International Geology Review, Vol. 42, 2000, p. 499–515.
Copyright © 2000 by V. H. Winston & Son, Inc. All rights reserved.

Advances in the Hydrogeochemistry and Microbiology of Acid Mine Waters

D. KIRK NORDSTROM

U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303-1066

Abstract

The last decade has witnessed a plethora of research related to the hydrogeochemistry and microbiology of acid mine waters and associated tailings and waste-rock waters. Numerous books, reviews, technical papers, and proceedings have been published that examine the complex biogeochemical process of sulfide mineral oxidation, develop and apply geochemical models to site characterization, and characterize the microbial ecology of these environments. This review summarizes many of these recent works, and provides references for those investigating this field. Comparisons of measured versus calculated Eh and measured versus calculated pH for water samples from several field sites demonstrate the reliability of some current geochemical models for aqueous speciation and mass balances. Geochemical models are not, however, used to predict accurately time-dependent processes but to improve our understanding of these systems and to constrain possible processes that contribute to actual or potential water quality issues. Microbiological studies are demonstrating that there is much we have yet to learn about the types of different microorganisms and their function and ecology in mine-waste environments. A broad diversity of green algae, bacteria, archaea, yeasts, and fungi are encountered in acid mine waters, and a better understanding of their ecology and function may potentially enhance remediation possibilities as well as our understanding of the evolution of life.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

Introduction

MINERAL RESOURCE PRODUCTION is vital to modern, industrialized societies. Scientific, technological, health, educational, and overall economic benefits that developed countries enjoy would not be possible without the products of the minerals industry. Unfortunately, mineral production can damage, and has damaged, other needed resources. Huge tracts of land are moved and sometimes destroyed. Serious degradation of air, water, and soil resources has occurred and continues to occur on a large scale. It is estimated that 24 billion tons of non-fuel minerals are extracted each year, with about 2.7 billion tons in non-overburden waste (Young, 1992). The U.S. produces about 1 billion tons of non-fuel mineral wastes (including overburden) each year. The global amount of earth moved from mining is nearly twice the average annual sediment load of the world's rivers (Young, 1992). Acid mine waters, produced from metal sulfide mining activities, have destroyed aquatic life, crops, and livestock, and they have endangered the health and livelihood of many communities. In late December, 1991, the Nangiles mine portal plug at the Wheal Jane, Cornwall, UK, unexpectedly burst and released 50,000 m^3 (13 million gallons) of acid mine drainage and sent a colorful plume into the Fal Estuary (Banks et al., 1997). On April 24–25, 1998, a large mine impoundment at the Aznacollar–Los Frailes mine complex, about 1 km across, failed and released 6 million cubic meters of acid water (4 million m^3) and sulfidic tailings (2 million m^3) into the Guadiamar River, near Seville, Spain, threatening a major wildlife refuge at Doñana National Park, covering a total of 4,286 hectares of farmland, river banks, and river channel, and destroying all aquatic life (see www.csic.es; Grimalt and Macpherson, 1999). The cyanide spill from a 4 km long impoundment at a gold leaching operation in Romania on January 30–31, 2000, entered the Tisza River, and destroyed aquatic and bird life for hundreds of miles into Hungary (see www.unep.org and search: Tisza River). The cyanide spill also put thousands of fisherman out of work, contaminated water supplies for several towns and rural communities, and caused contamination all the way into the Danube River.

In addition to the degradation and depletion of water resources, soils have been removed or contaminated, and the air quality has been compromised. The global atmosphere has become enriched in trace metals, especially Hg, As, Pb, Zn, Cd, Cu,

0020-6814/00/462/499-17 $10.00

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

and Sb, as well as in SO_2 and SO_4. More than 50% of the anthropogenic As, Cd, and Zn emitted into the atmosphere is derived from the nonferrous metals industry. Mercury and Pb in atmospheric particles are primarily derived from fossil fuel combustion. Antimony is primarily associated with copper production and is most likely associated with smelting activities.

Increased concern for the effects of mining on the environment has led to renewed efforts by researchers and regulators to learn more about the problems and processes associated with sulfide mineral oxidation and the effects of residual metals on environmental health. Many economic geologists have become environmental geochemists. New studies have focused on water-rock-microbe interactions involving sulfide minerals. New techniques in surface spectroscopy, restored interest in geomicrobiology, new experiments on sulfide oxidation kinetics, advances in computer codes for simulating aqueous geochemical reactions, and alternative ideas for remediation have revitalized a focus on causes, consequences, and clean-up possibilities for acid rock drainage. The number of conferences on the topic of acid rock and acid mine drainage has increased substantially, to the point where important international meetings are occurring simultaneously—e.g., Sudbury '99: Mining and the Environment II, in Ontario, Canada (Goldsack et al., 1999) was held the same week as Mine, Water, and Environment for the 21st Century in Sevilla, Spain (Fernandez-Rubio, 1999).

The purpose of this paper is to review recent research (mostly during the last decade) on sulfide mineral oxidation, especially on hydrogeochemistry and microbiology related to acid mine water formation. There are far more recent papers on this subject than could be included in this review, so this paper makes no claim to be comprehensive nor complete. It can only be hoped that by including some of the more recent documents, related references can be located more easily.

General References

Three relevant books have been published on environmental geochemistry related to the mining and processing of metallic sulfides. Alpers and Blowes (1994) have edited a volume covering research on field, lab, isotope, analytical, and remedial design aspects of mineral sulfide oxidation and consequences in 39 chapters. Jambor and Blowes (1994) have edited a short-course handbook containing 13 chapters that emphasizes the mineralogy and hydrogeology and some of the basic principles. Plumlee and Logsdon (1999) and the companion volume (Filipek and Plumlee, 1999) have provided 30 chapters and 583 pages of fundamental principles, processes, health topics, and case studies on the environmental geochemistry of mineral deposits.

The Mineral Policy Center has surveyed the problems associated with abandoned mines in Lyon et al. (1993) and have more extensively treated the subject of mining impacts on hydrology and water quality in Da Rosa and Lyon (1997). The annual Fort Collins meeting on tailings and mine waste has continued to grow in size, and the 1999 meeting resulted in a volume of more than 800 pages and 88 short papers (Tailings and Mine Waste '99). The U.S. Geological Survey (USGS) has for many years published investigations related to acid mine waters as part of its Toxic Substances Hydrology program. In 1997, the USGS implemented the Abandoned Mine Lands (AML) Initiative to assist other federal agencies in their efforts to clean up mine-waste hazards on federal lands. The most recent Toxic Substances Hydrology program meeting produced a separate volume devoted to investigations on contamination from hard-rock mining (Morganwalp and Buxton, 1999). The second Mining and the Environment meeting (or Sudbury '99, Goldsack et al., 1999) has been a popular one for the international community (also see Sudbury '95, Hynes and Blanchette, 1995). The California Mining Association published a book on Mine Waste Management (Hutchinson and Ellison, 1992) and more recently Marcus (1997) has produced a 785-page Mining Environmental Handbook. Noteworthy for coal mine drainage issues is the Brady et al. (1998) volume published by and for the State of Pennsylvania. Evangelou (1995) published a CRC book and Evangelou and Zhang (1995) produced a major review paper on pyrite oxidation and the control or prevention of acid mine drainage. The most recent summaries and results of research on the geochemistry of acid mine waters can be found in Schmiermund and Drozd (1997), Rose and Cravotta (1998), and Nordstrom and Alpers (1999).

On the World Wide Web, a valuable home page for up-to-date information and discussions on mine waste issues is maintained (www.enviromine.com). The USGS maintains a home page for its Mine Drainage Interest Group as well (mine-drainage.usgs.gov/mine/).

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

Geochemical Modeling of Acid Mine Waters

Tremendous advances have been made with the application of geochemical modeling to pyrite oxidation, formation of acid mine waters, and remediation consequences. The most recent review on this subject can be found in Alpers and Nordstrom (1999). The discussion in this section will follow that review, with condensation and additions from other recent studies.

Several important points need to be raised about modeling and its application. First, modeling does not necessarily imply a computer code nor does it necessarily imply mathematics. As pointed out by Greenwood (1989), "a model is a well-constrained logical proposition, not necessarily mathematical, that has necessary and testable consequences." The goal is to improve and refine our conceptual model. Experimental models, mathematical models, and computerized models all are tools that help us to reach our goal.

Second, a geochemical model is a theoretical construct of chemical principles developed for geologic (or hydrogeologic) systems. These constructs can be developed and applied in a variety of ways but usually have some similar properties, such as speciation, to be described below.

Third, users of geochemical models must have some basis for determining the model reliability for the intended range of application. For aqueous speciation calculations, it has been suggested that the seawater and river water test cases of Nordstrom et al. (1979b) be used for checking the consistency of speciation calculations. Some speciation, such as redox species, some free ion activities, and some organically bound metals, can be analytically determined and should be compared to computed speciation to evaluate reliability (Nordstrom, 1996). Ball and Nordstrom (1991) contributed two additional ground-water test cases that include expanded redox options and an Se(IV/VI) determination. Test cases that include mass transfer, mixing, ion exchange, evaporation, adsorption, and reactive transport have been described with the PHREEQC program (Parkhurst, 1995; Parkhurst and Appelo, 1999).

Fourth, models are only as reliable as the input data and auxiliary assumptions allow. Input data are of two general types: field or analytical parameters and physicochemical parameters. Physicochemical parameters include thermodynamic and kinetic data. Examples of sensitivity analyses for thermodynamic and analytical data applied to geochemical modeling are reported by Schecher and Driscoll (1987, 1988) and Nordstrom and Ball (1989). Numerous sources of thermodynamic data can be found and such data should be checked for accuracy, precision, and consistency. The thermodynamic data of Nordstrom et al. (1990) are commonly employed for aqueous geochemical modeling with supplementary data such as those found in Appelo and Postma (1993), Langmuir (1997), Johnson et al. (1992), and Nordstrom and Munoz (1994). Aqueous geochemical modeling should be based on water-chemistry, hydrological, mineralogical, and geological data. The more that it is based on data from a specific site, the more it can be used for site-specific applications. The less site data that are available, the less useful and the more uncertain are any conclusions.

Fifth, the background training and experience of the modeler is of critical importance to any modeling activity and its interpretation. Peer review can help in this regard and should always be utilized, but the adequacy, efficiency, and quality of a modeling exercise will reflect the capabilities of the person or group who carries out the task.

There are many aspects to geochemical modeling. Most models use *aqueous speciation*, or the equilibrium distribution of aqueous species among free ions and complexes. Heterogeneous reactions involve *mass transfer*, or the transfer of mass between two or more phases (such as dissolution or precipitation reactions). *Mass balances* are used in several different senses. In the context of this paper, mass balances refer to the conservation of mass that must exist when minerals undergo mass transfer reactions between the solid phase and the aqueous phase. *Mass transport* refers to solute movement by fluid flow. *Reaction transport* combines mass transfer with mass transport.

Modeling acid mine waters

The following three examples give an idea of how well our current speciation, redox, and mass transfer computations can simulate measurements made on the chemistry and mineralogy of actual mine water samples. The first is a comparison of computed versus measured redox-potential measurements for the Fe(II/III) redox couple. The second is a comparison of computed versus measured pH changes on oxidation of mine water samples, and the third is a comparison of computed versus measured pH and mass

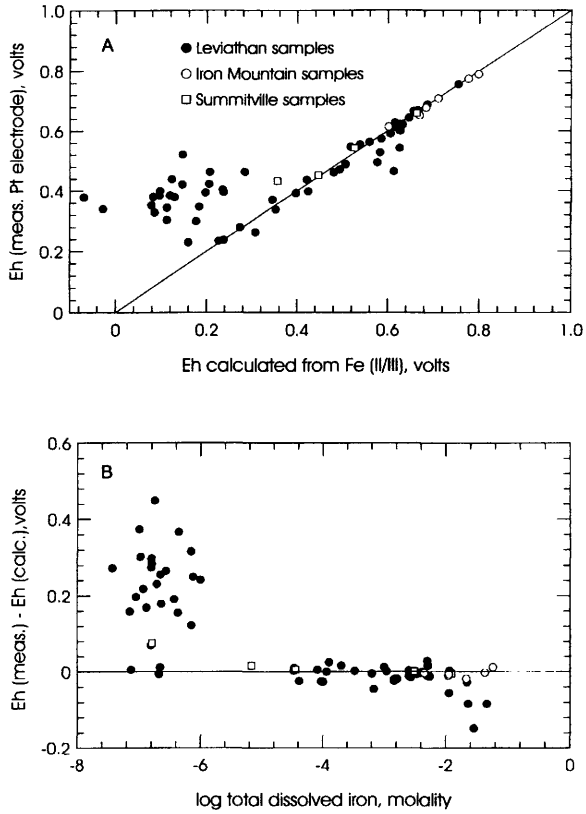

FIG. 1. A. Comparison of Eh measured by platinum electrode with Eh calculated from a speciation model based on complete water analyses and Fe(II/III) determinations. B. Difference between measured and calculated Eh as a function of the total dissolved iron concentrations.

transfer parameters for water samples collected from two mine sites in Brazil.

Aqueous speciation of acid mine waters is a difficult task. It requires careful and reliable determinations of numerous dissolved constituents, including Fe(II) and Fe(III). Without high quality control, including reasonable charge balances (≤10%), the analyses are not adequate for speciation calculations. Without sufficient knowledge of speciation for actual mine waters, more complex calculations that depend on speciation may be seriously in error. A new method for the direct determination of Fe(III) helps to decrease errors when the Fe(III) concentration is a small proportion of the total dissolved iron (To et al., 1999).

Redox equilibrium between redox couples for dissolved species usually is not attained (Lindberg and Runnells, 1984). Redox equilibrium between the platinum electrode and aqueous redox species is reached for only two constituents in aquatic systems: dissolved iron and dissolved sulfide. There is some indication that for some few ground waters, uranium redox species may actually equilibrate with the platinum electrode (Ahonen et al., 1994). Nordstrom et al. (1979a) and Nordstrom (1996) showed that excellent correspondence could be achieved between the electrode-measured Eh values and the Eh calculated values based on Fe(II/III) determinations (To et al., 1999) and speciation calculations to determine the activities of Fe(II) and Fe(III). The figure showing this comparison in Nordstrom (1996) is updated here in Figure 1A with data from the Iron Mountain Mine site (Nordstrom, 1977), and the Summitville Mine site (Nordstrom et al., pers. commun., 1999) added to the original data of the Leviathan Mine site (Ball and Nordstrom, 1989). This agreement corroborates the reliability of the iron speciation computation for acid mine waters. Simi-

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

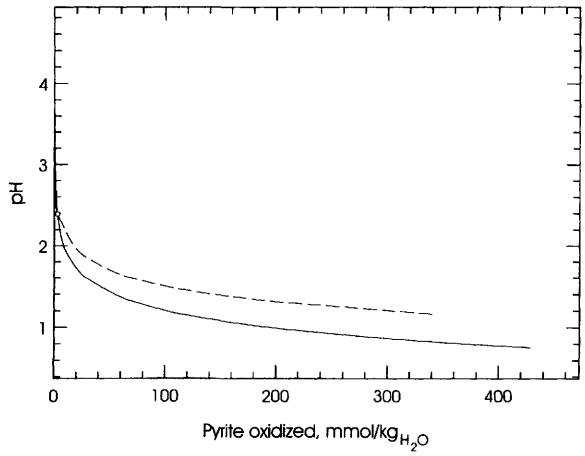

FIG. 2. The pH decrease as a function of the amount of pyrite oxidized simulated by the PHREEQC code (Parkhurst and Appelo, 1999). Lower solid line is the pH when no aqueous iron is oxidized, and the dashed line results when the aqueous ferrous iron is oxidized and allowed to precipitate ferrihydrite with a log K_{sp} = 3.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

lar results were obtained by Stipp (1990) for a range of pH and iron sulfate concentrations synthesized in the laboratory. At concentrations of iron below about 0.5 mg/L or 10^{-5} molal, the electroactivity weakens and the competition from oxygen produces a mixed potential. This effect causes the measured Eh to become progressively greater than the calculated Eh at decreasing concentrations of iron, as shown in Figure 1B.

Alpers and Nordstrom (1999) showed how pyrite oxidation can be simulated by reaction with oxygen and pure water. Their calculation was done with the PHRQPITZ code (Plummer et al., 1988) using the Pitzer specific ion interaction approach. The objective was to look at the formation of very low pH mine waters, and no Fe(III) was allowed to form because of the lack of Fe(III) Pitzer parameters. This example can be expanded upon to consider the oxidation of Fe(II) by using the ion association model and maintaining the pH range above 0.5 using the PHREEQC code (Parkhurst, 1995). The result can be seen in Figure 2, where the pH increases after oxidation of the solubilized Fe(II). On this log-linear plot, however, the pH values above the location of the open circle, about 2.4, cannot be seen.

The results at higher pH can better be seen in the log-log plot of Figure 3. Here, three lines are shown: a solid line representing pyrite oxidation with no oxidation of dissolved Fe(II), a dotted line representing the pH after pyrite oxidation *and* oxidation of the dissolved Fe(II) but no precipitation of an iron oxyhydroxide phase, and a dashed line representing the pH after pyrite oxidation, Fe(II) oxidation, and precipitation of an iron oxyhydroxide phase with a log K_{sp} = 3.0, comparable to a low-solubility ferrihydrite. Ferrihydrite, a common and widespread hydrous ferric oxide precipitate (Jambor and Dutrizac, 1998), is taken as a proxy for a range of hydrous ferric oxide minerals known to precipitate in acid mine waters. The stoichiometry is assumed to be the same as $Fe(OH)_3$, which gives the same dissolution stoichiometry for the aqueous ions as that for goethite:

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O, \quad (1)$$

$$FeOOH + 3H^+ = Fe^{3+} + 2H_2O. \quad (2)$$

The range of log K_{sp} values for hydrous ferric oxides ranges from about –0.2 for goethite (D'yakonov et al., 1994; Sergeeva et al., 1999) to an estimated 3 to 5 for ferrihydrite (Nordstrom et al., 1990).

In Figure 3, there are two crossover points: one for the Fe(II)-oxidation-without-precipitation line at a pH of 3.26 and the other for the Fe(II)-oxidation-with-precipitation line at a pH of 2.39. Hence, at pH values higher than the crossover point, oxidation of dissolved Fe(II) leads to a decrease in pH, while oxidation at lower pH values leads to an increase in pH. The inflection seen near the pH = 2.39 crossover is indicative of buffering by Fe(III) hydrolysis and may help to explain why most acid mine waters

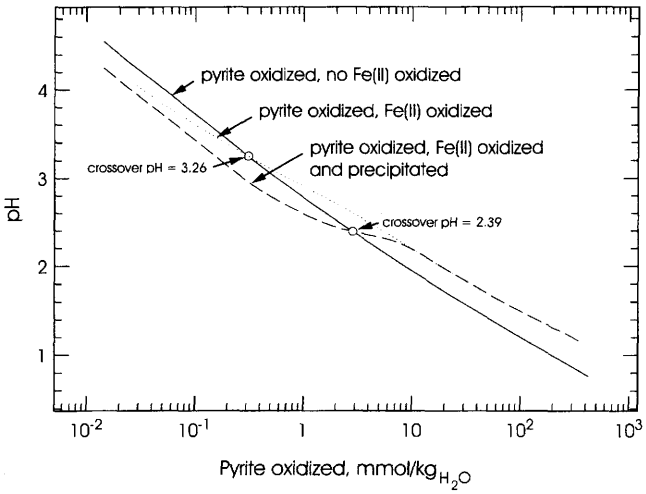

FIG. 3. The pH plotted as a function of the logarithm of the amount of pyrite oxidized, with no aqueous ferrous iron oxidized (solid line), with aqueous ferrous iron oxidized but not allowed to precipitate (dotted line), and with ferrous iron oxidation and precipitation of ferrihydrite of log $K_{sp} = 3$ (dashed line).

rarely achieve pH values below 2 without significant evaporation or extreme conditions, such as at Iron Mountain (Nordstrom and Alpers, 1999). These crossovers represent the point at which the proton consumption reaction:

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

is balanced by the proton production reaction:

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+. \quad (4)$$

When precipitation occurs, an additional 2 protons are produced:

$$FeOH^{2+} + 2H_2O = Fe(OH)_3 + 2H^+, \quad (5)$$

so that the crossover point occurs at a lower pH. Note that pyrite oxidation always causes a decrease in pH (the solid line in Figure 3), but oxidation of the resultant aqueous Fe(II) may cause either an increase or a decrease in pH, depending on the initial pH value (determined in Figure 3 by the mass amount of pyrite that was oxidized) relative to the pK values for hydrolysis and precipitation.

The next aspect of this example is to determine how well these calculations match observations of pH changes in oxidized mine waters. For most acid mine waters the mass balances have not been obtained to determine the amount of pyrite dissolved to produce a particular composition. Hence, it is not possible to reproduce a plot such as Figure 3 for acid mine waters. There are sufficient data, however, from the Leviathan mine study (Ball and Nordstrom, 1989), augmented by some unpublished data from Iron Mountain (Nordstrom, pers. commun., 1976) and from other mines in Colorado and Montana (Verplanck, pers. commun., 1999) to make a comparison. Instead of plotting pH against amount of pyrite dissolved, the final pH can be plotted against the initial pH before oxidation. The actual pH values measured after a variety of mine water samples had fully oxidized in the laboratory are shown by the solid circles in Figure 4. These results are complemented with arrows to designate a pH decrease at high initial pH, and a pH increase at low initial pH. The linear solid line indicates the initial pH (= final pH) and the curved solid line shows the pH change from computer calculations used to derive Figure 3.

Three conclusions can be drawn from this plot. First, at low initial pH, the measured pH change agrees with the simulated pH change. Second, the measured crossover point agrees with the simulated crossover point, indicating that the choice of K_{sp} is reasonable for iron precipitates in mine waters stored for a few weeks. Third, for higher measured pH changes, the measured values tend to be much lower than the simulated pH changes, although they are both in the correct direction (i.e., shifted down from the initial pH line). The pH values do not agree

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

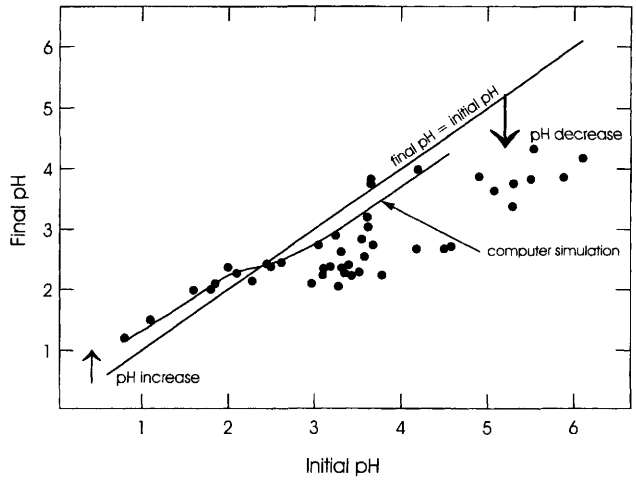

FIG. 4. The final pH plotted as a function of the initial field pH for mine waters that have been allowed to oxidize upon contact with the air for a few weeks.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

well above 2.4 because the initial pH values are not only a result of pyrite oxidation but also a result of carbonate and silicate weathering reactions that tend to neutralize the water. If the initial pH of a water sample is 6 because of carbonate weathering reactions, but initially contains 10 mg/L of ferrous iron, it will decrease in pH much more than if it began at a pH of 3 (with no carbonate dissolution) and had the same amount of ferrous iron to oxidize. If the amount of neutralization were determined by mass balances, it should be possible to model the entire pH change. The next example will demonstrate this approach. The pH change at high pH is always greater the higher the initial pH because the initial concentration of protons is much lower. Thus, the amount of pH decrease is a function of both the initial pH and the amount of reduced iron available for oxidation and hydrolysis. The agreement between calculated and measured pH values in this example is another corroboration of the reliability of geochemical modeling for acid mine waters and acid rock drainage.

The third and final example in this section is a comparison of pH computed from mass balance (or inverse modeling) and mass transfer assumptions with measured pH. These results are based on a study of water-rock interactions at the Osamu Utsumi mine and the Morro do Ferro thorium and rare-earth-element deposit near Poços de Caldas, Brazil (Chapman et al., 1993). Both sites have experienced about 75 million years of weathering of pyrite, carbonates, and silicates. Ground waters were pumped from several wells and the samples analyzed for all major and most trace elements, including the redox species of iron.

An important aspect of the geochemical modeling at these sites was the application of mass balances to determine the relative amounts of minerals that might have dissolved and precipitated to produce the observed water compositions (Plummer and Back, 1980; Plummer et al., 1983). The basic concept requires water composition data, mineralogy for the reactive phases in the system, and a knowledge of the ground-water flow system. From at least two points along a ground-water flow path, water compositions are chosen and the amount of mass transfer is calculated. With available computer programs (Parkhurst and Appelo, 1999; Plummer et al., 1994) additional constraints such as mixing of different waters and isotopic mass balances can be included. A simple example should clarify how this approach works. Consider a two-component system composed of calcium and carbon and two phases that can dissolve in water, calcite and carbon dioxide. This example could be a simplified limestone aquifer system. Well 1 contains 1.2 mmol/kg (millimolal) of Ca and 0.3 mmol/kg of C. Well 2, downgradient from Well 1, contains 3.3 mmol/kg of Ca and 3.0 mmol/kg of C. The mass amounts of calcite and carbon dioxide that have

TABLE 1. Mass Balance Results for Three Wells near Pocos de Caldas, Brazil, $mmol/kg_{H2O}$[1]

Mineral	MF12	PC-GW-42	F1
Fluorite	0.140	0.0092	0.0108
Calcite	0.072	0.002	0.0009
K-spar	0.02865	0.33	0.325
Albite	0.0365	0.0091	0.0087
Chlorite	–	0.0007	0.0006
Barite	–	–	0.0009
Kaolinite	–0.377	–0.1697	–0.1663
Chalcedony	–0.156	–0.120	–0.1095
Pyrite	0.056	0.0814	0.0822
Sphalerite	0.004	0.0012	0.0013
Ferrihydrite	–0.043	–0.0696	–0.0560
MnOOH	0.0306	0.0033	0.0035

[1]MF12 is at the Morro do Ferro site; the other two are at the Osamu Utsumi site. Values are amounts of minerals dissolved (positive) or precipitated (negative) in deriving the ground-water composition from infiltration of pure water.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

dissolved or precipitated can be solved by solution of simultaneous equations:

$$\begin{aligned} Ca_{(final)} - Ca_{(initial)} = \Delta Ca = \\ 2.1 mmol\ kg^{-1} = \alpha_{calcite} \\ C_{(final)} - C_{(initial)} = \Delta C = \\ 2.7 mmol\ kg^{-1} = \alpha_{calcite} + \alpha_{CO_2} \end{aligned} \quad (6)$$

where the α coefficients are the mass amounts transferred per kg of water. The only two phases specified were calcite and carbon dioxide, so that 2.1 mmol/kg of calcite must have dissolved. The increase in dissolved carbon is 2.7 mmol/kg, of which 2.1 mmol/kg is from calcite dissolution, so that 0.6 mmol/kg of carbon dioxide must have dissolved. This method has been called "inverse modeling" because the amounts of minerals that undergo mass transfer are backed out from known data on the mineralogy of the aquifer and known ground water compositions along flow paths. Forward modeling differs in that only an initial condition is known, say a given mineralogical assemblage and a starting water composition, and assumptions inherent in the computer code (or those applied by the user) about what geochemical reactions are allowed to occur. Inverse modeling is, of course, much better constrained than forward modeling because it uses much more site-specific field data.

Table 1 lists the mass balance results describing the chemical evolution from rainwater (pure water) to the ground-water composition for three wells near Poços de Caldas. Table 2 compares the measured pH with the pH calculated from the PHREEQE program (Parkhurst et al., 1990) based on the mass balances from Table 1. The comparison demonstrates nearly identical results between measured and calculated pH values, lending a high degree of confidence in the model calculations. The minerals used in the mass balances were based on careful investigations by Waber et al. (1992) and Waber (1992). These results show that the mass balance approach can be very effective in simulating the chemistry of water-rock interactions when the mineralogy and the ground-water compositions are known.

Examples of both forward modeling, to explain why it would not be desirable to plug a mine such as the Richmond mine at Iron Mountain, CA (Nordstrom and Alpers, 1999), and inverse modeling, to determine whether or not a hydrologic connection existed between two mines at Iron Mountain, demonstrate the effectiveness of geochemical calculations in regulatory decision making for remediation of mine sites (Nordstrom and Alpers, 1999).

Reactive transport modeling in ground waters

Considerable advances have been made with respect to the combined reaction and transport of water and air through mined areas and mine wastes.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

age can be found in the development and application of the OTIS/OTEQ codes (Runkel Bencala et al., 1996; Runkel, McKnight et al., 1996; Runkel, 1998; Runkel et al., 1999). Hydrologic parameters for these types of models often are estimated using results from tracer-dilution studies, preferably ones involving constant-flow injection (Broshears et al., 1993). A good test of this code was the simulation of an experiment in which sodium carbonate was added temporarily to neutralize an acid mine water (Broshears et al., 1996). Other applications of the OTIS/OTEQ code to streams affected by acid mine waters include investigations in the Upper Animas River basin, Colorado (Walton-Day et al., 1999) and the Wightman Fork–Alamosa River basin near Summitville, Colorado (Bencala and Ortiz, 1999; Ball et al., 1999).

Pyrite Oxidation Mechanisms

The oxidation of pyrite is a complex hydrobiogeochemical process involving three important catalysts: the semiconductive surface of pyrite, chemolitho-autotrophic bacteria, and aqueous Fe(III). The strong oxidant aqueous Fe(III) is considered a catalyst because after it is reduced (upon reaction with the pyrite surface) it can be rapidly converted back to Fe(III) by iron-oxidizing enzymes in microorganisms.

Nordstrom (1982) pointed out that the seven electrons lost by the sulfur in pyrite to form sulfate cannot be lost in a single step and several possible intermediate sulfur species might form. Goldhaber (1983) and Moses et al. (1987) demonstrated the formation of thiosulfate, polythionates, and sulfite during pyrite oxidation, but only when oxygen was the oxidant. These intermediates did not appear when Fe(III) was the oxidant. The lack of detectable intermediate sulfoxyanions in the presence of Fe(III) suggests that Fe(III) reacts so rapidly with sulfoxyanions that they cannot be detected. The electroconductive surface of pyrite also may play a role in the fast degradation of sulfoxyanions by Fe(III).

Luther (1987, 1990) used arguments based on molecular orbital theory to conclude that thiosulfate formation could be the first step in the oxidation of the sulfur in pyrite. Thiosulfate and other sulfoxyanions are a source of energy for most species in the *Thiobacillus* genus (Ehrlich, 1996; Nordstrom and Southam, 1997). Furthermore, Xu and Schoonen (1995) have shown that thiosulfate is catalytically oxidized in the presence of pyrite to tetrathionate. Williamson and Rimstidt (1993) showed that ferric iron rapidly decomposes thiosulfate to tetrathionate. These studies indicate that thiosulfate is formed during the oxidation of pyrite and that it is easily oxidized by the pyrite surface, by bacteria, and by Fe(III). From thiosulfate oxidation, the main product is tetrathionate, which should undergo similar but slower oxidation to sulfate. Tetrathionate can be further oxidized by microorganisms to sulfate. These processes may help to explain the rapid transformation of sulfur in pyrite to sulfate. The rates of these processes are fast enough that it would be unusual to find any sulfoxyanion other than sulfate in an acid mine water.

Another complication in the reaction mechanism for sulfide mineral oxidation is that metal monosulfides, such as sphalerite and galena, produce H_2S in acid solutions. Once H_2S is formed, it rapidly oxidizes to thiosulfate in the presence of air and a separate pathway has been initiated to form thiosulfate and other oxyanions (see Zhang and Millero, 1994; Xu et al., 1998). Thiosulfate readily disproportionates in acid solutions to form elemental sulfur and sulfite. The sulfite oxidizes to sulfate and elemental sulfur becomes an energy supply for autotrophic bacteria. Sulfur also is formed from pyrite at moderately elevated temperatures (Bergholm, 1955), but it is not clear whether this sulfur is formed from H_2S or from thiosulfate or from the disulfide in pyrite. It is possible that the thiosulfate seen in the studies by Goldhaber (1983) and Moses et al. (1987) is from either a small amount of H_2S or elemental sulfur formed during the reaction and that the presence of Fe(III) eliminates or decomposes reduced sulfur too quickly to observe any thiosulfate formation. Schippers et al. (1996) have resolved most of these questions in a revealing study in which they determined the products of pyrite oxidation by a bacterium that only oxidizes iron, *Leptospirillum ferrooxidans*, and demonstrated the formation of tetrathionate, pentathionate, and a considerable amount of elemental sulfur. These results, similar to abiotic experiments using only Fe(III) to oxidize pyrite, contrasted with those found when they used *Thiobacillus ferrooxidans*, a bacterium that oxidizes both ferrous iron and reduced sulfur compounds. With *T. ferrooxidans*, elemental sulfur was formed, but at much lower concentrations and no polythionates were detected. This study confirms that the sulfur-oxidizing microorganisms are primarily responsible for the rapid conversion of the disulfide component in

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

pyrite to aqueous sulfate, preventing the accumulation of detectable sulfoxyanion intermediates.

Microbiology of Acid Mine Waters

As long ago as 1919, Powell and Parr suggested that acidic drainage from coal deposits was caused by pyrite oxidation catalyzed by bacteria. Rudolfs and Helbronner (1922) demonstrated the catalytic oxidation of zinc sulfide by bacteria, but the iron- and sulfur-oxidizing autotroph, *Thiobacillus ferrooxidans*, was not isolated from coal-mine drainage until 1947 (Colmer and Hinkle, 1947). By the 1960s its role in the catalysis of both aqueous Fe(II) and pyrite oxidation was well established, and hydrometallurgical applications of these bacteria for metal extraction and the cleaning of pyrite and marcasite from coal were being pursued (Kuznetsov et al., 1963; Zajic, 1969). Today, *T. ferrooxidans* probably has been studied more than any other autotroph and the latest genomic characteristics have been reported by Irazabal et al. (1997). Unfortunately, the microbial ecology of mine waters and the role of other microorganisms is poorly understood. This fact is surprising because the astounding microbial diversity in acid waters has been known for many decades (Lackey, 1938; Joseph, 1953; Ehrlich, 1963).

Several recent reviews related to the oxidation of sulfide minerals by microorganisms reflect strong continuing interest in this topic (Suzuki, 1994; Suzuki et al., 1994; Ledin and Pedersen, 1996; Kelly et al., 1997; Nordstrom and Southam, 1997; Kelly, 1999; Johnson, 1998). At the same time, conventional concepts of the role of microbes in sulfide oxidation and acid mine waters are changing.

The role of *T. ferrooxidans* has been found to be supplemented and even replaced in some environments. The widespread association of *T. thiooxidans* (which oxidizes sulfur but not iron) with *T. ferrooxidans* has long been known (Zajic, 1969; Sokolova and Karavaiko, 1964; Scala et al., 1982). More recent studies have found *Leptospirillum ferrooxidans* to be of comparable importance (Sand et al., 1992; Schrenk et al., 1998). Darland et al. (1970) first reported the unusual occurrence of an Archaean mycoplasma (a cell without a cell wall), *Thermoplasma acidophilum*, from self-heating coal refuse piles. This species optimally grew at 55°C and pH about 2. At the Iron Mountain Mine site, a new iron-oxidizing Archaeon has been found, *Ferroplasma acidarmanus* (Edwards et al., 2000), along with *Thiobacillus caldus* at temperatures of ~40°C and a pH of about 0.7. Iron Mountain contains some of the most acidic waters that have ever been reported, with pH values as low as –3.6 (Nordstrom et al., 2000). The lowest pH reported for which microbes have been found is –0.06 (and a temperature of ~60°C) for the Archaean mycoplasm, *Picrophilus oshimae* (Schleper et al., 1995). Other microbes that have been identified at Iron Mountain through cloning and RNA analysis include *Acidimicrobium ferrooxidans* and *Sulfobacillus thermosulfooxidans* (Bond et al., 1999). Other acidophilic Archaea genera include the aerobes *Metallosphaera* and *Sulfurococcus* (Johnson, 1998). Two Archaea genera are facultative anaerobes, *Thermoplasma* and *Acidianus*, and a single species, *Stygiolobus azoricus*, is obligately anaerobic.

The occurrence of mycoplasma at higher temperatures and low pH requires an unusually "tough skin," because the internal pH of their cells must be 6–7 to carry out metabolic functions. The lipopolysaccharide of their cell membrane consists of a tetraether lipid with mannose and glucose units. This composition makes these microbes stable in hot acid conditions (Madigan et al., 1997). A succession from *T. thioparus* at neutral pH to *T. ferrooxidans* at low pH has been observed at the Kidd Creek tailings (Blowes et al., 1995) and helps to explain the mineralogical observations, such as the occurrence of ferric oxyhydroxide rims in the low pH section of the tailings.

A multitude of microorganisms, including Bacteria, Eukarya, and Archaea, have been found in acid mine waters. Yeasts, fungi, green algae (but not cyanobacteria; Brock, 1973), amoebas, and actinomycetes have all been found in acid waters, but little is known about their ecology, community structure, limits of growth as a function of pH, and mechanisms of low pH tolerance. Several species of acidophilic yeasts and filamentous fungi have been identified that live at pH values as low as 1–2 (Magan, 1997). Examples include *Acontium*, *Candida*, *Cephalosporium*, *Cladosporium*, *Penecillium*, *Rhodotorula*, *Saccharomyces*, and *Trichosporon* (Nordstrom and Southam, 1997; Magan, 1997). Both autotrophic and heterotrophic bacteria can be found and heterotrophs may be living symbiotically or at least commensally with the autotrophs (Ledin and Pedersen, 1996; Nordstrom and Southam, 1997). At least six species of *Acidiphilium*, a genus of acidophilic heterotrophs, have been identified in acid mine waters. One of the most recent ones is *Acid-*

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

iphilium multivorum (Wakao et al., 1994). Natural photosynthesis in *Acidiphilium rubrum* using a novel Zn-containing bacteriochlorophyll was discovered by Wakao et al. (1996). Other acidophilic heterotrophs include *Pseudomonas, Bacillus, Micrococcus, Sarcina, Crenothrix, Microsporium, Aerobacter,* and *Caulobacter.* Common green algae found growing in acid waters include *Chlamydomonas, Chlorella, Chroomonas, Euglena, Hormidium,* and *Ulothrix.*

The dissolved and particulate carbon in some of these waters could be substantially elevated from microbial growth and decay. The waste products and decay of one community could become the food for the next trophic level. Ciliates and rotifers have been found in microbial slimes with pH of 1.5 at the Iron Mountain site in California (Robbins et al., 2000). Some studies have been done on green algae in acid mine waters and metal uptake has been observed. Research gained from such studies might help to improve the efficiency of biohydrometallurgical processes and might be utilized in metal attenuation for streams acidified by mine drainage. Our understanding of microbial ecology in these environments is very limited and many more important discoveries have yet to be made.

Conclusions

The hydrogeochemistry and microbiology of mining and mineral processing sites can be very complex; the sites can be extremely costly and time-consuming to clean up. The physical and chemical trauma to the environment and the risks to human health can be alleviated if proper planning for minimizing environmental contamination is incorporated into the initial plans for mining and processing. The long-term costs and liability also are greatly reduced. Some of the tools that can be applied to comparing risks, predicting geochemical consequences, and understanding the effects of sulfide oxidation on water quality are outlined in this review. The application of geochemical models has greatly enhanced the quantification of these processes and made it easier to predict probable consequences of mining activities. The microbiology of acid mine drainage is less advanced in terms of understanding environmental processes and rates, but holds promise for incorporating potential remedial alternatives into clean-up activities.

Some of the greatest difficulties in applying models and biogeochemical processes are in the scaling up of rates and mechanisms from laboratory studies to the field. At field sites, our knowledge of water flow paths is very limited and our knowledge of the reactive surfaces available to air and water flow is even worse. The types and amounts of microbial colonization (essential for understanding reaction rates) along flow paths is largely unknown. Often there are severe temperature gradients. Underground mines are often inaccessible for direct observations. We cannot predict local and seasonal weather conditions with much accuracy. Hence, applying models to site-specific conditions involves considerable uncertainties and extensive averaging of properties, in addition to the large number of assumptions that most models utilize. The objective, however, is to improve our conceptual understanding of how these complex systems work rather than to make accurate predictions. Models often can address specific questions very well. If the major factors that lead to acid mine water production at a site can be determined and models can be applied with reasonable confidence, then the best formulation for cost-effective remediation should be possible.

Recent advances in the hydrogeochemistry and microbiology of acid mine waters have greatly increased our ability to understand and predict the causes and consequences of mining activities. As this knowledge is employed and incorporated into mining and engineering practices and remediation activities with proper hydrogeological studies, we can expect to see more responsible mining activities and more environmentally safe conditions (e.g., Plumlee and Logsdon, 1999). Hydrogeochemistry and microbiology are interdependent and integrated subjects in reality; they are only treated as separate subjects here for the sake of convenient discussion. Hopefully, this knowledge can be incorporated into engineering practice, so that disasters such as the waste impoundment failure in Spain (see the Seville proceedings [Fernandez-Rubio, 1999] and the special issue of Science of the Total Environment [Grimalt and Macpherson, 1999]), the cyanide spill in Romania, and the deleterious consequences of mine plugging can be avoided (Nordstrom, 1999).

Acknowledgments

It is a great pleasure for me to dedicate this paper to such a prominent geochemist, inspirational scientific leader, and fine individual as Prof. Konrad Krauskopf. I consider myself very fortunate to have

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

had him on my Ph.D. committee and to have known him personally for over 25 years. Few scientists have combined the pursuit of excellent science with the integrity needed to face political confusion (as in the area of radioactive waste disposal) and some of the best writing skills I have seen, as Konnie. I am grateful to my two reviewers, Rob Runkel and George Parks, who made several important editing suggestions that led to a much improved manuscript. I am also very grateful to Prof. Gary Ernst, who encouraged me and patiently waited for this overdue paper. This work was supported by the National Research Program of the U.S. Geological Survey.

REFERENCES

Ahonen, L., Ervanne, H., Jaakola, T., and Blomqvist, R., 1994, Redox chemistry in uranium-rich groundwater of Palmottu uranium deposit, Finland: Radiochim. Acta, v. XX, p. 1–7.

Alpers, C. N., and Blowes, D. W., eds., 1994, Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Series 550, 681 p.

Alpers, C. N., and Nordstrom, D. K., 1999, Geochemical modeling of water-rock interactions in mining environments, *in* Plumlee, G. S., and Logsdon, M. J., eds., Environmental geochemistry of mineral deposits: Littleton, CO, Soc. Econ. Geol., p. 289–323.

Appelo, C. A. J., and Postma, D., 1993, Geochemistry, groundwater, and pollution: Rotterdam, Balkema, 536 p.

Bain, J. G., Blowes, D. W., Robertson, W. D., and Frind, E. O., 1999, Modelling of sulfide oxidation with reactive transport at a mine drainage site: Jour. Contam. Hydrol., v. 41, p. 23–47.

Ball, J. W., and Nordstrom, D. K., 1989, Final revised analyses of major and trace elements from acid mine waters in the Leviathan mine drainage basin, California and Nevada–October 1981 to October 1982: U.S. Geol. Surv. Water-Resour. Invest. Report 89-4138, 46 p.

_____, 1991, User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geol. Surv. Open-File Report 91-183, 189 p.

Ball, J. W., Runkel, R. L., and Nordstrom, D. K., 1999, Transport modeling of reactive and non-reactive constituents from Summitvillle, Colorado: Preliminary results from the application of the OTIS/OTEQ model to the Wightman Fork/Alamosa River system, *in* Morganwalp, D. W., and Buxton, H. T., eds., (1999) U.S. Geological Survey Toxic Substances Hydrology Program—Proc. Tech. Meeting, Charleston, South Carolina, March 8–12, 1999, v. 1: U.S. Geol. Surv. Invest. Report 99-4018A, p. 305–312.

Banks, D., Younger, P. L., Arnesen, R.-T., Iversen, E. R., and Banks, S. B., 1997, Mine-water chemistry: The good, the bad, and the ugly: Env. Geol., v. 32, p. 157–174.

Bencala, K. E., and Ortiz, R. F., 1999, Theory and(or) reality: Analysis of sulfate mass-balance at Summitville, Colorado poses process questions about the estimation of metal loadings, *in* Morganwalp, D. W., and Buxton, H. T., eds., U.S. Geological Survey Toxic Substances Hydrology Program–Proc. Tech. Meeting, Charleston, South Carolina, March 8–12, 1999, v. 1: U.S. Geol. Surv. Invest. Report 99-4018A, p. 119–122.

Bergholm, A., 1955, Oxidation av pyrit: Jernkontorets Annaler, v. 139, p. 531–549 (translated by D. Baxter, D. and edited by Nordstrom, D. K. , DeMonge, J. M., and Lövgren, L., 1995, U.S. Geol. Surv. Open-File Report 95-389, 20 p.).

Blowes, D. W., 1994, Remediation and prevention of low-quality drainage from tailings impoundments, *in* Jambor, J. L., and Blowes, D. W., eds., Environmental geochemistry of sulfide mine-wastes: Nepean, Ont., Min. Assoc. Can. Short Course Handbook, v. 22, p. 365–380.

Blowes, D. W., Al, T., Lortie, L., Gould, W. D., and Jambor, J. L., 1995, Microbiological, chemical, and mineralogical characterization of the Kidd Creek mine tailings impoundment, Timmins area, Ontario: Geomicrobiol. Jour., v. 13, p. 13–34.

Blowes, D. W., and Ptacek, C. J., 1994, Acid-neutralization mechanisms in inactive mine tailings, *in* Jambor, J. L., and Blowes, D. W., eds., Environmental geochemistry of sulfide mine-wastes: Nepean, Ont., Min. Assoc. Can. Short Course Handbook, v. 22, p. 271–292.

Bond, P. L., Edwards, K. J., Gihring, T. M., Bond, P. L., and Banfield, J. F., 1999, Microbial ecology of an acid mine drainage environment [abs.]: Geol. Soc. Amer. Abs. Prog., October 24–28, 1999, Denver, CO, p. A-448.

Brady, K. B. C., Smith, M. W., and Schueck, J., eds., 1998, Coal mine drainage prediction and pollution prevention in Pennsylvania: Harrisburg, PA, Penn. Dept. Env. Protect.

Brock, T. D., 1973, Lower pH limit for the existence of blue-green algae: Evolutionary and ecological implications: Science, v. 179, p. 480–483.

Broshears, R. E., Bencala, K. E., Kimball, B. A., and McKnight, D. M., 1993, Tracer-dilution experiments and solute-transport simulations for a mountain stream, Saint Kevin Gulch, Colorado: U.S. Geol. Surv. Water-Resources Invest. Report 92-4081, 18 p.

Broshears, R. E., Runkel, R. L., Kimball, B. A., McKnight, D. M., and Bencala, K. E., 1996, Reactive solute transport in an acidic stream: Experimental pH

increase and simulation of controls on pH, aluminum, and iron: Env. Sci. Tech., v. 30, p. 3016–3024.

Cathles, L. M., 1994, Attempts to model the industrial-scale leaching of copper-bearing mine waste, *in* Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Ser. 550, p. 123–131.

Chapman, N. A., McKinley, I. G., Shea, M. E., and Smellie, J. A. T., 1993, The Poços de Caldas Project: Natural analogues of processes in a radioactive waste repository: Amsterdam, Elsevier, 603 p.

Colmer, A. R., and Hinkle, M. E., 1947, The role of microorganisms in acid mine drainage: Science, v. 106, p. 253–256.

Darland, G., Brock, T. D., Samsonoff, W., and Conti, S. F., 1970, A thermophilic, acidophilic mycoplasma isolated from a coal refuse pile: Science, v. 170, p. 1416–1418.

Da Rosa, C. D., and Lyon, J. S., 1997, Golden dreams, poisoned streams: Washington, DC, Mineral Policy Center.

D'yakonov, I. I., Khodkovsky, I. L., Schott, J., and Sergeeva, E. I., 1994, Thermodynamic properties of iron oxides and hydroxides I. Surface and bulk properties of goethite (α-FeOOH) up to 500 K: Eur. Jour. Mineral., v. 6, p. 967–983.

Dzomback, D. A., and Ali, M. A., 1993, Hydrochemical modeling of metal fate and transport in freshwater environments: Water Pollut. Res. Jour. Canada, v. 28, p. 7–50.

Edwards, K. J., Bond, P. L., Gihring, T. M., and Banfield, J. F., 2000, An archaeal iron-oxidizing extreme acidophile important in acid mine drainage: Science, v. 287, p. 1796–1799.

Ehrlich, H. L., 1963, Microorganisms in acid drainage from a copper mine: Jour. Bacteriol., v. 86, p. 350–352.

_____, 1996, Geomicrobiology, third ed.: New York, Marcel Dekker, 719 p.

Evangelou, V. P., 1995, Pyrite oxidation and its control: Boca Raton, FL, CRC Press, 285 p.

Evangelou, V. P., and Zhang, Y. L., 1995, A review: Pyrite oxidation mechanisms and acid mine drainage prevention: Crit. Rev. Env. Sci. Tech., v. 25, p. 141–199.

Fernandez-Rubio, R.,ed., 1999, Mine water and environment: Int. Congress, Int. Mine Water Assoc., Sept. 13–17, 1999, Sevilla, Spain.

Filipek, L. H., and Plumlee, G. S., eds., 1999, The environmental geochemistry of mineral deposits: Littleton, CO, Soc. Econ. Geol., Rev. Econ. Geol., v. 6B.

Glynn, P., and Brown, J., 1996, Reactive transport modeling of acidic metal-contaminated ground water at a site with sparse spatial information, *in* Lichtner, P. C., Steefel, C. I., and Oelkers, E. H., eds., Reactive transport in porous media: Mineral. Soc. Amer. Rev. Mineral., v. 34, 377–438.

Goldhaber, M. B., 1983, Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6–9 and 30°C: Amer. Jour. Sci., v. 283, p. 193–217.

Goldsack, D., Belzile, N., Yearwood, P., and Hall, G., eds., 1999, Sudbury '99: Mining and the Environment II, Proc. Int. Symp., v. 1, 2, and 3, Sudbury, Ontario, Oct. 13–16, 1999.

Greenwood, H. J., 1989, On models and modeling: Can. Mineral., v. 27, p. 1–14.

Grimalt, J. O., and Macpherson, E., 1999, The environmental impact of the mine tailing accident in Aznalcollar (south-west Spain): Sci. Total Env., v. 242 (nos. 1–3), p. 1–323.

Hutchinson, I. P. G., and Ellison, R. D., 1992, Mine waste management, California Mining Association: Boca Raton, FL, Lewis Publ., 654 p.

Hynes, T. P., and Blanchette, M. C., eds., 1995, Proceedings of Sudbury '95—Mining and the Environment, Sudbury, Ontario, May 28 – June 1, 1995, 3 volumes.

Irazabal, N., Marin, I., and Amils, R., 1997, Genomic organization of the acidophilic chemolithoautotrophic bacterium *Thiobacillus ferrooxidans* ATCC 21834: Jour. Bacteriol., v. 178, p. 1946–1950.

Jambor, J. L., and Blowes, D. W., 1994, Environmental geochemistry of sulfide mine wastes: Nepean, Ont., Min. Assoc. Can., Short Course Handbook, v. 22, 438 p.

Jambor, J. L., and Dutrizac, J. E., 1998, Occurrence and distribution of natural and synthetic ferrihydrite, a widespread iron oxide: Chem. Rev., v. 98, p. 2549–2585.

Johnson, D. B., 1998, Biodiversity and ecology of acidophilic microorganisms, FEMS Microbiol. Ecol., v. 27, p. 307–317.

Johnson, R. H., Blowes, D. W., Robertson, W. D., and Jambor, J. L., 1999, The hydrogeochemistry of the Nickel Rim mine tailings impoundment, Sudbury, Ontario: Jour. Contam. Hydrol., v. 41, p. 49–80.

Johnson, J. W., Oelkers, E. H., and Helgeson, H. C., 1992, SUPCRT92—A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000°C: Computers and Geosci., v. 18, p. 899–947.

Joseph, J. M., 1953, Microbiological study of acid mine waters—Preliminary report: Ohio Jour. Sci., v. 53, p. 123–127.

Kelly, D. P., 1999, Thermodynamic aspects of energy conservation by chemolithotrophic sulfur bacteria in relation to the sulfur oxidation pathways: Arch. Microbiol., v. 171, p. 219–229.

Kelly, D. P., Shergill, J. K., Lu, W.-P., and Wood, A. P., 1997, Oxidative metabolism of inorganic sulfur compounds by bacteria: Antonie Van Leeuwenhoek, v. 71, p. 95–107.

Kuznetsov, S. I., Ivanov, M. V., Lyalikova, N. N., 1963, Introduction to geological microbiology: New York, McGraw-Hill Book Co., 252 p.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

Lackey, J.B., 1938, The flora and fauna of surface waters polluted by acid mine drainage: Public Health Report 53, p. 1499–1507.

Langmuir, D., 1997, Aqueous environmental geochemistry: Englewood Cliffs, NJ, Prentice Hall, 600 p.

Ledin, M., and Pedersen, K., 1996, The environmental impact of mine wastes—Roles of microorganisms and their significance in treatment of mine wastes: Earth Sci. Rev., v. 41, p. 67–108.

Lichtner, P.C., 1994, Time-space continuum formulation of supergene enrichment and weathering of sulfide-bearing ore deposits, *in* Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Ser. 550, p. 153–170.

_____, 1996, Continuum formulation of multicomponent-multiphase reactive transport, *in* Lichtner, P. C., Steefel, C. I., and Oelkers, E. H., eds., Reactive transport in porous media: Mineral. Soc. Amer., Rev. Mineral., v. 34, p. 1–81.

Lichtner, P. C., and Waber, N., 1992, Redox front geochemistry and weathering: Theory with application to the Osamu Utsumi uranium mine: Jour. Geochem. Explorat., v. 45, p. 521–564.

Lindberg, R. D., and Runnells, D. D., 1984, Ground water redox reactions—An analysis of equilibrium state applied to Eh measurements: Science, v. 225, p. 925–927.

Luther, G. W., II, 1987, Pyrite oxidation and reduction—Molecular orbital theory considerations: Geochim. et Cosmochim. Acta, v. 51, p. 3193–3199.

_____, 1990, The frontier-molecular-orbital theory approach in geotechnical processes, *in* Stumm, W., ed., Aquatic chemical kinetics: John Wiley and Sons, Inc., New York, p. 173–198.

Lyon, J. S., Hilliard, T. J., and Bethell, T. N., 1993, Burden of gilt: Washington, DC, Mineral Policy Center.

Madigan, M. T., Martinko, J. M., and Parker, J., 1997, Brock biology of microorganisms, eighth ed.: Upper Saddle River, NJ, Prentice Hall, 986 p.

Magan, N., 1997, Fungi in extreme environments, *in* Esser, K., and Lemke, P. A., eds., 1997, The Mycota, part IV. Environmental and microbial relationships: Berlin, Springer-Verlag, p. 99–115.

Marcus, J. J., 1997, Mining environmental handbook: Effects of mining on the environment and American environmental controls on mining: London, Imperial College Press, 785 p.

Mayer, K. U., Benner, S. G., and Blowes, D. W., 1999, The reactive transport model MIN3P: Application to acid mine drainage generation and treatment—Nickel Rim mine site, Sudbury, Ontario, *in* Goldsack, D., et al., eds., Mining and the environment II, Sudbury '99, Sept. 13–17, 1999, Sudbury, Ontario, p. 145–154.

Morganwalp, D. W., and Buxton, H. T., eds., 1999, U.S. Geological Survey Toxic Substances Hydrology Program—Proc. Tech. Meeting, Charleston, South Carolina, March 8–12, 1999, v. 1: U.S. Geol. Surv. Invest. Report 99-4018A, 324 p.

Moses, C. O., Nordstrom, D. K., Herman, J. S., and Mills, A. L., 1987, Aqueous pyrite oxidation by dissolved oxygen and by ferric iron: Geochim. et Cosmochim. Acta, v. 51, p. 1561–1571.

Nordstrom, D. K., 1977, Hydrogeochemical and microbiological factors affecting the heavy metal chemistry of an acid mine drainage system: Unpubl. Ph.D. dissertation, Stanford University, 210 p.

_____, 1982, Aqueous pyrite oxidation and the consequent formation of secondary iron minerals, *in* Kittrick, J. A., Fanning, D. S., and Hossner, L. R., eds., Acid sulfate weathering: Soil Sci. Soc. Amer. Spec. Pub. No. 10, p. 37–56.

_____, 1996, Trace metal speciation in natural waters: Computational vs. analytical: Water, Air, Soil Poll., v. 90, p. 257–267.

_____, 1999, Consilience and conciliation: The need for less human impact and more humane impact, *in* Armannsson, H., ed., Geochemistry of the earth's surface: Proc. 5th Int. Symp., Reykjavik, Iceland, Aug. 16–20, 1999: Rotterdam, Balkema, p. 139–142.

Nordstrom, D. K., and Alpers, C. N., 1999, Geochemistry of acid mine waters, *in* Plumlee, G. S., and Logsdon, M. J., eds., The environmental geochemistry of mineral deposits: Soc. Econ. Geol., Rev. Econ. Geol., v. 6A.

Nordstrom, D. K., Alpers, C. N., Ptacek, C. J., and Blowes, D. W., 2000, Negative pH and extremely acidic mine waters from Iron Mountain, California: Env. Sci. Tech., v. 34, p. 245–258.

Nordstrom, D. K., and Ball, J. W., 1989, Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytic errors: Sci. Geol. Bull., v. 42, p. 269–280.

Nordstrom, D. K., and Munoz, J. L., 1994, Geochemical thermodynamics, second ed.: Oxford, Blackwell Scientific, 493 p.

Nordstrom, D. K., Jenne, E. A., and Ball, J. W., 1979a, Redox equilibria of iron in acid mine waters, *in* Jenne, E. A., ed., Chemical modeling in aqueous systems: Amer. Chem. Soc. Symp. Series 93, p. 51–80.

Nordstrom, D. K., McNutt, R. H., Puigdomenech, I., Smellie, J. A. T., and Wolf, M., 1992, Ground water chemistry and geochemical modeling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Pocos de Caldas, Minas Gerais, Brazil: Jour. Geochem. Explorat., v. 45, p. 249–288.

Nordstrom, D. K., Plummer, L. N., Langmuir, D., Busenberg, E., May, H. M., Jones, B. F., and Parkhurst, D. L., 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitations, *in* Melchior, D. C., and Bassett, R. L., eds., Chemical modeling in aqueous systems II: Amer. Chem. Soc. Symp. Series 416, p. 398–413.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

Nordstrom, D. K., Plummer, L. N., Wigley, T. M. L., Wolery, T. J., Ball, J. W., Jenne, E. A., Bassett, R. L., Crerar, D. A., Florence, T. M., Fritz, B., Hoffman, M., Holdren, G. R., Jr., Lafon, G. M., Mattigod, S. V., McDuff, R. E., Morel, F. M. M., Reddy, M. M., Sposito, G., and Thrailkill, J., 1979b, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, *in* Jenne, E. A., ed., Chemical modeling in aqueous systems: Amer. Chem. Soc. Symp. Series 93, p. 857–892.

Nordstrom, D. K., and Southam, G., 1997, Geomicrobiology of sulfide mineral oxidation, *in* Banfield, J. F., and Nealson, K. H., eds., Geomicrobiology: Interactions between microbes and minerals: Min. Soc. Amer., Rev. Mineral., v. 35, p. 361–390.

Parkhurst, D. L., 1995, User's guide to PHREEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: U.S. Geol. Surv. Water-Resource Invest. Report 95-4227, 143 p.

Parkhurst, D. L., and Appelo, C. A. J., 1999, User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geol. Surv. Water-Resource Invest. Report 99-4259.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1990, PHREEQE—A computer program for geochemical calculations: U.S. Geol. Surv. Water-Resource Invest. 80-96, revised and reprinted edition, 195 p.

Plumlee, G. S., and Logsdon, M. J., eds., 1999, The environmental geochemistry of mineral deposits: Soc. Econ. Geol., Rev. Econ. Geol., v. 6A.

Plummer, L. N., and Back, W., 1980, The mass balance approach: Applications to interpreting the chemical evolution of hydrologic systems: Amer. Jour. Sci., v. 280, p. 130–142.

Plummer, L. N., Parkhurst, D. L., and Thorstenson, D. C., 1983, Development of reaction models for groundwater systems: Geochim. et Cosmochim. Acta, v. 47, p. 665–685.

Plummer, L. N., Prestemon, E. C., and Parkhurst, D. L., 1994, An interactive code (NETPATH) for modeling *net* geochemical reactions along a flow *path*, version 2.0: U.S. Geol. Surv. Water-Resource Invest. Report 94-4169, 130 p.

Plummer, L. N., Parkhurst, D. L., Fleming, G. W., and Dunkle, S. A., 1988, A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines: U.S. Geol. Surv. Water-Resource Invest. Report 88-4153, 310 p.

Powell, A. W., and Parr, S. W., 1919, Forms in which sulfur occurs in coal: Bull. Amer. Inst. Metall. Eng., p. 2041–2049.

Ritchie, A. I. M., 1994, Rates of mechanisms that govern pollutant generation from pyritic wastes, *in* Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Ser. 550, p. 108–122.

Robbins, E. I., Rodgers, T. M., Alpers, C. N., and Nordstrom, D. K., 2000, Ecogeochemistry of the subsurface food web at pH 0–2.5 in Iron Mountain, California, USA: Hydrobiologia, in press.

Rose, A. W., and Cravotta, C. A., III, 1998, Geochemistry of coal mine drainage, *in* Brady, K. B. C., Smith, M. W., and Schueck, J., eds., Coal mine drainage prediction and pollution prevention in Pennsylvania: Harrisburg, PA, Penn. Dept. Env. Protect., p. 1-1–1-22.

Rudolfs, A., and Helbronner, A., 1922, Oxidation of zinc sulfide by microorganisms: Soil Sci., v. 14, p. 459–464.

Runkel, R. L., 1998, One-dimensional transport with inflow and storage (OTIS): A solute transport model for streams and rivers: U.S. Geol. Surv. Water-Resource Invest. Report 98-4018, 73 p.

Runkel, R. L., and Bencala, K. E., 1995, Transport of reacting solutes in rivers and streams, *in* Singh, V. P., ed., Environmental hydrology: Dordrecht, Kluwer Acad. Publ., p. 137–164.

Runkel, R. L., Bencala, K. E., Broshears, R. E., and Chapra, S. C., 1996, Reactive solute transport in streams 1. Development of an equilibrium-based model: Water Resources Res., v. 32, p. 409–418.

Runkel, R. L., Bencala, K. E., McKnight, D. M., and Kimball, B. A., 1999, Reactive solute transport in streams –A surface complexation approach for trace metal sorption: Water Resources Res., v. 35, p. 3829–3840.

Runkel, R. L., McKnight, D. M., Bencala, K. E., and Chapra, S. C., 1996, Reactive solute transport in streams 2. Simulation of a pH modification experiment: Water Resources Res., v. 32, p. 419–430.

Sand, W., Rohde, K., Sobotke, B., and Zenneck, C., 1992, Evaluation of *Leptospirillum ferrooxidans* for leaching: Appl. Env. Microbiol., v. 58, p. 85–92.

Scala, G., Mills, A. L., Moses, C. O., and Nordstrom, D. K., 1982, Distribution of autotrophic Fe and S-oxidizing bacteria in mine drainage from sulfide deposits measured with the FAINT assay [abs.]: Abstr. Amer. Soc. Microbiol., Ann. Mtg.

Scharer, J. M., Nicholson, R. V., Halbert, B., and Snodgrass, W. J., 1994, A computer program to assess acid generation in pyritic tailings, *in* Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Ser. 550, p. 132–152.

Schecher, W. D., and Driscoll, C. T., 1987, An evaluation of uncertainty associated with aluminum equilibrium calculations: Water Resour. Res., v. 23, p. 525–534.

———, 1988, An evaluation of the equilbrium calculations within acidification models: The effect of uncertainty in measured chemical components: Water Resour. Res., v. 24, p. 533–540.

Schippers, A., Jozsa, P.-G., and Sand, W., 1996, Sulfur chemistry in bacterial leaching of pyrite: Appl. Env. Microbiol., v. 62, p. 3424–3431.

Downloaded by [Tshwane University of Technology] at 07:00 29 January 2014

Schleper, C., Puhler, G., Kuhlmorgen, B., and Zillig, W., 1995, Life at extremely low pH: Nature, v. 375, p. 741–742.

Schmiermund, R. L., and Drozd, M. A., 1997, Acid mine drainage and other mining-influenced waters (MIW), in Marcus, J. J., ed., Mining environmental handbook, p. 599–617.

Schrenk, M. O., Edwards, K. J., Goodman, R. M., Hamers, R. J., and Banfield, J. F., 1998, Distribution of *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*: Implications for generation of acid mine drainage: Science, v. 279, p. 1519–1521.

Sergeeva, E. I., Suleimenov, O. M., Evstigneev, A. V., and Khodakovsky, I. L., 1999, Solubility of hematite, Fe_2O_3 (cr, α) at 200°C and the standard entropy of Fe^{3+} ion in aqueous solution: Geochem. Int. v. 37, p. 1097–1107.

Sokolova, G. A., and Karavaiko, G. I., 1964, Physiology and geochemical activity of Thiobacilli: Moscow, Nauka, 282 p. (in Russian).

Stipp, S. L.,1990, Speciation in the Fe(II)-Fe(III)-SO_4-H_2O system at 25°C: Env. Sci. Tech., v. 24, p. 699–706.

Suzuki, I., 1994, Sulfur-oxidizing enzymes: Method. Enzymol., v. 243, p. 455–462.

Suzuki, I., Chan, C. W., and Takeuchi, T. L., 1994, Oxidation of inorganic sulfur by *Thiobacilli*, *in* Alpers, C. N., and Blowes, D. W., eds., Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Series 550, p. 60–67.

To, B. T., Nordstrom, D. K., Cunningham, K. M., Ball, J. W., and McCleskey, R. B., 1999, New method for the determination of dissolved Fe(III) concentrations in acid mine waters: Env. Sci. Tech., v. 33, p. 807–813.

Waber, N., 1992, The supergene thorium and rare-earth element deposit at Morro do Ferro, Poços de Caldas, Minas Gerais, Brazil: Jour. Geochem. Explorat., v. 45, p. 113–158.

Waber, N., Schorscher, H. D., and Peters, T., 1992, Hydrothermal and supergene uranium mineralization at the Osamu Utsumi mine, Poços de Caldas, Minas Gerais, Brazil: Jour. Geochem. Explorat., v. 45, p. 53–112.

Wakao, N., Nagasawa, N., Matsuura, T., Matsukura, H., Matsumoto, T., Hiraishi, A., Sakurai, Y., and Shiota, H., 1994, *Acidiphilium multivorum sp. nov.*, an acidophilic chemoorganotrophic bacterium from pyritic acid mine drainage: Jour. Gen. Appl. Microbiol., v. 40, p. 143–159.

Wakao, N., Yokoi, N., Isoyama, N., Hiraishi, A., Shimada, K., Kobayashi, M., Kise, H., Iwaki, M., Itoh, S., Takaichi, S., and Sakurai, Y., 1996, Discovery of natural photosynthesis using Zn-containing bacteriochlorophyll in an aerobic bacterium *Acidiphilium rubrum*: Plant Cell Physiol., v. 37, p. 889–893.

Walton-Day, K., Runkel, R. L., Kimiball, B. A., and Bencala, K. E., 1999, Application of the route-transport models OTIS and OTEQ and implications for remediation in a watershed affected by acid mine drainage, Cement Creek, Animas River Basin, Colorado, *in* Morganwalp, D. W., and Buxton, H. T., eds., U.S. Geological Survey Toxic Substances Hydrology Program–Proc. Tech. Meeting, Charleston, South Carolina, March 8–12, 1999, v. 1: U.S. Geol. Surv. Invest. Report 99-4018A, p. 37–46.

Williamson, M. A., and Rimstidt, J. D., 1993, The rate of decomposition of the ferric-thiosulfate complex in acidic aqueous solutions: Geochim. et Cosmochim. Acta, v. 57, p. 3555–3561.

Wunderly, M. D., Blowes, D. W., Frind, E. O., and Ptacek, C. J., 1996, Sulfide mineral oxidation and subsequent reactive trasnport of oxidation products in mine tailings impoundments: A numerical model: Water Resource Res., v. 32, p. 3173–3187.

Xu, Y., and Schoonen, M. A. A., 1995, The stability of thiosulfate in the presence of pyrite in low-temperature aqueous solutions: Geochim. et Cosmochim. Acta, v. 59, p. 4605–4622.

Xu, Y., Schoonen, M. A. A., Nordstrom, D. K., Cunningham, K. M., and Ball, J. W., 1998, Sulfur geochemistry of hydrothermal waters in Yellowstone National Park: I. The origin of thiosulfate in hot spring waters: Geochim. et Cosmochim. Acta, v. 62, p. 3729–3743.

Young, J. E., 1992, Mining the earth: Worldwatch Institute, Worldwatch Paper 109, 53 p.

Zajic, J. E., 1969, Microbial biogeochemistry: New York, Academic Press, 345 p.

Zhang, J.-Z., and Millero, F. J., 1993, The products from the oxidation of H_2S in seawater: Geochim. et Cosmochim. Acta, v. 57, p. 1705–1718.

_____, 1994, Kinetics of oxidation of hydrogen sulfide in natural waters, *in* Alpers, C. N., and Blowes, D. W., eds., Environmental geochemistry of sulfide oxidation: Amer. Chem. Soc. Symp. Series 550, p. 393–409.