus miniers hautement contaminés

Quel est le problème et que savent les chercheurs à ce sujet?

L'altération des minéraux sulfurés contenus dans les résidus miniers libère des acides et des métaux dans l'environnement. Dans certains cas, cette libération peut s'échelonner sur de nombreuses décennies, voire des siècles. Au cours des dernières décennies, on a largement eu recours à des modèles informatiques pour prédire la libération de contaminants par les sites de résidus miniers. Dans un sous-ensemble de dépôts, les eaux interstitielles et les eaux souterraines associées aux haldes de résidus peuvent renfermer des concentrations anormalement élevées de métaux dissous. À ces endroits, les modèles informatiques classiques n'ont pas été concluants en raison des très fortes concentrations en cause, et les prédictions de la libération des métaux peuvent être erronées.

Pourquoi l'INRE a-t-il effectué cette étude?

Les sites où les eaux interstitielles sont très concentrées sont les plus susceptibles de lessiver des concentrations élevées de métaux dans l'environnement. Toutefois, les outils de modélisation de ces sites en sont aux stades de mise au point initiaux. La présente étude résume les outils de modélisation existants et fournit plusieurs exemples d'applications de modèles spécialisés à ces sites hautement contaminés.

Quels sont les résultats?

Pour les principaux contaminants des sites miniers, dont le fer, les sulfates et l'acide, les prédictions des modèles concordent avec les observations sur le terrain. Pour les contaminants à l'état de traces, les prédictions sont soit inexistantes, soit contradictoires. Toutefois, les contaminants à l'état de traces peuvent être très toxiques. Il est donc recommandé de raffiner le modèle afin d'inclure ces contaminants.

Comment ces résultats seront-ils utilisés?

Les résultats peuvent servir à améliorer les prédictions de la libération à long terme d'acides et de métaux par les sites miniers hautement contaminés. Ils peuvent également faciliter la conception de systèmes d'assainissement propres à ces sites.

Quels étaient nos principaux partenaires dans cette étude?

Université de Waterloo.

Geochemistry of Concentrated Waters at Mine Waste Sites

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1. Introduction

The oxidation of sulfide minerals at mine sites leads to the release of high concentrations of dissolved SO_4, H^+ and metals to drainage waters. At some sites, the concentrations of these constituents can reach very high levels, beyond the range of accuracy of conventional geochemical modelling approaches (e.g. Blowes et al., 1991; Nordstrom and Alpers, 1999; Nordstrom et al., 2000, Frau, 2000). Over the past four decades geochemical speciation/mass transfer models have been widely used for delineation of geochemical processes in natural systems and at waste sites. These models have been continually expanded and refined and now cover a variety of geochemical reactions, including precipitation-dissolution, oxidation-reduction, adsorption-desorption, cation exchange, and metal complexation. The majority of geochemical models use relatively simple methods to calculate activity coefficients and rely on the use of ion-pairs to account for deviations from ideality. These models are generally limited to calculating geochemical relations for relatively fresh waters.

Approximately two decades ago, the Pitzer ion-interaction method of estimating activity coefficients was applied to a geochemical system (Harvie and Weare, 1980). The introduction of this method allowed the extension of geochemical models to a much broader range of concentrations and compositions. There is a need to calculate mineral solubility relations and ion activities for concentrated mine drainage waters. The Pitzer theory is well suited to these problems.

Application of geochemical models to natural and contaminated systems requires a well-formulated model, thermodynamic data and input data, and field measurements. Deficiencies in model databases and field measurements have been, and continue to be, the primary shortcoming when using geochemical models to interpret or infer geochemical processes. Several recent additions to the model input data have improved the capability of the ion interaction model to predict mineral solubilities and ion activities at mine sites. This chapter describes these improvements.

1. 1. Occurrence of concentrated drainage waters

Excavation of ore and metal extraction processes increases the exposure of sulfide minerals. These sulfide minerals can oxidize, through abiotic and biotic pathways, leading to the release of elevated concentrations of SO_4^{2-}, H^+ and dissolved metals to drainage waters. The oxidation of pyrite, one of the most common sulfide minerals, leads to the release of Fe(II), SO_4^{2-} and acid:

$$FeS_{2(s)} + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

The Fe(II) released can be further oxidized to Fe(III):

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \qquad (2)$$

The Fe(III) can also oxidize pyrite, producing Fe(II):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (3)$$

The above reactions are described in detail in Chapters ?, ? and ? by Blowes et al. (this volume), Jambor (this volume) and Nordstrom (this volume). Depending on the degree of Fe(II) oxidation, a variety of Fe-bearing secondary solids can form (Jambor, this volume). Examples of these Fe-bearing secondary minerals are Fe(II) sulfate salts such as melanterite and its dehydration products, mixed Fe(II)-Fe(III) sulfate minerals such as copiapite, or oxidized Fe(III) oxide, hydroxide and sulfate-bearing solids (Jambor, this volume).

Pyrite can contain metal impurities, and elevated concentrations of these metals can be released as a result of pyrite oxidation. In addition to pyrite, a wide variety of other sulfide and metal-bearing minerals are present at mine sites. These minerals can oxidize or dissolve under the acidic conditions that prevail at many mine sites. If these low-pH metal-rich waters contact country-rock minerals, acid-neutralization rocks will occur, resulting in the attenuation of some dissolved species, and the addition of others to drainage waters. The composition of drainage waters, therefore, can be highly variable both in terms of relative concentrations and total concentrations. At sites that contain an abundance of sulfide minerals and at sites with a high potential for evaporation, the oxidation of sulfide minerals can result in the generation of drainage waters that are highly concentrated, containing in excess of 100,000 mg/L of dissolved solids. For example, drainage waters at the Richmond mine contain > 700,000 mg/L SO_4, >100,000 mg/L Fe and high concentrations of Cu (>4000 mg/L), Zn (>23,000 mg/L), As (>300 mg/L) and other dissolved constituents (Nordstrom et al., 2000). At the Heath Steele mine in New Brunswick, pore waters extracted from the vadose and saturated zone of a weathered tailings impoundment contained to 85,000 mg/L SO_4, up to 48,000 mg/L Fe and high concentrations of Zn, Pb and Cu (up to 3690, 10 and 70 mg/L, respectively; Blowes et al., 1991). At the Sherridon mine in northern Manitoba, pore waters in the tailings contain > 250,000 mg/L SO_4, > 80,000 mg/L Fe, > 50,000 mg/L Zn, > 5000 mg/L Al, > 1500 mg/L Cu, and high concentrations of As and other metals (Moncur et al., 2003). At the Brunswick Mines No. 6 open pit mine, St. Arnaud and Aiken (1991) describe groundwater in the vicinity of the open pit mine which contains very high concentrations of Zn (>3000 mg/L), Fe (> 7000 mg/L) and SO_4 (>25,000 mg/L).

The above examples illustrate the large range in composition that can be observed, and the exceedingly high concentrations of dissolved metals that can be maintained in solution. The occurrence of very high concentrations of dissolved metals is attributed to increased rates of sulfide oxidation due to the increased surface area of sulfide minerals exposed in mine workings and mine wastes, especially mill tailings, and the effect of evaporation in natural arid regions or in response to high temperatures generated by sulfide-oxidation reactions. Mine workings have rough wall surfaces and can be particularly prone to increased aeration and concentrated drainage waters (Figure 1). The reactive surface area of pit mine walls has been estimated to be 27 to 161 times that of an ideal, smooth two-dimensional surface, due to the increased roughness of pit wall surfaces and fractures penetrating into the rock walls (MEND, 1995). Mill tailings are typically ground to < 25 μm to 1 mm in size, leading to substantial increases in the surface area available for reaction (Blowes et al., 2003). Concentrated pore waters are present in tailings pore waters, often near the zone of active oxidation (Figure 2). Mines located in arid regions are prone to evaporation, and concentration of dissolved constituents (Figure 3). The oxidation of sulfide minerals is an exothermic process, leading to the generation of heat in mine workings and waste pore spaces. This heat promotes further evaporation, leading to even greater increases in solute concentrations. Temperatures as high as 47 °C were observed in the Richmond underground workings (Nordstrom et al., 2000). Harries and Ritchie (1985) report temperatures as high as 50 °C within the Rum Jungle waste rock pile.

Sites with concentrated waters have been documented in a range of climatic settings. Some of the highest concentrations of dissolved solids have been reported for northern California (Nordstrom et al., 2000) and southern Italy (Frau, 2000), relatively warm and arid climates; but also for northern Canada in the subarctic (Moncur et al., 2003) and eastern Canada in a temperate zone (Blowes et al., 1991).

Sites with extreme concentrations often contribute the greatest to the degradation of groundwater and surface waters (Nordstrom and Alpers, 1999). Discharge of even a modest volume of water from these sites can lead to large total mass loadings because of the extreme concentrations. It is prudent, therefore, to develop modelling approaches which provide accurate predictions of geochemical processes leading to these high concentrations and processes that provide maximum limits on the concentrations. These models are fundamental tools that can be used for predicting the release of metals from mine sites, and for developing effective remediation strategies.

1. 2. Modelling approaches for concentrated waters

A geochemical model requires a theoretically sound mathematical formulation for calculating ion-activity coefficients, acid-base reactions, oxidation-reduction reactions and solid, liquid and gas-phase mass transfer to effectively predict natural geochemical processes. In addition, thermodynamic data bases for use with the models require comprehensive sets of constants for all components in solution, including ion-association and complexation constants, mineral-solubility constants, gas-phase partitioning constants and accurate constants for use with the activity correction equations for all ions and neutral species.

Geochemical speciation models were first developed in the 1960s (Garrels and Thompson, 1965) and have been continually improved over the last four decades. The earliest geochemical models were based on the ion-pair modelling approach and had limited data bases. Over time, the capabilities of geochemical models expanded, as did the model data bases. Early geochemical models such as MINEQL (Westall et al., 1976) and PHREEQE (Parkhurst et al., 1985) used the ion-association model for actiivty correction. This model relies on the use of ion-pair constants, acid-base constants, and mineral solubility data, together with simple activity correction equations such as the extended Debye Hückel equation or the Davies equation. These geochemical models provide excellent predictions of acid/base, oxidation/reduction and mineral precipitation/dissolution reactions for waters that have ionic strengths of < 0.5? (Parkhurst, 1990).

Mine drainage waters typically contain elevated concentrations of SO_4, Fe(II), Fe(III), H^+, and lesser amounts of Ca, Mg, and trace metals. It was soon recognized that these models were limited for application to acid-mine drainage settings, and improvements to the models were made for these settings For example, Ball and Nordstrom (1987), developed the geochemical speciation model (WATEQ4F) that is well suited to application to mine drainage settings. WATEQ4F includes complexation and ion-pair constants that account for associations between Fe(II), Fe(III), SO_4 and HSO_4, and used extended forms of the Debye Hückel equation to account for longer-range interactions. These additions led to improved predictions of mineral solubilities and ion-activities for mine drainage waters. These constants have been added to other data bases, such as that of MINTEQA2 (Allison et al., 1990), resulting in even greater improvements in predictive modelling at mine sites with moderate concentrations of dissolved solids (*e.g.*, Blowes and Jambor, 1990).

At mine sites with higher concentrations of dissolved solids, the choice of models is more limited. In the 1980's, models based on Pitzer ion-interaction equations for predicting ion activities were developed for application to saline lakes and groundwater (Harvie and Weare, 1980; Harvie et al., 1982, 1984). This model was incorporated into the geochemical computer code PHRQPITZ (Plummer et al., 1988) making the Pitzer modelling approach widely available to the geochemical community. PHRQPITZ, however, was not developed for application to mine drainage sites. Efforts have been made to expand the PHRQPITZ data base for application to mine drainage settings, as described in Ptacek and Blowes (2000). The expanded model now provides estimates of activity coefficients for a wider range of dissolved metals commonly observed at mine sites. This chapter summarizes the state of development of the Pitzer based models and describes recent applications of the Pitzer model to concentrated mine drainage sites.

1. 3. Solids associated with concentrated mine waters

The oxidation of sulfide minerals leads to the formation of a series of secondary solids, ranging from insoluble to highly soluble phases (Jambor, this volume). At sites where low concentrations of sulfide-oxidation products are present in mine waters, insoluble phases (*e.g.*, ferrihydrite and goethite) and moderately soluble phases (*e.g.* jarosite and gypsum), can precipitate. At sites where very high concentrations of sulfide oxidation products are released, saturation of the water with respect to highly soluble phases (*e.g.*, melanterite) can be attained, and these phases precipitate. At most sites with highly concentrated mine drainage waters, pyrite or pyrrhotite are present in very large volumes. Oxidation of these sulfide minerals leads to the release of Fe and SO_4 and H^+. Other sulfides are typically present in lesser amounts, therefore oxidation of these sulfides contributes to the dissolved solids, but are generally present as a minor portion of the total dissolved solids. The secondary solids that precipitate from these waters are often dominated by highly soluble iron- and sulfate-bearing secondary solids. The water in contact with these soluble solids may, therefore, contain elevated concentrations of only a few constituents (*e.g.* Fe and SO_4 from 10,000s to 100,000s mg/L). Other constituents often are present in lower concentrations due to lower solubility limits and/or a stronger affinity for adsorption sites. Contact between rain or snowmelt waters with the most soluble phases leads to their dissolution, increasing dissolved-phase concentrations. The initial model development requires accurate prediction of the highly soluble phases commonly encountered at sites with extreme concentrations.

2. Model Development

2. 1. Fundamentals of Pitzer ion-interaction models

The Pitzer ion-interaction theory of activity correction (Pitzer, 1973, 1991) has been applied to a variety of natural geochemical settings (*e.g.*, Harvie et al., 1984; Monnin and

Schott 1984; Felmy and Weare, 1986; Langmuir and Melchior, 1985, Spencer et al., 1990; Clegg and Whitfield, 1991; Monnin and Ramboz, 1996) and mine waste sites (Blowes et al., 1991; Ptacek and Blowes, 1994, 2000; Nordstrom et al., 2000). These applications involve equations for estimating activity coefficients of dissolved species, together with relations representing partitioning between solid and gaseous phases. For a simple equilibrium reaction, using a metal sulfate salt as an example:

$$MeSO_{4(s)} \Leftrightarrow Me^{2+} + SO_4^{2-} \qquad (4)$$

a mass expression can be written as:

$$K_{sp} = a_{Me^{2+}} a_{SO_4^{2-}} = m_{Me^{2+}} m_{SO_4^{2-}} \gamma_{Me^{2+}} \gamma_{SO_4^{2-}} \qquad (5)$$

where a represents the activity, m the single-ion molality (mol/kg solvent) and ☎ the single-ion activity coefficient. According to equation 5, calculation of the concentration of a single species $m_{Me^{2+}}$ in equilibrium with a solid phase requires estimates of m_{SO4}, ☎$_{Me2+}$ and ☎$_{SO4}$. Values of ☎, which depend strongly on the solution composition and concentration, are calculated using the Pitzer ion-interaction theory. These estimates are combined with general equations representing mineral solubilities, oxidation/reduction, gas-phase partitioning and solution equilibria. The development of specific models based on the Pitzer theory to predict mineral solubility in natural waters requires ion interaction parameters and mineral free energy data compiled in an internally consistent manner (Ptacek and Blowes, 2000).

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Estimates of ☎ are made using the following equations:

$$\ln\gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \psi_{Mca}\right)$$

$$+ \sum_{a<} \sum_{a'} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \qquad (6)$$

and

$$\ln\gamma_X = z_X^2 F + \sum_c m_c(2B_{cX} + ZC_{cX}) + \sum_a m_a(2\Phi_{Xa} + \sum_c m_c \psi_{Xac})$$

$$+ \sum_{c<}\sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} \qquad (7)$$

where the subscripts M, c, and c' represent cations, X, a, and a' represent anions. The summation index c represents the sum over all cations in the system, the double summation $c < c'$ represents the sum over all distinguishable pairs of dissimilar cations. Similar definitions for a and $a < a'$ apply for anions in the system. The quantity F includes the Debye-Hückel term. These and additional parameters are fully defined elsewhere (Harvie et al., 1984; Plummer et al., 1988)

Data required to apply equations 6 and 7 are acquired from statistical fits of solution behaviour for the dominant cations, anions, neutral species in solution. The terms ♋$^{(0)}$, ♋$^{(1)}$, ♋$^{(2)}$ and C*, which are included in the variables B and C in equations 6 and 7 are determined from statistical fits of experimental data, usually osmotic coefficient data for binary salt solutions. The parameters ●*, to describe cation-cation and anion-anion interactions, and ☼ to describe cation-cation-anion, and anion-anion-cation interactions are obtained from solutions containing more complex mixtures of electrolytes.

Geochemical applications of the Pitzer theory have relied mainly on the original model formulation of Harvie and Weare (1980) and Harvie et al. (1984) to model geochemical reactions in the Na-K-Mg-Ca-SO_4-Cl-CO_2-H_2O system. The Harvie et al. (1984) database was incorporated into the geochemical computer code PHRQPITZ (Plummer et al. 1988). Applications of PHRQPITZ typically involve calculation of mineral saturations and reaction pathways using the titration or reaction options of the computer code. The degree of saturation is expressed as a saturation index, *SI*, usually defined as $SI = log\ IAP - log\ K$, where $SI = 0$ represents equilibrium conditions, $SI < 0$ undersaturated conditions, and $SI > 0$ supersaturated conditions. To calculate saturation indices, the solubility constant *K* is usually corrected for deviation in temperature from standard conditions, and *IAP* is calculated using temperature corrected constants.

2. 2. Expansion of model databases for mine drainage applications

The Pitzer theory has been applied to interpret geochemical conditions in natural water systems, including evaporation of sea water or continental river waters. Application of the Pitzer theory to mine drainage problems involved expansion of the databases to represent geochemical processes in metal-sulfate solutions covering a range in pH from hyperacidic to neutral in pH.

Calculations of reaction pathways and chemical equilibria in systems containing elevated concentrations of acid are important for a variety of chemical systems. Ion-interaction parameters have been reported for a range of metal-sulfate solutions for predicting solution properties in encountered in manufacturing and ore extraction processes (*e.g.*, Paige et al. 1992, 1998; Schuiling and van Gaans 1997), in studies of the geochemistry of mine drainage waters (*e.g.*, Blowes et al. 1991; Ptacek and Blowes 1994; Ridley et al. 1997, 1999; Nordstrom and Alpers 1999; Nordstrom et al. 2000), and in studies of acid sulfate aerosols associated with highly evaporative conditions (e.g., Clegg et al. 1998). Although ion interaction coefficients for use in Pitzer models have been developed for these specific applications, much of the information is directly transferable among these systems or to other unrelated systems.

The aqueous properties of H_2SO_4 using Pitzer's equations were first represented by assuming complete dissociation of H_2SO_4. Later, the inclusion of the bisulfate species HSO_4^- improved the predictions for this system to concentrations up to 6 m H_2SO_4 (e.g., Reardon and Beckie 1987). Hovey et al. (1993) and Clegg et al. (1994) introduced a mole fraction-based version of the ion interaction equations and introduced an ionic-strength dependent third virial coefficient which further improved predictions in the H_2SO_4 system. Hachimi et al. (1996) derived parameters for the H_2SO_4 system between 0 and 27 mol kg^{-1}.

Ion-interaction parameters for the $FeSO_4$-H_2SO_4-H_2O between 0 and 90 °C are available for H_2SO_4 concentrations up to 6 m, together with solubility products for melanterite ($FeSO_4 \cdot 7H_2O$) and szomolnokite ($FeSO_4 \cdot H_2O$) (Reardon and Beckie, 1986). Parameters for the system $NiSO_4$-H_2SO_4-H_2O, together with solubility isotherms for three hydrates of $NiSO_4$, are provided at 25 °C and up to 6 m H_2SO_4 (Reardon, 1989). Baes et al. (1993) describe parameters for the $CuSO_4$-H_2SO_4-H_2O at 25 °C, Baes et al. (1993) and solubility relations for $CuSO_4 \cdot 5H_2O$ versus H_2SO_4 up to a concentration of 6 m H_2SO_4.

In a series of papers focusing on application to the processing of uranium ore, Paige et al. (1992, 1998) evaluated solution equilibria in the systems $PbSO_4$-H_2SO_4-H_2O, $PbSO_4$-Na_2SO_4-H_2O, $BaSO_4$-H_2SO_4-H_2O and $RaSO_4$-H_2SO_4-H_2O. Concentrations of H_2SO_4 ranged between 0 and 6.19 mol kg^{-1}. The parameterization by Paige et al. relied on that of the H_2SO_4 system by Reardon and Beckie (1987). In this case, a HSO_4^- species was incorporated into the data analysis, but ion pairs were not.

Hovey et al. (1993) described the thermodynamics of $Na_2SO_4(aq)$ between 0 and 100 °C for mixtures containing H_2SO_4 and Na_2SO_4. Hovey et al. (1993) included new experimental data for this system, and modelled data presented by Rard (1992). The analysis by Hovey et al. (1993) explicitly considered the formation of the HSO_4^- species, and provided a molarity-based analysis to 6 m and a molality-based analysis to 15 m. Archer and Rard (1998), Rard (1997) and Rard and Clegg (1999) provided experimental data and analysis with the Pitzer model for $MgSO_4$ mixtures, including H_2SO_4 at 298 K. Their analysis included the formation of a $MgSO_4^0$ ion pair, and the HSO_4^- species. Solubility curves for $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 5H_2O$, and $MgSO_4 \cdot H_2O$ as a function of H_2SO_4 concentration were provided.

Reardon (1988) expanded the concentration range for the binary parameters for Al-SO_4 mixing, from which an $Al_2(SO_4)_3 \cdot 17H_2O$ solubility product was obtained. Reardon (1988) provided solubility isotherms for mixing in the ternary systems between $Al_2(SO_4)_3$ and $CuSO_4$, $FeSO_4$, $MgSO_4$, $NiSO_4$, or $CaSO_4$.

Ion interaction parameters were summarized for a series of metal sulfate salts by Pabalan and Pitzer (1991), including sulfate solubility in the aqueous ternary mixtures Na-Li-SO_4, Na-Cu-SO_4, Na-Ni-SO_4, Na-Co-SO_4, Na-Mn-SO_4, Cu-Li-SO_4, Ni-Li-SO_4, Fe(II)-Li-SO_4, Co-Cl-SO_4, Ni-Cl-SO_4, Mg-Cd-SO_4, Al-Mg-SO_4, and Al-Fe(II)-SO_4 at 25 °C. Pabalan and Pitzer (1991) also provided solubility relations in the quaternary mixtures Na-Li-Cu-SO_4 and Na-Co-Cl-SO_4 at 25 °C, and enthalpy and other thermal data for the crystalline phases.

Ion interaction parameters and solubility products for mixing in the ternary systems Fe(II)-Na-SO_4 and Fe(II)-Cl-SO_4 were evaluated by Ptacek (1992). Also evaluated were the solubility products for melanterite, mirabilite, and a mixed Fe,Na hydrated sulfate phase at other temperatures.

In a study to evaluate the effect of carbonate neutralization reactions in mine drainage settings, Ptacek (1992) describes interaction parameters for the system Fe(II)-Na-SO_4-Cl-CO_2-H_2O, including solubility relations for siderite as a function of P_{CO2} and a range in salt concentration to melanterite, halite and mirabilite saturation. In this study new parameters were derived and added to the original database of Harvie et al. (1984).

Christov (1999) summarized solubility data for a study which included measurements in the system K-Ni-SO_4 and K-Cu-SO_4. The study described previously determined Pitzer parameters for the binary systems $NiSO_{4(aq)}$ and $CuSO_{4(aq)}$, and solubility products were calculated for K_2SO_4, $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, and the double salts $K_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ and $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$. Christov also determined the free energy of mixing for $K_2SO_4(Ni,Cu)SO_4 \cdot 6H_2O$, which is expected to form in solutions containing both Ni and Cu. van Gaans (1998) described the efforts of Herbert and Monig (1997) to include Cd and Zn in the original Harvie et al. (1984) model. These authors investigated the interaction of Cd and Zn with Cl and SO_4.

3. Case Studies

3.1 Sherridon mine tailings, Manitoba

The Cu-Zn ore body at Sherridon, Manitoba (65 km north east of Flin Flon, Manitoba) was mined between 1928 and 1951. Tailings generated between 1928 and 1931 were deposited in a 40 hectare "old" pile. After 1931, Zn recovery began, and the wastes were deposited in a second "new", larger pile. The tailings contain between 40 and 60 wt. % sulfides, predominantly pyrrhotite and pyrite, with lesser amounts of sphalerite, arsenopyrite and marcasite. The area has an annual precipitation of approximately 485 mm (Hydrological Atlas of Canada, 1978; Climate Atlas Climatique - Canada, 1984a,b) and mean lake evaporation of about 487 mm annually (Hydrological Atlas of Canada, 1978). Average monthly temperatures in the area range between -24 ^{0}C and 17 ^{0}C (Climate Atlas Climatique - Canada, 1984), and evapotranspiration is about 350 mm annually (Hydrological Atlas of Canada, 1978).

Samples of tailings pore water were collected during summer 2000 from the vadose zone, using a pore-water squeezing technique (Blowes and Jambor, 1990) and from the saturated zone using drive-point piezometers. The results of the sampling indicate the pore waters contain very high concentrations of dissolved SO_4 and metals, both in the vadose zone and the deeper saturated zone of the tailings. In the "old" part of the tailings impoundment, where the tailings have oxidized for over 70 years, very low pH values were observed, as low as pH 0.6 (Figure 4). These values gradually increase with depth to 5.8 as the result of acid-neutralization processes.

Concentrations of Fe as high as 129,000 mg/L and SO_4 as high as 280,000 mg/L were observed in the tailings pore waters (Figure 4). The Fe is predominantly present as Fe(II), however concentrations of Fe(III) are sufficiently elevated above the sulfide oxidation zone that the color of the pore waters are deep black. Below the oxidation zone, the pore waters turn green, then blue, and finally clear with increasing depth. Concentrations of other metals are high, up to 54,900 mg/L Zn, 5,710 mg/L Al , 97 mg/L

Cd, 105 mg/L Co , 1,620 mg/L Cu, 3.1 mg/L Cr, 262 mg/L Mn, 15.3 mg/L Ni, 5.2 mg/L Pb, and 41 mg/L As were observed (Figure 4). In a newer area of the impoundment where the tailings have oxidized for 50 years, high concentrations of Fe (107,000 mg/L), SO_4 (244,000 mg/L), Zn (4,800 mg/L), Al (6,170 mg/L), Cd (10 mg/L), Co (55 mg/L), Cu (375 mg/L), Cr (3.1 mg/L), Mn (71 mg/L), Ni (8 mg/L), Pb (5 mg/L), and As (55 mg/L) were observed. High concentrations of some metals are limited mostly to the low pH zones, including As, Co, and Ni. The concentrations of other metals, including Cr, Mn, Cd, Fe, and Zn, are elevated throughout most of the cross-section. The very high concentrations of Zn are attributed to the fact that Zn was not recovered from the ore during the first few years of mine operation, and the relatively rapid oxidation kinetics of sphalerite. Very high concentrations of Zn were observed in the pore waters of the "old" tailings (> 50,000 mg/L). These are some of the highest reported for mine waste sites (Table 1). The new tailings were produced after Zn recovery was initiated. As a result, Zn concentrations are substantially lower than in the "old" tailings. Concentrations of other constituents are lower, but still are many times higher than typically observed in low-sulfide deposits.

Mineralogical study indicates that the tailings are partially oxidized to a depth of 0.5 m, with pyrrhotite depleted to that depth, and pyrite partially oxidized, but present to the tailings surface. A number of soluble and insoluble secondary solids, including melanterite, goethite, jarosite and gypsum. Accumulation of these secondary minerals on the surfaces and within voids between the tailings grains, has resulted in the formation of discontinuous layers of hardpan in the upper oxidized zone of the tailings, and a 50 cm-thick, continuous hardpan just below the oxidation front. Acid-neutralization reactions have lead to the depletion of carbonate and aluminosilicate minerals. There are no measurable carbonate minerals in shallow samples, and <1% in deeper core materials. Aluminosilicate minerals are strongly depleted in the upper meter of the tailings. The presence of a significant mass of residual sulfides in the vadose zone of the tailings suggest that the tailings will remain acid-generating for many years to come.

Mineral saturation indices were calculated for the tailings pore water using the computer code PHRQPITZ, to which additional ion-interaction coefficients were added to the model data base (Ptacek and Blowes, 1994, 2000). The model calculations indicate that the pore water is at saturation with respect to melanterite and gypsum at the depths these phases were observed. In the deeper tailings in the "new" impoudment, the pore water is near saturation with respect to siderite, consistent with the first observation of alkalinity in the tailings pore water. Equilibrium with respect to these soluble phases is expected, given the long transit times expected for pore water in the fine-grained tailings. Application of an ion-association model indicates strongly supersaturated conditions with respect to gypsum and near saturation with respect to melanterite. For these waters, the ion-interaction approach appears to provide a more reasonable description of the geochemistry than obtained with the ion-association model.

The occurrence of the very high concentrations of Fe and SO_4 and extensive formation of melanterite are attributed to a number of factors, including the rapid oxidation kinetics of pyrrhotite, the long duration of oxidation and the relatively low precipitation rates in the region. This accumulation of melanterite represents a source of stored Fe, SO_4 and H^+. The melanterite was observed to form readily at seeps and within the tailings in response to slight declines in temperature, and then was observed to dissolve upon warming or after intensive rains. This Fe(II) is available for release to surface waters, where oxidation reactions can lead to the production of additional acidity.

2. 3. Heath Steele mine tailings, New Brunswick

Pore waters with very high concentrations of dissolved solids have been observed in the old tailings impoundment at the Heath Steel mine site, near New Castle, N.B. The Heath Steele tailings contain approximately 85 wt% sulfide minerals, principally pyrite, with lesser amounts of pyrrhotite, sphalerite and chalcopyrite (Blowes et al., this volume). Tailings, which had been deposited in a 10 hectare impoundment between 1957 and 1963, were allowed to oxidize for 30 years at the time of sampling (Blowes et al., 1991). High concentrations of SO_4 (up to 100 g/L), Fe(II) (up to 50 g/L), and low pH conditions (pH as low as 0.5) were present in the pore waters of the tailings. These concentrations were sufficiently high to lead to the formation of a massive hardpan below the zone of active oxidation, coincident with an increase in pH.

Blowes et al. (1991) applied a modified version of PHRQPITZ (Plummer et al., 1988) to calculate mineral saturation indices for a range of minerals for the Heath Steele tailings. Temperature-dependent Fe(II)-SO_4-HSO_4 interaction parameters were added to the PHRQPITZ data base to improve the model calculations. The Heath Steele pore waters were approximately 10 °C, requiring temperature corrections for components and phases with highly temperature dependent solubility constants and interaction coefficients. Ptacek and Blowes (1994) expanded the calculations to include siderite in the data base. Calculated saturation indices for gypsum ranged between -0.049 and 0.060. Gypsum was observed to be present throughout the depth of the tailings. Saturation indices for melanterite ranged from -1.023 at the base of the impoundment, to -0.292 at 50 cm below the impoundment surface. Saturation indices for melanterite reached a maximum at the depth of a cemented hardpan layer, 30 to 50 cm below the impoundment surface.

Mineralogical study indicated that the hardpan layer was composed of tailings cemented by secondary precipitates, principally gypsum and melanterite. The melanterite was crystalline and ranged in color from clear to pale green. Energy-dispersion analyses indicated that samples that had crystallized in situ in the tailings were almost pure $FeSO_4$. Blowes et al. (1991) estimated Fe(III) activities through field-measured Pt-electrode Eh values and the Nernst equation. Calculations indicated the pore water to be undersaturated with respect to $Fe(OH)_3$ near the impoundment surface. As the pH increased toward the hardpan layer, the water became supersaturated with respect to $Fe(OH)_3$. Saturation indices calculated for jarosite indicated supersaturated conditions throughout the impoundment. Jarosite and goethite were detected in samples of the tailings materials, but accumulations of ferric iron-bearing minerals were negligible. Calculations of saturation indices were also made using the geochemical code MINTEQA2 (Allison et al., 1990), to which the WATEQ4F data base (Ball and Nordstrom, 1987) was added. These calculations indicated highly supersatured conditions with respect to gypsum, inconsistent with the rapid precipitation rates expected for this phase.

2. 4. Richmond mine workings, California

Some of the most acidic metal-laden mine waters ever reported occur at the Richmond mine of the Iron Mountain copper deposit, near Redding California (Nordstrom and Alpers, 1999; Nordstrom et al., 2000). Ag, Au, Cu, Fe, Zn and pyrite were produced from the Iron Mountain group of mines beginning in the early 1860s and ending in 1962. The mineral deposits are massive sulfide lenses containing up to 95% pyrite, and lesser amounts of chalcopyrite and sphalerite. Nearly optimal conditions are present within the underground workings of the Richmond mine for the production of acid drainage (Nordstrom and Alpers, 1999; Nordstrom et al., 2000). The heat generated by pyrite oxidation promotes convective air transport, continually replenishing O_2 to the mine walls. Temperatures of 47 ^{o}C have been recorded in the recent past, and higher temperatures have been recorded in the past (Nordstrom and Alpers, 1999). During dry seasons, accumulation of sulfide oxidation products results in the formation of extensive deposits of secondary Fe-bearing minerals. During the wet season, groundwater flow through fractured country rock provides abundant water for flushing the accumulated oxidation products. As a result, there are pools of water with extremely low pH values, as low as -3.6, elevated Fe concentrations > 100,000 mg/L and exceptionally high SO_4 concentrations (up to 760,000 mg/L).

Calculations of H^+ ion activity and mineral equilibria were made using the Pitzer model for Richmond Mine waters by Nordstrom et al. (2000). A revised version of PHRQPITZ (Plummer et al., 1988) was used for the calculations (Ptacek and Blowes, 1994, 2000; Nordstrom et al. 2000). This version included temperature corrections for the Fe(II)-SO_4-HSO_4 system over the entire range of temperatures observed in the mine (up to 47 °C). Hydrogen ion activities were calculated for standard curves for electrode calibration and for determining the effect of Fe(II) addition on the activity calculations. It was concluded that the presence of Fe(II) had a minimal influence on the calculated H^+ activities. At this time there are no reliable Pitzer parameters for addition of Fe(III) to the Fe(II)-SO_4-HSO_4 system. The influence of Fe(III) on the geochemical model calculations cannot be fully assessed. Other efforts directed at the measurement of pH in concentrated waters are those by Harvie et al. (1984), Knauss et al. (1990, 1991), Mesmer (1991), Ptacek (1992), Dorta-Rodr[illegible]guez et al. (1997).

3.4. Genna Luas mine wastes, Sardinia, Italy

Highly concentrated mine drainage waters have developed at the Genna Luas mine site, southwestern Sardinia, as the result of sulfide oxidation and evaporation processes (Frau, 2000). The mine operated for ~100 years, up until the early 1980s, with the most intensive stage taking place between 1960 and 1980. The mineralization consisted of pyrite-melnikovite, with minor amounts of sphalerite, and traces of galena and chalcopyrite. The pyrite is described as cryptocrystalline pseudo-colloidal in texture and highly susceptible to oxidation. Oxidation of pyritiferous waste rock and mill tailings, deposited on site in heaps, has resulted in the generation of concentrated mine drainage waters (Table 1) that have seeped from the waste piles into an quarry-like open-pit (Frau, 2000). Effluent waters with concentrations of $SO_4 > 200,000$ mg/L, Fe > 77,000 mg/L, Zn > 10,000 mg/L and Al > 2500 mg/L were reported for the site. Evidence of weathering of sulfides is widespread. The secondary minerals melanterite, epsomite, copiapite, gypsum, halotrichite, pickeringite and Fe(III) (oxy)hydroxides are readily observed in association with oxidation of the massive sulfide on mine walls (Frau, 2000). Frau (2000) describes abundant occurrences of melanterite, formed as a result of direct crystallization on the surfaces of pyrite grains, and through precipitation from hyperacidic Fe(II)-SO_4 rich waters emanating from the waste piles.

Frau (2000) applied the geochemical model PHRQPITZ (Plummer et al., 1988) to calculate mineral saturation indices for surface waters collected in the former open-pit and from a bore-hole located inside the quarry. Highest concentrations were observed for the bore-hole samples. Using the original version of PHRQPITZ (Plummer et al., 1988), which includes a solubility product for melanterite, but not temperature dependent Pitzer parameters for the Fe(II)-HSO_4-SO_4 system, Frau (2000) calculated saturation indices of 0.151 for melanterite, and 0.139 for gypsum, and an ionic strength of 8.2 *m* for the bore-hole water. Mineralogical analysis indicated the presence of gypsum and abundant melanterite at the site. The composition of the melanterite was reported to be $(Fe_{0.091}Zn_{0.05}Mg_{0.04})SO_4{\cdot}7H_2O$ indicating uptake of Zn and Mg in the melanterite structure. This composition is quite similar to that reported for the Iron Mountain site.

Equilibrium with respect to melanterite and gypsum is typically achieved fairly rapidly (hours to days), and equilibrium is expected between samples collected adjacent to these phases. The PHRQPITZ calculations indicated slight supersaturated conditions for the borehole water with respect to melanterite and gypsum. This slight supersaturation could be associated with kinetic limitations on the precipitation rates, the presence of impurities in the mineral phases, or the limitations of the original PHRQPITZ database. Saturation indices calculated with PHREEQE (Parkhurst et al., 1980; 1990 revision) and

SOLMINEQ.88 with the Pitzer option (Kharaka et al., 1989) indicated undersaturated conditions with respect to melanterite (Frau, 2000).

The abundant melanterite formed as the result of pyrite oxidation is considered the single-most important phase controlling the composition of drainage waters at the site. The melanterite acts as a transient storage of Fe(II), H^+ and SO_4 through both the dissolution of melanterite, and through the subsequent oxidation of Fe(II):

$$FeSO_4 \cdot 7H_2O + \frac{1}{4}O_2 \rightarrow Fe(OH)_3 + SO_4^{2-} + 2H^+ + \frac{9}{2}H_2O \qquad (8)$$

Laboratory studies confirm that acid is released upon dissolution of melanterite using samples from the Genna Luas site and reagent-grade melanterite (Frau, 2000).

The Genna Luas site has a mean annual rainfall of 800 mm, with a pronounced dry season lasting between May and October and a wet season between November and January. The mean annual temperature at the site is 17 °C, with values rarely < 0 °C and often > 40 °C. Frau (2000) describes the release of waters with extreme concentrations occurs during heavy rains, and attributes that release from the stored melanterite and related salts during the drier periods in the year.

3.4. Metal refinery site

Geochemical reactions that occur in an waste pond at a TiO_2 plant at Armyansk, Crimea, Ukraine were described by Schuiling and van Gaans (1997) and van Gaans and Schuiling (1997). At this site waste acid and fine-grained phosphogypsum were discharged into an isolated bay since 1969. The pH of the pond water has gradually decreased to 0.85 over the course of its operation. Acid initially disposed in the pond was neutralized through reactions with underlying carbonate-rich muds. Eventually, however, an extensive hardpan formed and further neutralization of the acid was limited. As a result, concentrations of acid gradually increased as a result of evaporative processes. As the water evaporates precipitation of natrojarosite was documented (Schuiling and van Gaans, 1997). The formation of gypsum was also documented, with the source of Ca being attributed to the underlying carbonate sediments. Many trace metals, including V, Cr, and Ni were incorporated in the jarosite. Calculations of reaction pathways were made using PHRQPITZ to describe the geochemical evolution of this acid pond (van Gaans and Schuiling 1997). The titration option of this computer code was used to carry out the simulations. Predicted changes in the geochemical evolution of the pond agreed closely with the observed chemistry over the history of the pond.

3. Summary and Conclusions

Pore waters and seepage waters within and in the direct vicinity of mine wastes and mine workings can contain very high concentrations of dissolved solids. It is common for highly soluble secondary solids to precipitate from these waters. Advanced modelling techniques, based on the Pitzer ion-interaction model, are available to predict pore-water compositions that will form in contact with these soluble solids, and to predict the potential phases that can precipitate from mine waters. Application of the Pitzer model to mine and refinery waste sites as summarized in several case studies has yielded results consistent with mineralogical observations. Soluble sulfate salts which form from concentrated mine waters, often in copious quantities, are prone to resolubilization during wet seasons. Increases in temperature also affect the stability of these phases. Ion-interaction based models are currently limited to predicting solubility relations among several common sulfate salts and hydroxide and carbonate solids, simple oxidation-reduction and acid-base reactions and gas-phase transfer. These processes dominate the geochemical composition of mine effluent waters at many mine sites that exhibit extreme concentrations. Current versions of Pitzer-based models are sufficiently advanced to describe the major ion chemistry at a variety of mine drainage sites where extreme water compositions are encountered. As mine sites age, the number of mine sites with water compositions that are more extreme in concentration is expected to increase. Model calculations of the major ion chemistry described in the case studies is the first step in geochemical model development for these types of sites.

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Table 1. Composition of waters at high-sulfide mine sites in different localities in the world.

Parameter (concentrations expressed in g/L)	**Heath Steele** **Eastern Canada** Blowes et al. (1991) (tailings pore water)	**Iron Mountain** **Western U.S.** Nordstrom and Alpers (1999) (mine shafts/tunnels)	**Genna Luas** **Southern Italy** Frau (2000) (surface water)	**Sherridon** **Northern Canada** Moncur et al. (2003) (tailings pore water)
pH	1	-3.6	0.62	0.67
Cu	0.6	4.8	0.22	1.6
Zn	6	23.5	10.8	55
Cd		0.17	0.06	0.1
As		0.34	0.07	0.05
Fe_{total}	48	111	77	129
SO_4	85	760	203	280

Chemistry (concentrations expressed in g/L)	**Other Sites**	**Type**	**Source** *(after Nordstrom and Alpers, 1999)*
pH	0.67	(deep mine shafts/tunnels)	Goleva *et al.*(1970)
Cu	48	likely shafts	Clarke (1916)
Zn	50	likely shafts	Braeuning (1977)
Cd	0.04	(deep mine shafts/tunnels)	Lindgren (1928)
As	0.4	likely shafts	Goleva (1977)
SO_4	209	(deep mine shafts/tunnels)	Lindgren (1928)

LIST OF FIGURES

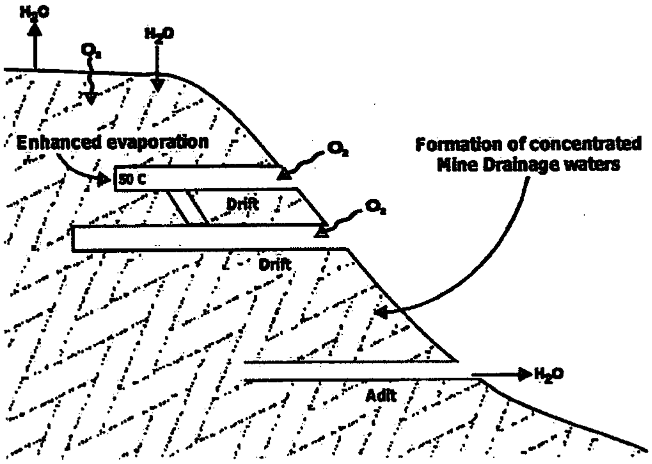
H2O
O2
H2O
Enhanced evaporation
50 C
O2
Drift
O2
Drift
Formation of concentrated Mine Drainage waters
H2O
Adit

Figure 1.

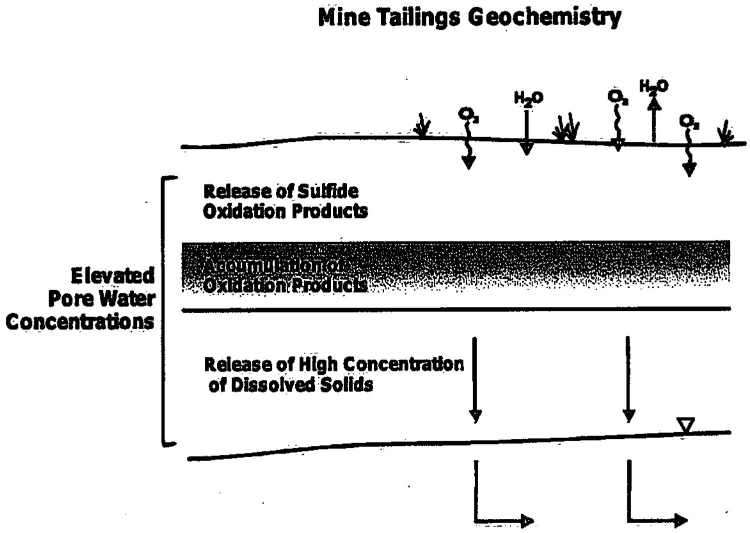
Mine Tailings Geochemistry
O_2
H_2O
O_2
H_2O
O_2
Release of Sulfide Oxidation Products
Accumulation of Oxidation Products
Elevated Pore Water Concentrations
Release of High Concentration of Dissolved Solids

Figure 2.

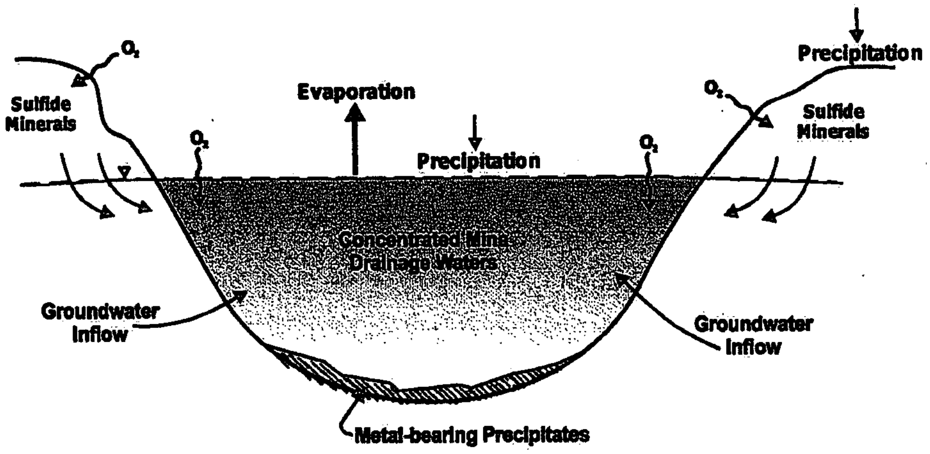O_2
Sulfide Minerals
Evaporation
Precipitation
O_2
Sulfide Minerals
O_2
Precipitation
O_2
Concentrated Mine Drainage Waters
Groundwater Inflow
Groundwater Inflow
Metal-bearing Precipitates

Figure 3.

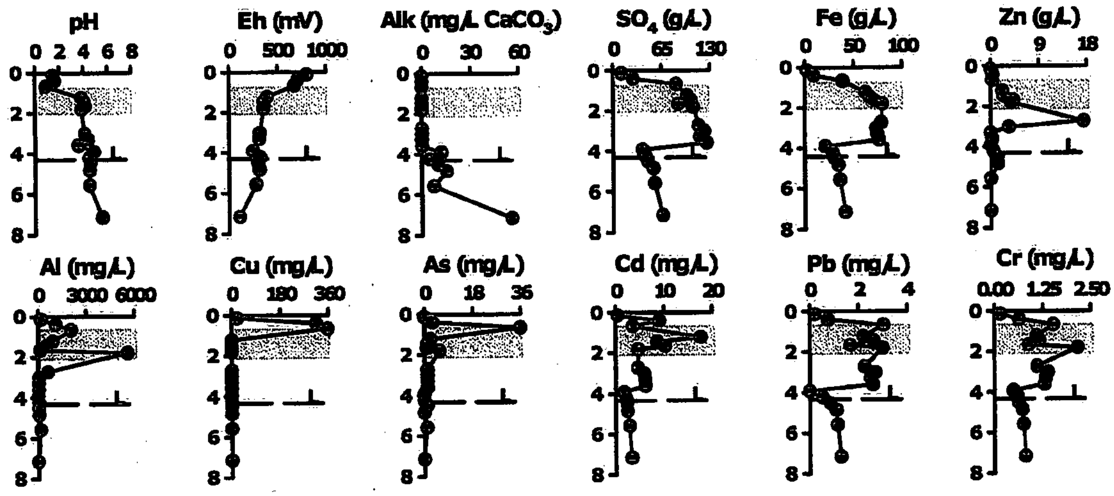

Figure 4. Vadose-zone pore water and groundwater chemistry in tailings after 70 years of oxidation (after Moncur et al., 2003).

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