

Chapter 14

GEOCHEMICAL MODELING OF WATER-ROCK INTERACTIONS IN MINING ENVIRONMENTS

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INTRODUCTION

Geochemical modeling is a powerful tool for evaluating geochemical processes in mining environments. Properly constrained and judiciously applied, modeling can provide valuable insights into processes controlling the release, transport, and fate of contaminants in mine drainage. This chapter contains

- 1) an overview of geochemical modeling,
- 2) discussion of the types of models and computer programs used,
- 3) description of a procedure for screening water analyses for modeling input, and
- 4) examples of the application of modeling for interpreting geochemical processes in mining environments.

Three general strategies in current use to interpret water-rock interactions are statistical analysis, “inverse” modeling, and “forward” modeling. Multivariate correlation analysis, factor analysis, cluster analysis, and other statistical techniques can group water-chemistry data into sets that may relate to hydrogeochemical processes (Drever, 1988; Puckett and Bricker, 1992). In the field of geochemical exploration, statistical analysis is used widely to treat large data sets of rock and sediment chemistry (e.g., Garrett, 1989). No physical or chemical principles are involved directly in these statistical treatments, hence they are not considered further in this chapter. Nevertheless, statistical analysis can be a useful tool in organizing complex geochemical data for interpretation.

Inverse modeling uses field data to interpret water analyses in terms of water-rock interactions. Chemical and isotopic data for water and rocks along a known flow path are used to test hypotheses regarding geochemical processes by mass-balance considerations. Several possible combinations of geochemical reactions are considered simultaneously to narrow the choice to a minimum number of feasible reactions. Although inverse modeling is based primarily on mass balance and mineral compositions without any thermodynamic or kinetic data, it can be further constrained by detailed mineralogic information, by mineral saturation states determined with speciation calculations, and by a general knowledge of kinetic rates of mineral dissolution and precipitation.

Forward modeling predicts or simulates the consequences of particular geochemical reactions given assumptions regarding the initial state of a system and its boundary conditions. Forward models attempt to answer questions such as “What would be the result if a rock of composition A were to react with a water of composition B?” From user-supplied reactions with associated thermodynamic data and assumptions regarding equilibrium, the consequences of specific geochemical reactions can be computed.

Reactions that may be modeled include mineral dissolution and precipitation, oxidation-reduction, gas evolution, and sorption. Forward geochemical models have been combined with hydrologic models that incorporate physical transport processes to create “coupled reaction-transport” models. Forward geochemical models can be used in mining environments for a variety of applications. Examples include estimating pre-mining water-quality conditions (Runnells et al., 1992), determining optimal conditions and reagent requirements for water treatment, predicting consequences of remediation alternatives, and predicting downstream water-quality conditions resulting from mining and remediation.

Modeling is not an exact science and its application has numerous pitfalls, uncertainties, and limitations. As a precautionary note we first discuss the philosophy behind modeling, a theme to which we return at the end of the chapter. Next, we describe the screening of water analyses and the formulation of preliminary hypotheses using ion plots. A fundamental aspect of most modeling computations is the aqueous speciation calculation, which should be done only with water analyses that survive the scrutiny of the screening procedures. Following a section on aqueous speciation, we describe inverse modeling and forward modeling, with brief discussions of advanced forward models that simulate sorption, solid solutions, and coupled reaction-transport.

MODELING PHILOSOPHY AND PERSPECTIVES

Scientific models are evolving ideas, ways of capturing into communicable language certain aspects of physical reality, embodiments of hypotheses (Konikow and Bredehoeft, 1992), and ways of looking at the world; they are best thought of as guides to our thinking. We adopt the following definition for a model: “a *testable* idea, hypothesis, theory, or combination of theories that provides...insight or a new interpretation of an old problem.” (Nordstrom, 1994). A chemical model is a theoretical construct that permits the calculation of physicochemical processes and properties of substances (such as thermodynamic, kinetic, and quantum mechanical properties); a geochemical model is a chemical model developed for geologic systems (Nordstrom, 1994).

The goals of modeling are to improve and refine a conceptual model (Greenwood, 1989). A model is not reality, nor is it a reliable, correct, or valid representation of reality. A model is not a computer code, *per se*. A conceptual model begins as an idea that has logical and testable consequences. It can sometimes be translated into a mathematical model; mathematical models can usually be converted into numerical models which can then be pro-

grammed as computer codes. The resulting computer programs may include chemical and numerical models, but are not considered geochemical models until applied to a specific geologic or geochemical system. Hence, we have come full circle back to a revised conceptual model after a formal translation (mathematics), and an approximate solving routine (numerical methods), using an electronic managing and accounting device (the computer).

The geochemical model itself can never be proven to be true nor shown to be valid in an absolute sense; the computed results are only valuable insofar as they improve or disprove the original conceptual model (Nordstrom, 1994). Hazardous waste engineers, managers, and regulators need to know about the reliability of models and use the term "model validation" to refer to provisional acceptance according to predefined criteria. However, the concept of "model validation" remains a highly controversial and contentious area of debate. Recent discussions (e.g., Konikow and Bredehoeft, 1992; Oreskes et al., 1994; Nordstrom, 1994) contend that both hydrologic and geochemical models cannot be validated (i.e., proven to be true or valid) *per se* because the models are merely approximations of reality intended to test the implications of hypotheses. The term "model verification" is most often used in the sense of comparing the results of complex numerical codes to analytical solutions (e.g., Lichtner, 1993) and does not relate to the issue of whether or not the model or analytical expression provides an adequate description of the system under consideration. Models can disprove but never prove hypotheses. Even when a prediction by a model is shown later by independent means to have been correct, this does not indicate that the model (or set of hypotheses) will be correct when applied to other systems; it may have been right for the wrong reasons, or somehow incomplete or inadequate in ways that were not tested.

Why do earth scientists make models? Models help guide our thinking, opening up new possibilities, insights, and hypotheses that might not have been possible without them. Models are tools that increase our understanding and are not ends in themselves. Models are necessarily limited and approximate. In science, they are often on the forefront of knowledge and may contain huge uncertainties. They are continually revised and updated as more information becomes available and as more ideas are tested. Consequently, the knowledge a person brings to bear on a problem is far more important than the sophistication of a certain computer program in determining the usefulness of a modeling result. Knowledge and experience with both practical and theoretical hydrogeochemistry as well as general knowledge of hydrologic and geologic processes are essential for successful geochemical modeling.

With an appropriate sensitivity to the inherent limitations and uncertainties of geochemical models and modeling, it is possible to use the modeling approach to gain considerable insight into processes that may be occurring at a contaminated mine site, to test hypotheses regarding major controls on the mobility of selected contaminants, and to assess the probable consequences of various remediation strategies without costly field experiments.

DATA SCREENING AND ION PLOTS

When using water analyses as a basis for geochemical modeling, the data must be carefully screened. Major ion concentrations should be determined well enough that electrical charge imbalances are minimized. One method for computing charge imbalance

(CI) is the following formula (modified from Ball and Nordstrom, 1991):

$$CI (\%) = \frac{[\sum_i m_i^+ z_i^+ - \sum_i m_i^- z_i^-] * 100}{[\sum_i m_i^+ z_i^+ + \sum_i m_i^- z_i^-] / 2} \quad [1]$$

where m_i^+ and m_i^- are the molalities of cation and anion species, respectively, and z_i^+ and z_i^- represent the charge on each species. Water samples with CI values less than 10% are preferred as input for geochemical modeling.

Several other tests of analytical quality should have been completed by the analysts in the laboratory according to accepted quality assurance/quality control (QA/QC) procedures, including spiked recoveries, standard additions, replicate analyses to determine precision, alternate standards, alternate methods, standard reference materials, tests for matrix interferences, and relevant statistical tests (Elving and Kienitz, 1978). Numerous standard reference materials that have undergone interlaboratory comparisons are available to provide the basis for accuracy estimates. From these results, analytical errors on individual constituents can be derived for error propagation and sensitivity analysis as part of geochemical modeling (e.g., Nordstrom and Ball, 1989).

Less common but very useful techniques for screening water analyses include comparisons of measured with calculated total dissolved solids (TDS) and measured with calculated specific conductance. Furthermore, because sulfate is usually the dominant anion in acid mine waters, sulfate concentrations should correlate very well with both TDS and specific conductance. Ball and Nordstrom (1989) used this technique to evaluate mine water analyses from the Leviathan mine, California. Because sulfate analyses are often the least precise and least accurate of the major ions, these correlation tests can be very useful in identifying erroneous data. In areas where multiple samples have been taken over a period of time, time-series plots of concentrations and of ratios of certain constituents can be useful in identifying erroneous data or contaminated samples.

Analytical data for water samples used in speciation or mass-balance computations must be of high accuracy and precision. Relatively small errors in the analytical data can be exaggerated when propagated to produce results such as saturation indices or mass-balance coefficients. Errors in analytical data can be minimized by several procedures:

- 1) careful attention to water sample acquisition, field measurements, and proper filtration and preservation procedures,
- 2) appropriate choice of analytical procedures for the particular sample compositions, including correction or prevention of interferences, and
- 3) appropriate tests of analytical accuracy and precision by standard additions, alternative methods, and analysis of blanks, duplicates, and replicate samples according to standard QA/QC protocols.

It is important to choose analytical methods with sufficiently low detection limits for dissolved constituents. This is especially true for constituents that can be important complexing agents for trace elements despite low concentrations, e.g., PO_4 and F if concerned with controls on Al or U solubility.

Standard errors in analytical data should be clearly identified for purposes of error propagation when performing a sensitivity analysis. The appropriate number of significant figures should be

used for each analytical result, and the uncertainty in each analysis should be known, including errors introduced by dilution. The uncertainty on pH measurements should be based on the success in reproducing expected values for standard buffers that bracket the unknown pH value. Field values of pH are often reported with three significant figures; however, this level of precision can be obtained only if a check of standards is made both before and after the unknown measurement, and the standard buffers are within 0.05 units of the expected values. Uncertainties on laboratory analytical data range generally between 2 and 25% of the amount present, depending on numerous factors including the method used, the amount and number of dilutions, and proximity to the detection limit.

Iron species are commonly the dominant cations in acid mine waters. Therefore, analytical determinations of Fe(II) and Fe(III) as distinct constituents must be obtained on acid mine waters so that the charge balance and speciation calculations are reasonable. Standard methods for this procedure involve analysis of Fe(II) and Fe(total) by spectrophotometry using a ferroin complexing agent such as ferrozine (Stookey, 1970) or dipyridine (Brown et al., 1970), with calculation of Fe(III) by difference. It is strongly recommended that the same analytical method be used for both Fe(II) and Fe(total) so that analytical errors are minimized; in this way, systematic errors should cancel out in computation of Fe(III) concentrations. A new method (To et al., 1999) allows direct determination of Fe(III). There is often an excellent correlation between the activity ratio of Fe(III)/Fe(II) and the reduction-oxidation (redox) potential (Eh or pe) in iron-rich acid mine waters (e.g., Nordstrom et al., 1979a; Ball and Nordstrom, 1989). However, the field measurement of redox potential should be used as a check, rather than as a substitute, for analytical determination of both Fe(II) and Fe(III).

After the data are screened, simple ion plots are often helpful in formulating hypotheses concerning geochemical processes. For example, in a drainage system containing acid mine waters, any constituent which correlates strongly with sulfate is likely to be transported as a relatively conservative or nonreacting solute, analogous to chloride in most circum-neutral waters. Therefore, a plot of different constituents against sulfate may help to distinguish conservative from nonconservative constituents during downstream transport. Dissolved aluminum is a constituent which may exhibit either conservative or nonconservative behavior, depending on pH (Nordstrom and Ball, 1986). Other examples of the use of ion plots can be found in papers by Nordstrom et al. (1989, 1992) and by Plummer et al. (1990).

AQUEOUS SPECIATION MODELING

Aqueous speciation is the distribution of dissolved constituents among various aqueous complexes and individual free ions. The calculation of speciation is fundamental to most geochemical models and is used routinely to interpret water analyses for which all major ions have been determined. The speciation results are needed to compute the degree of saturation of an aqueous solution with respect to various minerals.

Speciation calculations can provide some bounding constraints on water-rock interactions but mostly they indicate which reactions are possible thermodynamically, not necessarily which reactions are likely to occur. Kinetic barriers may inhibit many mineral precipitation or dissolution reactions from taking place. For example, many surface waters and most shallow ground waters

have concentrations of $\text{SiO}_{2(\text{aq})}$ more than 6.3 mg/l, which is the equilibrium solubility of quartz at 25°C (Fournier and Potter, 1982). Despite quartz supersaturation for these waters, quartz does not form readily below 100°C (Fournier and Potter, 1982) because of very slow precipitation rates. Amorphous silica, which has an equilibrium silica solubility of about 120 mg/l at 25°C (Fournier and Rowe, 1977), tends to provide an upper limit to aqueous silica concentrations in natural waters; however, most low-temperature, non-geothermal waters have dissolved silica concentrations less than about 30 mg/l (Hem, 1985), suggesting control by other forms of crystalline silica such as chalcedony or cristobalite, or by a poorly-crystalline-to-amorphous clay mineral such as halloysite (Hem et al., 1973). The relations in the $\text{SiO}_2\text{-H}_2\text{O}$ system illustrate the complexity of low-temperature water-rock interactions, in which metastable phases may control or influence solubility because of kinetic barriers affecting thermodynamically stable phases.

Numerous minerals simply do not reach solubility equilibrium in natural waters at temperatures of 0–100°C. Minerals with slow precipitation rates are unlikely to control the aqueous concentrations of the relevant ions. Some knowledge of mineral reaction rates can be very helpful in the interpretation of the chemistry of natural waters using aqueous speciation and mineral saturation calculations (see Nordstrom and Alpers, 1999).

Quantitative knowledge of aqueous speciation is important for evaluating bioavailability and toxicity because certain aqueous species of a given element are much more toxic than others (see Smith and Huyck, 1999). For example, $\text{Cu}^{2+}_{(\text{aq})}$ is considered more toxic to fish than $\text{CuCO}_3^0_{(\text{aq})}$ or other complexed forms of copper (Hodson et al., 1979). Other useful results from speciation modeling include the elemental molalities needed as input for mass-balance and reaction-path models and the aqueous activities of individual ions. Correlation plots of aqueous activity values and activity ratios can be used to evaluate the stoichiometry of a precipitating phase that controls solubility (see Nordstrom and Alpers, 1999).

Speciation calculation

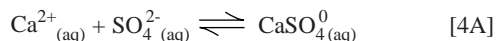
Speciation and mineral saturation are calculated by a sequence of steps containing both thermodynamic quantities and numerical approximations. The overall calculation seeks a minimum in the Gibbs free energy of the system. Although several techniques have been used to solve free energy minimization, they all seek a numerical solution for the combined non-linear set of mass-balance and mass-action equations that define the problem. Mass-balance equations of the form

$$m_{T(A)} = \sum_i m_{i(A)} \quad [2]$$

express the conservation of mass for all species that have a common component, where $m_{T(A)}$ is the total dissolved molality of a component A, and $m_{i(A)}$ is the molality of the i^{th} species containing the Ath component. For example, the mass-balance equation for calcium might be

$$m_{\text{CaT}} = m_{\text{Ca}^{2+}_{(\text{aq})}} + m_{\text{CaHCO}_3^+_{(\text{aq})}} + m_{\text{CaCO}_3^0_{(\text{aq})}} + m_{\text{CaSO}_4^0_{(\text{aq})}} \quad [3]$$

The mass-action equations express the equilibrium established among species by the equilibrium constant, K . For example, the association reaction for the CaSO_4^0 ion pair is



for which the mass-action equation is:

$$K_{\text{CaSO}_4^0_{(\text{aq})}}^{25^\circ\text{C}} = \frac{a_{\text{CaSO}_4^0_{(\text{aq})}}}{a_{\text{Ca}^{2+}_{(\text{aq})}} a_{\text{SO}_4^{2-}_{(\text{aq})}}} = 10^{2.30} \quad [4B]$$

The mass-balance and mass-action equations contain known quantities, and the condition of electroneutrality (charge balance) represents a known quantity, leaving the concentrations and activities of the individual aqueous species as the unknown quantities. For aqueous speciation calculations, the system is usually over-determined by one degree of freedom (Merino, 1979), so that finding a solution is a tractable problem. The distribution of aqueous species among free ions and complexes in the aqueous phase is assumed to be at homogeneous equilibrium.

Most (but not all) geochemical modeling codes assume at the start of the calculation that the total dissolved concentration is equivalent to the free ion concentration, i.e., for calcium

$$m_{\text{Ca}_{\text{T(aq)}}} = m_{\text{Ca}^{2+}_{(\text{aq})}} \quad [5]$$

For ion association models, the ionic strength, I , is computed from

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad [6]$$

where m_i and z_i are the molality and charge, respectively, of the i^{th} ion. The ionic strength is then used to calculate the activity coefficient of each ion, γ_i , according to the extended Debye-Hückel equation, the Davies equation, or a Brønsted-Guggenheim equation (e.g., Nordstrom and Munoz, 1994). The activity of each ion is then computed with the equation

$$a_i = \gamma_i m_i \quad [7]$$

After one iteration through a numerical approximation, a first estimate of speciation is made. The Newton-Raphson and continued-fraction methods are commonly used to find a numerical solution. An application using each of these methods is described by Nordstrom and Munoz (1994).

An alternative approach to calculating activity coefficients is with the Pitzer equations (Pitzer, 1973, 1979, 1987). This approach is known as the specific-ion interaction method because all ions are assumed to interact to some degree and these interactions are incorporated into terms that are added to an electrostatic Debye-Hückel term. The power of this approach is that activity coefficients can be fit to experimental data for ionic strengths up to 10 molal and higher in some chemical systems, whereas with the ion-association model, good fits to experimental data are limited to considerably lower ionic strengths.

Application of ion-association models to solutions with ionic strengths greater than about 0.1 molal can only be obtained with a linear term added on to the extended Debye-Hückel equation, i.e., a Brønsted-Guggenheim model. Such an expression can be considered a hybrid between the extended Debye-Hückel equation and the Pitzer approach. The hybrid model has been used in Sweden for many years with considerable success in the interpretation of aqueous electrolyte data (Grenthe et al., 1992).

There are two main drawbacks with application of the Pitzer approach to acid mine waters. One is that insufficient data are available to model the activity coefficients for all the principal trace elements found in acid mine waters. Considerable progress has been made on deriving the interaction parameters for some constituents in acid mine waters, specifically for the systems $\text{Fe(II)}\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Reardon and Beckie, 1987), $\text{Al-SO}_4\text{-H}_2\text{O}$ (Reardon, 1988), $\text{Ni-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Reardon, 1989), and $\text{PbSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Paige et al., 1992). However, interaction parameters for systems with Fe(III) , As(III/V) , Cu , and Zn are needed for a complete description of highly concentrated acid mine waters, and the temperature dependence of some interaction parameters remain uncertain or unknown (C. Ptacek and D. Blowes, written commun., 1995). The other drawback to the Pitzer method is the necessity to refit the interaction parameters for all elements whenever new data are added, so that consistency is maintained.

Redox reactions are important in the geochemistry of acid mine waters, yet most geochemical modeling codes assume erroneously that redox equilibrium is maintained. The redox chemistry must be determined by analyzing water samples for the individual redox states of elements such as Fe (II and III) and As (III and V) . Aqueous redox reactions and their rates are not understood well enough to assume any particular ratio of redox species based on platinum electrode measurements. Disequilibrium among redox couples is the rule not the exception (e.g., Lindberg and Runnells, 1984).

Once the speciation calculation has been made then the ion activity product (IAP) can be compared to the solubility product constant (K_{sp}) to test for mineral saturation. The saturation index, SI, is computed for each mineral in the data base from

$$\text{SI} = \log \left(\frac{\text{IAP}}{K_{\text{sp}}} \right) \quad [8]$$

The SI for an aqueous solution with respect to a particular mineral describes the thermodynamic tendency of that solution to precipitate or to dissolve that mineral. Positive values of SI indicate supersaturation and the tendency of the water to precipitate that mineral. Negative values of SI indicate undersaturation and the tendency of the water to dissolve a certain mineral. A value of $\text{SI} = 0$ indicates apparent equilibrium, a balance between the thermodynamic driving forces of dissolution and precipitation. Examples of SI values and their interpretation for various minerals in mine drainage environments are given in a later section of this chapter and in the chapter by Nordstrom and Alpers (1999).

Input data

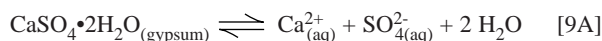
Two types of input data are used with computer codes that compute aqueous speciation: (1) analytical data on the water com-

position, and (2) thermodynamic data for aqueous species and minerals. Some computer programs have the thermodynamic data resident in the code or in an accessible data table; other programs require the thermodynamic data to be user-supplied. Regardless of the format, the thermodynamic data should always be considered as input data for which the reliability is the responsibility of the user.

Most computer programs that perform speciation modeling require input data for pH, temperature, and major ion concentrations as minimum parameters. For acid mine waters, dissolved oxygen, alkalinity (for samples with pH > 4.2), specific conductance, liquid density, and Eh (or pe) are also important input parameters, along with trace element concentrations of interest. Other aspects of analytical data evaluation were discussed in the previous section on Data Screening and Ion Plots.

Thermodynamic input data can be in the form of Gibbs free energies, enthalpies, entropies, heat capacities, and molar volumes for individual species that participate in a given reaction, or can be in the form of an equilibrium constant for the reaction (K) along with values or expressions for computing the enthalpy and heat capacity of reaction for determining the temperature dependence of K, and molar volumes of reaction for determining the pressure dependence. Some codes accept data in both forms. Some codes contain analytical expressions for log Ks of reactions as a function of temperature.

For example, the dissolution of gypsum in pure water is described by the reaction:



$$K_{\text{sp,gypsum}}^{25^\circ\text{C}} = \frac{a_{\text{Ca}_{(\text{aq})}^{2+}} a_{\text{SO}_{4(\text{aq})}^{2-}} a_{\text{H}_2\text{O}}^2}{a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(\text{gypsum})}}} = 10^{-4.58} \quad [9B]$$

For solids close to end-member composition, the solid activity term in the denominator can be set equal to 1. This approximation has been shown to be reasonable for gypsum from a field site in Arizona (Glynn, 1991a) but is not generally applicable to other solids of variable composition, as discussed in a later section on solid solutions. Setting the activity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in gypsum equal to 1 and taking the logarithm of equation [9B] gives

$$\log K_{\text{sp,gypsum}}^{25^\circ\text{C}} = \log a_{\text{Ca}_{(\text{aq})}^{2+}} + \log a_{\text{SO}_{4(\text{aq})}^{2-}} + 2 \log a_{\text{H}_2\text{O}} = -4.58 \quad [9C]$$

The association reaction for the CaSO_4^0 ion pair was given in equation [4A] and the corresponding mass action equation in equation [4B]. Taking the logarithm of equation [4B],

$$\log K_{\text{CaSO}_4}^{25^\circ\text{C}} = \log a_{\text{CaSO}_4^0} - \log a_{\text{Ca}_{(\text{aq})}^{2+}} - \log a_{\text{SO}_{4(\text{aq})}^{2-}} = 2.30 \quad [10]$$

For gypsum dissolution (equations [9A], [9B], and [9C]) in program WATEQ4F (Ball and Nordstrom, 1991), the temperature dependence of the equilibrium constant is calculated by the equation

$$\log K_{\text{sp,gypsum}} = 68.2401 - \frac{3221.51}{T} - 25.0627T \quad [11]$$

where T is temperature in Kelvins. For the ion association reaction (equations [4A], [4B], and [10]) the temperature dependence of the equilibrium constant is calculated using a value for $\Delta H_r^0 = 5.50 \text{ kJ} \cdot \text{mol}^{-1}$ in the Van't Hoff equation

$$\frac{-2.303 \, d(\log K_r)}{dT} = \frac{\Delta H_r^0}{RT^2} \quad [12]$$

Finding thermodynamic data for all water-mineral reactions of interest is a considerable challenge. Ideally, an internally consistent set of thermodynamic data would be preferred but this is not likely to be available. It is possible, however, to have a limited set of tolerably inconsistent thermodynamic data, in other words, a set in which the propagated errors in thermodynamic data do not significantly affect the speciation calculations or the resulting mineral saturation indices. The beginning of such a set can be found in Appendix D of Nordstrom and Munoz (1994). Programs that use the Pitzer equations tend to have a higher degree of internal consistency because it is a necessary consequence of deriving the fitting parameters. Thermodynamic data may not exist for many species of interest, especially trace-element association constants and mineral solubility constants. Sometimes these can be estimated (see Langmuir, 1979; Helgeson et al., 1981; Sverjensky, 1987; Shock and Helgeson, 1988, 1990; Shock et al., 1989, 1992; Shock and Koretsky, 1993). With or without estimation, the modeler is responsible for checking the adequacy of the critical stability constants for the geochemical system being studied.

Even if internal consistency were achieved, it would not be a guarantee of reliable data. Internal consistency simply refers to a consistent set of data according to the following criteria (Stipp et al., 1993; Nordstrom and Munoz, 1994):

- 1) Fundamental thermodynamic relationships (the basic laws and their consequences) are obeyed.
- 2) Common scales are used for temperature, energy, atomic mass, and fundamental physical constants.
- 3) Conflicts and inconsistencies among measurements are resolved.
- 4) An appropriate mathematical model is chosen to fit all temperature- and pressure-dependent data.
- 5) An appropriate aqueous chemical model is chosen to fit all aqueous solution data.
- 6) An appropriate choice of standard states is made and applied to all similar substances.
- 7) An appropriate starting point is selected for the development of a thermodynamic network.

As more of these criteria are met, greater consistency is achieved. With greater consistency, the probability that the data are reliable becomes greater, but there is still a finite probability that the data are incorrect.

The general absence of a sufficiently consistent and comprehensive thermodynamic data base increases the need for sensitivity analyses to be performed for those data that are critical to a geochemical interpretation. This aspect will be discussed further in the next section.

Interpretation of output

Aqueous speciation calculations for acid mine waters commonly reveal considerable complexation of metals with sulfate. For examples, we consider four acid mine water analyses that cover a range in pH values from about 5.0 to 0.5, with concentrations of sulfate from 206 to 118,000 mg/l and of iron from 4.7 to 20,300 mg/l. Complete analyses of the four samples are given in Table 14.1.

Analyses AMD-A and -B in Table 14.1 are for water samples from the Leviathan mine, which exploited an epithermal deposit containing elemental sulfur and cryptocrystalline pyrite located in Alpine County, California, near the Nevada border (Ball and Nordstrom, 1989). Analysis AMD-C is for combined discharge from the Hornet and Richmond mines, at Iron Mountain, in Shasta County, California (Nordstrom, 1977). At Iron Mountain, the oxidation of massive pyrite at or above the water table within a rhyolitic country rock having little neutralizing capacity has produced a concentrated acid mine water in which iron (II) is the dominant cation followed by iron (III), aluminum, zinc, magnesium, and copper. Analysis AMD-D in Table 14.1 represents an extreme case of "ultra-acid" water that flows from the Richmond mine at Iron Mountain, California (Alpers and Nordstrom, 1991); such extreme metal and sulfate concentrations are encountered only rarely, but serve to demonstrate the compositional limits of the ion-association modeling method.

Speciation of copper, sulfate, aluminum, and iron for samples AMD-A, -B, -C, and -D, computed with the computer program WATEQ4F (Ball and Nordstrom, 1991), is shown graphically as pie charts on Figure 14.1. With decreasing pH and increasing sulfate concentration, the degree of metal complexation with sulfate increases even though the ratio of sulfate to metals decreases. For the simple case of copper, the proportion of free $\text{Cu}^{2+}_{(\text{aq})}$ decreases from 85.5% in AMD-A to 43.4% in AMD-D because of the formation of the $\text{CuSO}_4^0_{(\text{aq})}$ ion pair. Similarly, the distribution of the free $\text{SO}_4^{2-}_{(\text{aq})}$ ion changes from 83.4% in AMD-A to 8.3% in AMD-D, with numerous metal-sulfate complexes competing for sulfate at the higher concentrations; the bisulfate ion ($\text{HSO}_4^-_{(\text{aq})}$) and metal-bisulfate complexes also compete for sulfate at pH values less than about 2. In addition to simple metal-sulfate ion pairs, double-sulfate complexes such as $\text{Zn}(\text{SO}_4)_2^{2-}_{(\text{aq})}$, $\text{Al}(\text{SO}_4)_2^-_{(\text{aq})}$ and $\text{Fe}(\text{SO}_4)_2^-_{(\text{aq})}$ become more abundant with higher sulfate concentrations.

Chemical equilibrium between sulfate and bisulfate ions is expressed by the reaction



The log K for reaction [13] is 1.99 at 25°C (Nordstrom et al., 1990), indicating that activities of sulfate and bisulfate are equal at pH values of about 2.0. At pH values less than 2.0, the bisulfate ion dominates sulfate equilibria, as in samples AMD-C and -D.

Although metal-bisulfate complexes for aluminum, zinc, and magnesium are in the database of WATEQ4F used in the computations, only the iron-bisulfate species $\text{Fe}^{\text{II}}\text{HSO}_4^+$ and $\text{Fe}^{\text{III}}\text{HSO}_4^{2+}$ are significant contributors to sulfate speciation in these samples (Fig. 14.1).

TABLE 14.1—Chemical data for four acid mine water samples. [Samples AMD-A and AMD-B correspond respectively to samples 82WA109 and 82WA110 from the Leviathan mine, Alpine County, California (Ball and Nordstrom, 1989); sample AMD-C corresponds to sample 76WA103 from the Hornet and Richmond mines, Iron Mountain, Shasta County, California (Nordstrom, 1977); sample AMD-D corresponds to sample 90WA103 from the Richmond mine at Iron Mountain (Alpers and Nordstrom, 1991).]

	AMD-A	AMD-B	AMD-C	AMD-D
Sample number	82WA109	82WA110	76WA103	90WA103
Water temperature (°C)	16.0	19.5	24.0	34.8
pH (field)	4.9	3.25	1.10	0.48
Constituent	(mg/l)			
Ca	44.7	82.2	240	183
Mg	13.5	23.6	720	821
Na	8.6	11.8	79.0	251
K	3.21	4.57	107	261
Cl	1.0	1.1	2.0	---
SO ₄	206	483	50,000	118,000
HCO ₃	---	0	0	0
SiO ₂	42.6	46.4	140	165
Ba	0.042	0.048	---	0.068
Al	5.06	19.8	1,410	2,210
F	0.30	0.52	2.0	---
Fe (total)	4.72	18.4	11,000 ³	20,300
Fe (II)	4.44	9.01	7,820	18,100
Fe (III) ²	0.28	9.39	3,180	2,200
Mn	1.26	3.04	11.0	17.1
Cu	0.09	0.23	360	290
Zn	0.04	0.15	1,860	2,010
Cd	.004	0.01	14.0	15.9
As (total)	0.01	0.02	---	56.4
As (III)	---	---	---	8.14
As (V) ⁴	---	---	---	48.3

¹---, not determined.

²Fe (III) computed as difference of Fe (total) and Fe (II).

³Value uncertain by up to 15%.

⁴As (V) computed as difference of As (total) and As (III).

Ferric iron and aluminum are similar in that both substances form trivalent free cations. However, iron and aluminum speciation differ to a large degree because the hydrolysis of ferric iron takes place at a much lower pH than that of aluminum. As discussed by Nordstrom and Alpers (1999), the first hydrolysis reactions for aluminum and iron can be expressed as follows:



$$K_{\text{Al}(\text{OH})^{2+}}^{25^\circ\text{C}} = \frac{a_{\text{Al}(\text{OH})^{2+}} a_{\text{H}^+}}{a_{\text{Al}^{3+}} a_{\text{H}_2\text{O}}} = 10^{-5.0} \quad [14\text{B}]$$

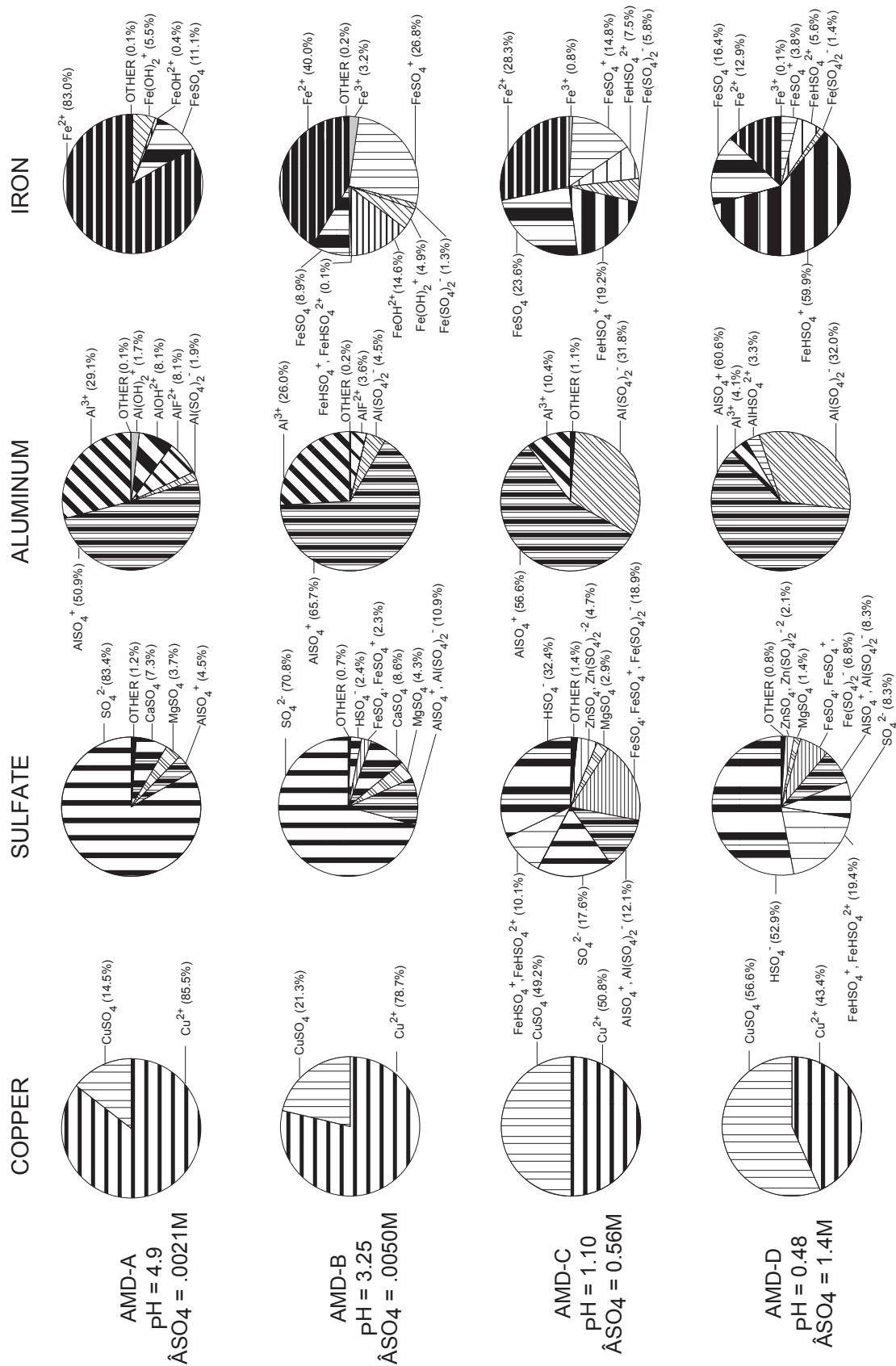


FIGURE 14.1—Pie charts showing results of aqueous speciation calculations in terms of relative molalities of copper, sulfate, aluminum, and iron species, using program WATEQ4F (Ball and Nordstrom, 1991) for acid mine water compositions in Table 14.1.

$$\log K_{\text{Al(OH)}^{2+}}^{25^\circ\text{C}} = \log a_{\text{Al(OH)}^{2+}} - \log a_{\text{Al}^{3+}} + \log a_{\text{H}^+} - \log a_{\text{H}_2\text{O}} = -5.0 \quad [14\text{C}]$$



$$K_{\text{Fe(OH)}^{2+}}^{25^\circ\text{C}} = \frac{a_{\text{Fe(OH)}^{2+}} a_{\text{H}^+}}{a_{\text{Fe}^{3+}} a_{\text{H}_2\text{O}}} = 10^{-2.2} \quad [15\text{B}]$$

$$\log K_{\text{Fe(OH)}^{2+}}^{25^\circ\text{C}} = \log a_{\text{Fe(OH)}^{2+}} - \log a_{\text{Fe}^{3+}} + \log a_{\text{H}^+} - \log a_{\text{H}_2\text{O}} = -2.2 \quad [15\text{C}]$$

The values of $\log K$ in equations [14C] and [15C] contribute to a sharp decrease in abundance of Al-hydroxide complexes at pH values below 5 (e.g., samples AMD-B, -C, and -D) and a similar decrease in Fe^{III} -hydroxide complexes at pH values below 2.2 (AMD-C and -D). The relation of these pH values to the $\log K$ values for the hydrolysis reactions can be seen by rearranging equations [14C] and [15C], while setting $a_{\text{H}_2\text{O}}$ equal to 1 ($\log a_{\text{H}_2\text{O}} = 0$) and using the definition $\text{pH} \equiv -\log a_{\text{H}^+}$ to yield

$$\log a_{\text{Al}^{3+}} - \log a_{\text{Al(OH)}^{2+}} + \text{pH} = 5.0 \quad [14\text{D}]$$

$$\log a_{\text{Fe}^{3+}} - \log a_{\text{Fe(OH)}^{2+}} + \text{pH} = 2.2 \quad [15\text{D}]$$

The value on the right hand side of equation [14D], equal to $-\log K$ for reaction [14A], corresponds to the pH value at which an equal activity of the free aluminum ion and the aluminum-hydroxide ion pair will coexist; the analogous relation for ferric iron is shown in equation [15D].

Hydrolysis of Fe^{2+} and other divalent metals (e.g., Cu, Zn, Cd, Pb, Co, Ni) is not a significant factor in the speciation of acid mine waters with pH values less than about 5. However, hydroxide complexes can be extremely important in speciation analysis of divalent metals in waters with circum-neutral pH. Significant uncertainties remain with regard to thermodynamic data for critical species such as $\text{Cu(OH)}_{2(\text{aq})}^0$. This underscores the need for users of speciation computer codes to use caution with regard to the quality, uncertainty, and internal consistency of thermodynamic data, as discussed earlier in this chapter.

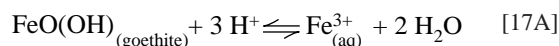
Table 14.2 contains computed molalities and activities for free ions in the four acid mine waters described in Table 14.1 and Figure 14.1, as well as saturation indices for several common secondary minerals, computed using program WATEQ4F (Ball and Nordstrom, 1991). Note that the difference between the logarithms of molality and activity for a given ion is represented by the logarithm of the individual ion activity coefficient, γ_i . Taking the logarithm of equation [7] yields

$$\log a_i = \log \gamma_i + \log m_i \quad [16]$$

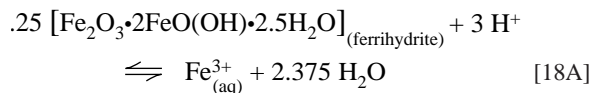
Values of γ_i deviate from 1 to a greater degree for more highly charged species and for solutions of high ionic strength (Garrels and Christ, 1965).

Mineral saturation indices in Table 14.2 indicate the thermodynamic tendency of the four water samples to precipitate or to dissolve certain minerals. All four samples show undersaturation with respect to gypsum. Supersaturation with respect to barite is evident in the three samples for which dissolved Ba data are available. Note that detection of Ba in samples with very high sulfate is problematic because of the low solubility of barite.

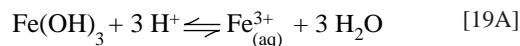
Interpretation of saturation indices for hydrous ferric oxides such as goethite, ferrihydrite, and ferric hydroxide is facilitated by writing the dissolution reactions for these phases in such a way that the K_{sp} expressions share the same exponents for the ferric and hydrogen ions.



$$K_{\text{sp,goethite}} = \frac{a_{\text{Fe}_{(\text{aq})}^{3+}} a_{\text{H}_2\text{O}}^2}{a_{\text{H}^+}^3} \quad [17\text{B}]$$



$$K_{\text{sp,ferrihydrite}} = \frac{a_{\text{Fe}_{(\text{aq})}^{3+}} a_{\text{H}_2\text{O}}^{2.375}}{a_{\text{H}^+}^3} \quad [18\text{B}]$$



$$K_{\text{sp,Fe(OH)}_3} = \frac{a_{\text{Fe}_{(\text{aq})}^{3+}} a_{\text{H}_2\text{O}}^3}{a_{\text{H}^+}^3} \quad [19\text{B}]$$

The only differences between the mass-action expressions in equations [17B], [18B], and [19B] are the values of the exponent applied to the activity of water (a quantity usually very close to unity) and the values of the equilibrium solubility constants. For goethite (equations [17A],[B]) and ferric hydroxide (equations [19A],[B]), the K_{sp} values differ by about 5.8 log units, which is the approximate difference between the SIs of these two phases for the four water samples shown in Table 14.2. As pointed out by Bigham (1994), "Ferrihydrite has become a popular but often misused synonym for 'amorphous' ferric hydroxide." Because goethite is less soluble than ferrihydrite or ferric hydroxide, it will always appear to be supersaturated in a low-temperature solution

TABLE 14.2—Molalities, activities, and saturation indices for four acid mine waters, computed using program WATEQ4F (Ball and Nordstrom, 1991) with chemical data in Table 14.1.

pH (field)	AMD-A 4.9		AMD-B 3.25		AMD-C 1.10		AMD-D 0.48	
	log m _i	log a _i	log m _i	log a _i	log m _i	log a _i	log m _i	log a _i
Species								
H ⁺	-4.87	-4.9	-3.21	-3.25	-0.98	-1.10	-0.35	-0.48
SO ₄ ²⁻	-2.74	-2.90	-2.45	-2.65	-1.01	-1.75	-0.92	-1.80
Cu ²⁺	-14.8	-14.9	-11.8	-11.8	-2.51	-3.02	-2.64	-2.93
Zn ²⁺	-6.26	-6.41	-5.77	-5.98	-1.95	-2.46	-1.92	-2.53
Cd ²⁺	-7.55	-7.70	-7.30	-7.51	-4.40	-4.91	-4.34	-4.64
Fe ²⁺	-4.15	-4.31	-3.88	-4.09	-1.22	-1.73	-1.26	-1.55
Fe ³⁺	-8.77	-9.11	-4.97	-5.44	-2.78	-3.91	-3.54	-4.20
Al ³⁺	-4.26	-4.61	-3.72	-4.19	-2.23	-3.37	-2.40	-3.07
Mineral	Formula	SI ²	SI	SI	SI	SI	SI	SI
		AMD-A	AMD-B	AMD-C	AMD-D			
Gypsum	CaSO ₄ •2H ₂ O	-1.48	-1.06	-0.33	-0.71			
Barite	BaSO ₄	0.40	0.52	---3	0.90			
Melanterite	FeSO ₄ •7H ₂ O	-4.88	-4.46	---	---			
Goethite	FeO(OH)	6.59	5.31	0.38	-1.79			
Ferric hydroxide [ferrihydrite ¹]	Fe(OH) ₃ ¹	0.70	-0.58	-5.52	-7.70			
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	0.64	2.66	-2.32	-5.85			
Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆	5.91	-1.64	-8.55	-9.81			
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	5.65	-3.01	-12.74	-14.61			
Gibbsite	Al(OH) ₃	1.46	-2.86	-8.25	-9.25			
Amorphous Al(OH) ₃	Al(OH) ₃	-1.31	-5.60	-10.95	-11.85			

¹For discussion of ferric hydroxide and ferrihydrite formulas, see Nordstrom and Alpers (1999).²SI, saturation index.³---, not computed.

that is saturated with respect to poorly crystalline, metastable hydrous ferric oxide such as ferric hydroxide, ferrihydrite, or schwertmannite, a sulfate-bearing ferric oxyhydroxide (see Nordstrom and Alpers, 1999).

Most other SI values in Table 14.2 are either greater than 1.0 or less than -1.0, indicating that solubility control by the listed phases is unlikely for the water samples under consideration. Other aspects of solubility control on acid mine water composition are discussed by Nordstrom and Alpers (1999).

In summary, the effect of sulfate complexing on metal concentrations is to decrease the free ion concentrations of metals and sulfate. These trends greatly affect saturation index calculations. Therefore it is critical to incorporate speciation analysis into any computations of mineral saturation or equilibrium with sulfate-rich waters common in mining environments.

Available programs and their evolution

The diagram on Figure 14.2 shows the evolution of selected aqueous speciation modeling programs. Figure 14.2 is not intended to be a comprehensive survey of available programs, but rather to provide a framework for understanding the origin of some of the programs in current usage. For more information on programs of this type, the reader is referred to the comparison of chemical models by Nordstrom et al. (1979b) and to the reviews by Waite (1989), Yeh and Tripathi (1989a), Bassett and Melchior (1990), Mangold and Tsang (1991), Plummer (1992), Wolery (1992a), and Nordstrom and Munoz (1994).

An early example of speciation calculations applied to natural waters was the pioneering work of Garrels and Thompson (1962) on the speciation of ocean water. One of the first available speciation computer codes was the HALTAFALL program, based on a successive-approximation algorithm (in ALGOL) developed by Ingri et al. (1967). This program was originally intended to simulate laboratory mixing procedures including titrations, precipitation separations, and solvent extractions. Other uses of the HALTAFALL program have been for the speciation of seawater (Dyrssen and Wedborg, 1974) and of estuarine waters (Dyrssen and Wedborg, 1980). Eriksson (1971, 1979) modified HALTAFALL to compute high-temperature equilibria and produced the new program SOLGASWATER (originally SOLGAS), which uses a Gibbs free energy minimization technique with Gaussian elimination. SOLGASWATER has been applied, primarily in Sweden, to both laboratory and field problems (Öhman, 1983; Lidén, 1983).

The REDEQL program was first described by Morel and Morgan (1972) as a speciation and phase-distribution program using a Newton-Raphson iteration. Numerous improvements and modifications have been made to this program, including REDEQL2 (McDuff and Morel, 1973), MINEQL (Westall et al., 1976), MICROQL (Westall, 1979), REDEQL.EPA (Ingle et al., 1978), and REDEQL.UMD (Harriss et al., 1984). MINTEQ (Felmy et al., 1984) combined MINEQL and the data base from WATEQ3 (Ball et al., 1981). Subsequent versions of MINTEQ include MINTEQA1 (Brown and Allison, 1987) and MINTEQA2 (Allison et al., 1991), which are products of the U.S. Environmental Protection Agency and are widely used for interpretation of exper-

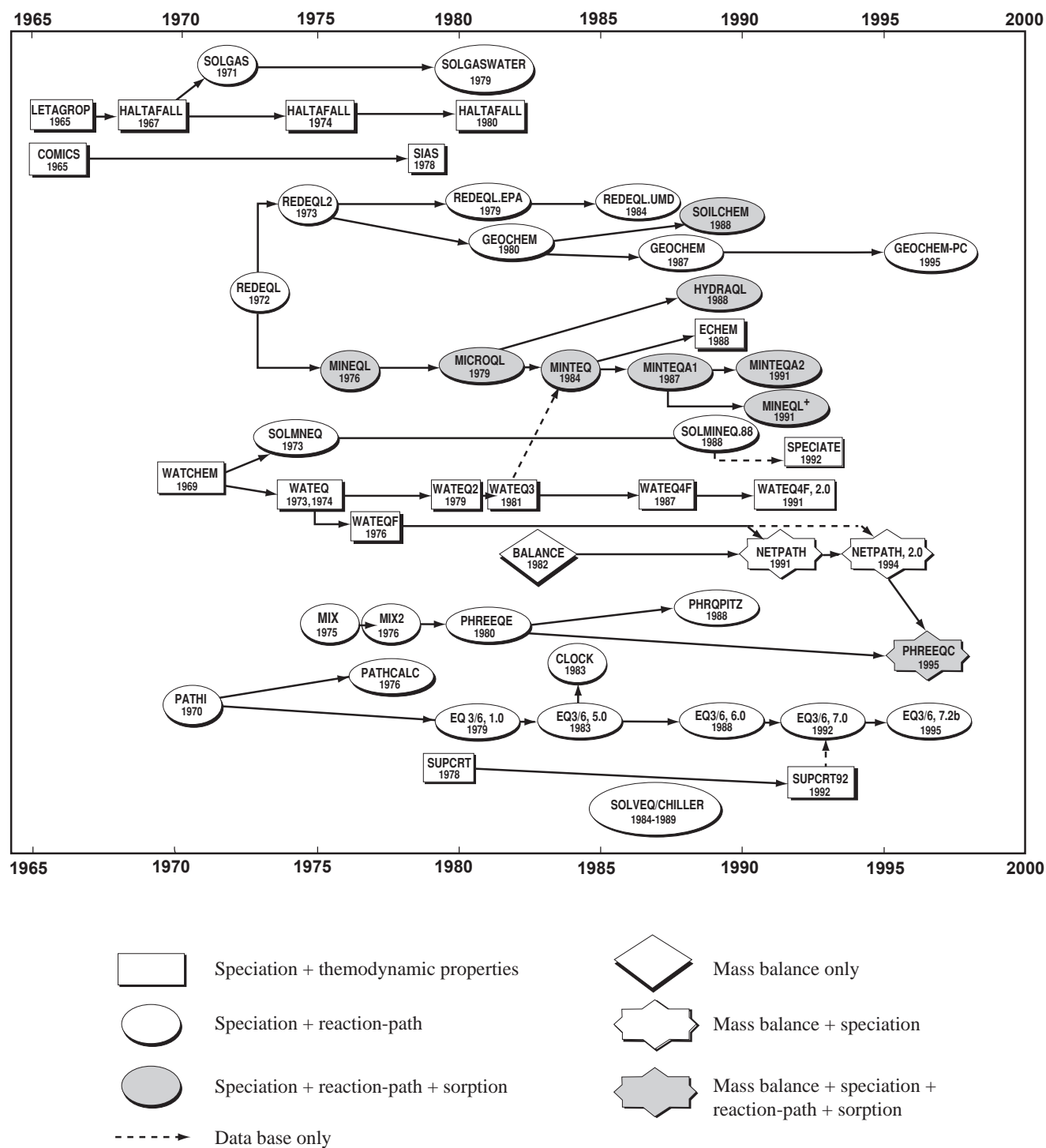


FIGURE 14.2—Evolution of selected geochemical modeling programs.

imental and field data. Other related programs are GEOCHEM for soil-water interactions (Sposito and Mattigod, 1980; Parker et al., 1987), updated as GEOCHEM-PC (Parker et al., 1995), SOILCHEM which includes a large number of organic species (Sposito and Coves, 1988), HYDRAQL (Papelis et al., 1988), ECHEM (Morrey, 1988), and MINEQL+, an interactive version of MINTEQA1 (Schecher and McAvoy, 1991). In addition to capabilities for computing aqueous speciation and mineral saturation indices, the MINTEQ series of programs can compute mass transfer (forward modeling) and can model adsorption, as discussed in later sections of this chapter and in the chapter by Smith (1999). MINTEQA2 is written in FORTRAN and runs on IBM-type personal computers. MacuQL (Muller, 1993) is a version of MICROQL that runs on Macintosh-type personal computers.

Another widely used series of speciation programs that compute mineral saturation indices is the WATEQ series developed by the U.S. Geological Survey, including WATEQ (Truesdell and Jones, 1973, 1974), WATEQF (Plummer et al., 1976), WATEQ2 (Ball et al., 1979, 1980), WATEQ3 (Ball et al., 1981), and WATEQ4F (Ball et al., 1987; Ball and Nordstrom, 1991). The latest version, WATEQ4F, v. 2.3 for IBM-type PC's, has an updated data base (Nordstrom et al., 1990) and was developed with an emphasis on trace metals and redox-sensitive species; the user may designate redox disequilibrium among the redox-sensitive elements, if desired.

The PHREEQE (pronounced "freak") program (Parkhurst et al., 1980) incorporates an aqueous model similar to programs in the WATEQ series. As in WATEQF and WATEQ4F, the user can choose between the Truesdell-Jones and the Davies models for computing aqueous activity coefficients. PHREEQE uses a dual-algorithm method that computes speciation with a continued fraction algorithm; forward modeling (mass transfer) is computed using a Newton-Raphson iteration. An advantage of the PHREEQE program relative to the WATEQ codes is the ease with which the user can add aqueous species, elements, and minerals to the model as part of the input file. This feature can facilitate the job of sensitivity analysis with regard to the thermodynamic data for individual minerals and aqueous species. The PHREEQC program (Parkhurst, 1995), written in C, is a recent update of PHREEQE that eliminates many of the deficiencies and limitations of the original code, such as the lack of mass balance on hydrogen and oxygen, and adds new capabilities including surface-complexation, ion-exchange, one-dimensional reactive transport, and inverse modeling (Parkhurst, 1995, 1997, 1998); several of these new capabilities are discussed in later sections of this chapter.

PHRQPITZ (pronounced "freak-pitz"; Plummer et al., 1988; Plummer and Parkhurst, 1990) is a version of the PHREEQE program that incorporates Pitzer's equations for analysis of solutions with high ionic strength. As with PHREEQE, the PHRQPITZ program can compute reaction paths (forward modeling) as well as aqueous speciation. A limitation of PHRQPITZ is that specific interaction parameters must be in the data base for all elements considered, which limits analysis to the system Na-K-Ca-Mg-H-Cl-CO₃-HCO₃-CO₂-SO₄-OH-H₂O. The PHRQPITZ data base has been extended to include parameters for the subsystems Fe^{II}SO₄-H₂SO₄-H₂O (Reardon and Beckie, 1987), Al-SO₄-H₂O (Reardon, 1988), and NiSO₄-H₂SO₄-H₂O (Reardon, 1989), although some problems remain with temperature coefficients (C. Ptacek and D. Blowes, written commun., 1995).

The EQ3NR program (Wolery, 1983; Wolery et al., 1990;

Wolery, 1992b) is another speciation program in wide use by geochemists. Its origin stems from the PATHI (pronounced "path-one") program of Helgeson et al. (1970) which was the first reaction-path (forward modeling) program in geochemistry. Output from EQ3 (Wolery, 1979) and the revised EQ3NR (Wolery, 1983, 1992b) can be used as input to the EQ6 program (Wolery and Daveler, 1992), which has forward modeling capabilities discussed in a later section of this chapter. A recent version of EQ3NR (v. 7.0, Wolery, 1992a, b) includes a hybrid Newton-Raphson solving algorithm that allows equilibrium and disequilibrium calculations, and five supporting data files that allow a choice between various applications of ion association and specific-ion interaction (Pitzer's equations) for the aqueous model, over a temperature range of 0–300°C. The EQ3/6 package of programs was developed at the Lawrence Livermore National Laboratory, and is distributed by the U.S. Department of Energy. Updates (v. 7.1 in 1993 and v. 7.2b in 1995; T. Wolery, written commun., 1995) have fixed bugs identified in earlier versions, and include a data base compatible with that from SUPCRT92 (Johnson et al., 1992), a program which facilitates computation of mineral-fluid equilibria over a temperature range of 0–1000°C and a pressure range of 0–5,000 bars. EQ3NR is written in FORTRAN and runs most easily on UNIX-based mainframe computers or workstations, although an earlier version (v. 6.0) was adapted to run on an IBM-type 486-based PC (S. McCauley, A. Williams-Jones, and C. Alpers, written commun., 1991). Updated versions (v. 7.2b and v. 8) were designed to run on Pentium-based PC's (Wolery, 1994; T. Wolery, written commun., 1995).

The program SOLMINEQ (Kharaka and Barnes, 1973) was developed at the U.S. Geological Survey concurrently with WATEQ and performs similar computations, with the additional capability to compute equilibria and mass transfer for geothermal waters at elevated temperature and pressure. An update, SOLMINEQ.88 (Kharaka and other, 1988; Perkins et al., 1990) was developed jointly by the U.S. Geological Survey and the Alberta Research Council. Several features are designed for analysis of geothermal fluids and oil-field brines, including fluid geothermometers, gas mixing and unmixing, and mineral-water mass transfers, discussed in a later section of this chapter. SOLMINEQ.88 has an option to use Pitzer's equations for brines, and several organic ligands are included in the data base. SPECIATE (Nesbitt et al., 1992) is a spreadsheet-based program that uses the SOLMINEQ.88 data base to calculate the aqueous speciation of radionuclides, organics, and major elements.

SOLVEQ (Reed, 1982; Spycher and Reed, 1989a) is a speciation program able to compute mineral-gas-solution equilibria. It was developed for hydrothermal conditions, particularly with regard to deposition of ore minerals by boiling and condensing processes, but is applicable also to low-temperature conditions. As with EQ3 and EQ6, the output from SOLVEQ can be used as input to CHILLER (Reed and Spycher, 1984), a forward modeling program discussed in a later section of this chapter.

"The Geochemist's Workbench™" is a proprietary package of geochemical modeling software developed by Bethke (1992a, 1998) at the University of Illinois, Hydrogeology Program. The code "React," successor to an earlier code known as "Gt," has the capability to compute aqueous speciation as well as mass transfer (forward modeling), with an option for using a Pitzer-based aqueous model. Other programs in the package include "Act2" and "Tact," which plot various types of stability diagrams, and "Rxn," which manipulates chemical reactions. An update to program

React has added the capability to decouple redox reactions and to compute sorption equilibria. Other capabilities of the package are discussed in later sections of this chapter.

Uncertainties and limitations

The use of speciation modeling programs can provide useful information concerning the geochemistry of water samples. Provided that a complete analysis of the water is available and that errors in analytical and thermodynamic data are minimal, it may be possible to determine which minerals are likely to dissolve or to precipitate in water of a given composition. Analysis of several water samples from one field area may provide support for a hypothesis that the solubility of a certain mineral or group of minerals controls the concentrations of certain metals. However, the correctness of such an interpretation depends in large part on the knowledge and experience of the modeler, especially his/her knowledge of hydrogeochemical processes.

The application of chemical models and their computer codes is limited to a range of water compositions. Waters with high ionic strength such as brines should be modeled where possible with the specific-ion interaction (Pitzer) approach, however critical data are not yet available for certain trace elements or for Fe(III), a major constituent of many acid mine waters with pH values below 3.

Redox disequilibrium is common in acid mine waters, but is often ignored in aqueous speciation calculations. Most commonly, this is due to a lack of analytical data for individual redox-active species. Individual redox species should be measured if at all possible, and a modeling program that can handle independent couples (e.g., WATEQ4F v. 2.0 or EQ3NR, v. 7.0 or later) should be used. Otherwise, interpretations concerning the geochemistry of redox-active metals such as Fe, As, and Mn are subject to extreme uncertainty and error.

INVERSE MODELING—MASS BALANCE

Inverse modeling using the mass-balance approach is one of the most powerful tools available for identifying the processes responsible for the chemistry of surface and ground water. Inverse modeling as a general approach to problem-solving refers to a problem where final results of a process are known and it is either the initial conditions or the nature of the processes themselves that are unknown. The mass-balance approach to geochemical modeling of water-rock interactions described here is based strictly on the compositions of water and of possible reactant and product minerals. The basic goal of mass-balance modeling is to determine one (or more) set(s) of reactions that are sufficient to account for known changes in water composition caused by mineral-water interactions. If water samples are available at two or more points along a flow path, then differences in concentration of various dissolved constituents can be used to determine possible sets of water-rock reactions that may have caused the changes in chemistry.

Compositional parameters may include elements, electrons (redox state) and stable isotopes. The mass-balance approach does not depend on thermodynamics or kinetics, *per se*. However, the user must be prepared to rule out unreasonable models that are inconsistent with the thermodynamics or kinetics of hydrogeochemical processes. For example, one should use the results of

speciation modeling (as discussed in the previous section of this chapter) to ensure that one does not hypothesize dissolution of a mineral into a solution supersaturated with that mineral; conversely, one should not hypothesize the precipitation of a mineral from a solution undersaturated with respect to that mineral. With regard to kinetics, it is necessary to use caution when invoking the participation of phases with very slow rates of precipitation or dissolution under the conditions being considered. In addition, one must consider the possibility that temperature and/or pressure conditions in the middle of a flow path may differ from those at the sampling points.

Theoretical basis and input data

A pioneering application of mass-balance principles to the geochemistry of weathering was the work of Garrels and McKenzie (1967) who used spring compositions to infer the relative reaction rates and stoichiometry of silicate mineral dissolution reactions in the granitic batholith of the Sierra Nevada, California. Other workers have used chemical mass-balance methods to derive elemental fluxes and rate constants for mineral dissolution using changes in water composition along flow paths in small watersheds and in aquifers, including Pačes (1983), Velbel (1985), Kenoyer and Bowser (1992), and Rowe and Brantley (1993).

The conceptual basis for computing net mass transfer to and from an aqueous solution between two points along a flow path was elucidated by researchers in the Water Resources Division of the U.S. Geological Survey, who applied the inverse modeling approach using the computer codes BALANCE (Parkhurst et al., 1982) and NETPATH (Plummer et al., 1991, 1992; Parkhurst and Plummer, 1993). The conceptual formulation of this approach is to find solutions to the following overall reaction (Plummer et al., 1983, 1991):



The initial and final water compositions, if known, are first converted to units of molality (moles per kg H₂O). A convenient way to compute molalities is to use a speciation program. Density data for the aqueous solutions must be known or estimated so that conversion to the molality scale can be made for the mass-balance computations to follow. The density correction can be important for some mine waters, which may have density values as high as 1.36 g/cm³ (Alpers et al., 1994). An approximate density for sulfate-rich waters can be estimated using data for mixtures of sulfuric acid and water. The next step is to compute values of Δ , the difference in concentration between the two water samples, for each element or compositional parameter of interest.

Other input data needed are the stoichiometric formulas of all minerals possibly interacting with the water along the flow path. For solid phases of variable composition (i.e., solid solutions) such as certain sulfides, feldspars, micas, and other rock-forming silicates and carbonates, compositional data from electron microprobe analysis, petrography, X-ray diffraction, energy dispersive analysis, or other means can provide an advantage during inverse modeling by allowing a solid-solution composition (e.g., Na_{0.96}Ca_{0.04}Al_{1.04}Si_{2.96}O₈ for albite feldspar) to take the place of

two or more end members. If significant variation of a solid-solution composition is observed or expected in the field, then input of two distinct compositions would allow the overall average composition to be determined by weighted average of the resulting mass-transfer coefficients. Ion-exchange and stable-isotope exchange reactions may also be included. Ion exchange reactions can be specified as simple exchange reactions, such as $\text{Ca}^{2+} \rightleftharpoons \text{Mg}^{2+}$, or $\text{Ca}^{2+} \rightleftharpoons 2 \text{K}^+$ without regard for the substrate; for example, cation exchange taking place on either phyllosilicate interlayer sites or on ferric hydroxide surfaces would be represented by a simple exchange reaction of the same form. Another type of mass transfer for which reaction coefficients may be computed is the flux of gasses in and out of solution.

Evaporation is an important process affecting water compositions in many environments, and can be considered in mass balance computations either explicitly or implicitly. Even if the hydrogen and oxygen in water are not considered as part of the mass balance, evaporation can be modeled as mixing with a solution of pure water with a negative mass transfer coefficient.

The mass-balance computation follows a simple matrix equation of the form $\mathbf{A} \cdot \mathbf{x} = \mathbf{B}$, where \mathbf{A} is a matrix with the stoichiometric coefficients of the possible reactant and product minerals and exchange reactions, \mathbf{B} is a column vector with the Δ values for each element, and \mathbf{x} is a column vector of unknown values corresponding to coefficients for the reactions represented by each row in matrix \mathbf{A} , in units of moles of reaction per kg H_2O (Fig. 14.3). To solve this matrix equation, the number of rows in column vectors \mathbf{B} and \mathbf{x} and in matrix \mathbf{A} must be equal; this corresponds to having the same number of equations as unknowns. So, the number of reactions among solid phases and gasses that can be considered at any one time is equal to the number of known compositional parameters in the Δ column vector (\mathbf{B}). In addition to major constituents in most waters, such as Ca, Mg, Na, K, Si, Cl, HCO_3 , and SO_4 , the elements abundant in most acid mine waters such as Fe, Al, Cu, Zn, and Mn can provide useful constraints. A redox parameter, such as the parameter RS of Parkhurst et al. (1982), should be included as a way of conserving electrons in any redox reactions to be considered. Stable and radiogenic isotopes of

hydrogen (δD and tritium) and of oxygen ($\delta^{18}\text{O}$) in water as well as isotopes of dissolved constituents such as carbon ($\delta^{13}\text{C}$ and ^{14}C), nitrogen ($\delta^{15}\text{N}$), sulfur ($\delta^{34}\text{S}$), and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) can also help to constrain the mass balance (e.g., Plummer et al., 1990, 1994). A similar mass-balance formulation may be derived for mixing of two or more water compositions, in combination with other water-rock reactions.

An inverse "model" is considered to be "a subset of the selected phases (and the computed mass-transfer coefficients) that satisfies all the selected constraints" (Plummer et al., 1991). This is consistent with the distinction made earlier between the conceptual model of a system and the computer code(s) used to test it.

Interpretation of output

In general, the output from inverse modeling will consist of one or more sets of reaction coefficients for the input hypothesized water-mineral reactions. It is important to realize that, although "models" derived by the inverse method may be exact, they are usually non-unique. Depending on the nature of the hypothesized reactions, the output from an inverse modeling program may consist of reaction coefficients for the moles of minerals dissolved and (or) precipitated, moles of gases in-gassed or out-gassed, moles of ion-exchange reactions, and (or) proportions of mixed solutions. Inverse models are subject to uncertainties from analytical data and from the underlying assumption of steady-state conditions.

Given multiple mass-balance models that are consistent with the input data, the choice of the most appropriate set of reactions and reaction coefficients should be based on consideration of questions such as the following:

- 1) Are the hypothesized reactant phases present in sufficient amounts in the host material?
- 2) Are the relative reaction coefficients consistent with relative kinetics of the hypothesized reactions?
- 3) Are the results compatible with the hydrogeologic setting?
- 4) Is the system open or closed with respect to gas fluxes?

$$\mathbf{A} \cdot \mathbf{x} = \mathbf{B}$$

moles Si mole albite	moles Si mole sericite	•	•	•	•	moles albite kg H_2O	=	moles Si kg H_2O
moles Al mole albite	moles Al mole sericite	•	•	•		moles sericite kg H_2O		moles Al kg H_2O
•	•	•	•	•		•		•
•	•	•	•	•		•		•
•	•	•	•	•		•		•

FIGURE 14.3—Matrix for mass-balance computations.

Available programs and their application

The program BALANCE (Parkhurst et al., 1982) was the first inverse geochemical modeling program to be applied widely to ground water problems. The original BALANCE program was limited to consideration of one combination at a time of possible reactions involving reactants and products, although the user could run multiple combinations sequentially by using an appropriately edited input file. It was also incumbent upon the BALANCE user to compute separately the saturation indices for water samples used in the modeling, so that thermodynamic constraints on mineral dissolution and precipitation were known.

The program NETPATH (Plummer et al., 1991, 1992, 1994) represents a significant enhancement of BALANCE (Fig. 14.2). The NETPATH program allows the user to consider more phases than the number of known compositional parameters by computing every possible combination of the correct number of phases. For example, if ten compositional parameters are known and there are eleven possible reactant and product minerals, then eleven different combinations of the compositional parameters will be tried, each combination leaving out one of the eleven possible reactant or product phases in turn. The user can streamline the process by indicating that certain phases should be allowed only to dissolve or precipitate, and can force the model to include certain phases in all possible solutions which can reduce considerably the number of possible combinations. Early versions of NETPATH had a companion program DB (Plummer et al., 1991) incorporating the speciation-saturation program WATEQF (Plummer et al., 1976) which can be used to compute elemental molalities for input to the mass-balance calculations and to compute saturation indices. A more recent version of NETPATH (v. 2.0, Plummer et al., 1994) includes a new speciation code, using the thermodynamic data base from PHREEQE, a subset of that from WATEQF. The revised version of NETPATH (Plummer et al., 1994) has the capability of mixing up to five waters and performing isotope mass balances and Rayleigh fractionation calculations for ^2H , ^{13}C , ^{14}C , ^{15}N , ^{18}O , ^{34}S , and ^{86}Sr . The program PHREEQC (Parkhurst, 1995) also has inverse modeling capabilities similar to those in NETPATH, v. 2.0. The most recent version of PHREEQC (v. 1.6) does not handle isotope mass balance; however, this capability is planned for later versions (v. 2.0; D. Parkhurst, written commun., 1998). Another improvement to the inverse modeling capability of PHREEQC is the consideration of analytical uncertainties (Parkhurst, 1995, 1998).

Example: Mass balance for Richmond mine water

An example follows of a relatively simple application of mass-balance modeling to a severe acid mine drainage problem. In this example, the goal of the modeling is to determine one or more sets of geochemical reactions that are responsible for the formation of a very concentrated mine water emanating from the Richmond mine at Iron Mountain, in the West Shasta mining district of northern California (Nordstrom, 1977; Alpers and Nordstrom, 1991; Alpers et al., 1992a). The composition of the mine water is given as sample AMD-D in Table 14.1; molalities were computed using the program WATEQ4F. At the Richmond mine, rainwater infiltrates through the mineralized zone, which consists of massive sulfide and stringer sulfide mineralization in an altered keratophytic (meta-dacitic) wall rock. The mine workings contain at

least 6 million tons of unmined pyritic Cu-Zn massive sulfide ore which remains above the water table, allowing ready access of oxygen by air convection and advection. The haulage level of the Richmond mine (2600 level) acts as an effective drain for the mine workings. The hydrogeologic setting is described further by Alpers et al. (1994). The concentrations of elements of interest in the initial rainwater solution are insignificant compared with those which leave the Richmond mine workings, so the water composition in Table 14.1 can be used as the Δ values.

The compositions of mineral phases likely to be dissolving and precipitating in the Richmond mine at Iron Mountain are given in Table 14.3. Compositions of chlorite, muscovite, epidote, and sphalerite determined by electron microprobe for samples from other mines in the West Shasta mining district (Reed, 1984) were used. Feldspar compositions were determined optically (Kinkel et al., 1956). The dacitic wall rock was metasomatized on the ocean floor prior to or during mineralization, so the majority of the feldspar is close to albite ($\text{Ab}_{.96}\text{An}_{.04}$) in composition. Because a range of feldspar compositions ($\text{Ab}_{1.00}$ to $\text{Ab}_{.80}\text{An}_{.20}$) was observed (Kinkel et al., 1956), sensitivity of the BALANCE model to the feldspar composition was tested, and was found to have little influence on computed reaction coefficients.

TABLE 14.3—Minerals considered in mass-balance computation for Richmond mine water.

Mineral	Formula	Source ¹
Albite	$\text{Na}_{.96}\text{Ca}_{.04}\text{Al}_{1.04}\text{Si}_{2.96}\text{O}_8$	1
Sericite	$\text{K}_{.70}\text{Na}_{.12}(\text{H}_3\text{O})_{.16}\text{Al}_{1.91}\text{Mg}_{.06}\text{Fe}_{.02}^{\text{II}}(\text{Al}_{.9}\text{Si}_{3.1})\text{O}_{10}(\text{OH})_2$	2
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	
Epidote ²	$\text{Ca}_{1.96}\text{Fe}_{.88}^{\text{II}}\text{Mg}_{.05}\text{Al}_{2.05}\text{Si}_{3.04}\text{O}_{12}(\text{OH})$	2
Chlorite	$\text{Mg}_{2.95}\text{Fe}_{.88}^{\text{II}}\text{Al}_{1.82}^{\text{Oct}}\text{Al}_{.81}^{\text{tet}}\text{Si}_{2.82}\text{O}_{10}(\text{OH})_8$	2
Quartz	SiO_2	
Calcite	CaCO_3	
Pyrite	FeS_2	
Chalcopyrite	CuFeS_2	
Sphalerite	$\text{Zn}_{.933}\text{Fe}_{.062}^{\text{II}}\text{Cu}_{.005}\text{S}$	2
Melanterite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	

¹Sources: (1) Kinkel et al. (1956); (2) Reed (1984).

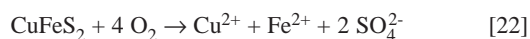
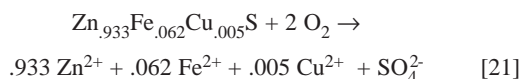
²Epidote formula included for reference only; phase not included in preferred mass-balance solution for water sample AMD-D.

Results from the mass-balance analysis for Richmond mine portal effluent, using input data from Tables 14.1 and 14.3, are shown in Table 14.4. Nearly one mole of pyrite has oxidized per kg of H_2O , along with much smaller amounts of sphalerite and chalcopyrite. The relative amounts of gangue minerals dissolved are also shown in Table 14.4; the largest contribution is from chlorite (0.013 mol/kg H_2O , equal to 7.5 g/kg H_2O), followed by sericite (0.011 moles or 4.3 g/kg H_2O) and albite (0.012 moles or 3.1 g/kg H_2O). In addition, dissolution of relatively small amounts of kaolinite (0.0063 mol/kg H_2O) and calcite (0.0047 mol/kg H_2O) is also indicated. Epidote (formula in Table 14.3) was included as a potential reactant, but no model solutions were found in which its dissolution was indicated. This result is consistent with slow kinetics of dissolution for epidote relative to the other gangue minerals considered.

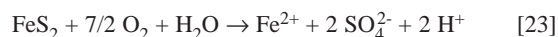
The principal reaction products indicated by the mass-balance solution are melanterite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$) and amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). An exceptionally large amount of melanterite precipitation (0.576 moles/kg H_2O) is indicated. An earlier attempt at mass balance for the Richmond portal effluent (Alpers and Nordstrom, 1989) used goethite (FeOOH) as the secondary iron phase, which seemed reasonable at the time given the abundance of this mineral in the gossan on top of Iron Mountain (Kinkel et al., 1956). However, renovation of the Richmond mine workings by the U.S. Environmental Protection Agency as part of a Superfund remediation program during 1989–90 made it possible to observe directly the secondary iron minerals forming in the underground mine workings (Alpers and Nordstrom, 1991; Alpers et al., 1991). It was found that melanterite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$) is the most abundant precipitate in areas of active mine-water flow during low-flow conditions, and that this and other Fe-sulfate minerals are likely to be dissolved during periods of high flow, including an annual flushing after the onset of the wet season (Alpers et al., 1991, 1992a, 1994). Thus, we expect that an inverse model based on water samples taken during a period of flushing would indicate dissolution of melanterite and (or) other soluble salts in contrast to the melanterite precipitation during the dry season indicated by the model shown in Table 14.4. Alpers et al. (1994) showed that melanterite formed in the Richmond mine has significant quantities of copper and zinc substituting for iron in solid solution. Although pure melanterite was used in the model shown in Table 14.4, a further refinement of the model would include a Cu-Zn-bearing melanterite as a reaction product, which would have the effect of requiring the oxidation of relatively more chalcocopyrite and sphalerite than shown in Table 14.4.

Note that water of hydration for the product phases is not considered in the mass balance because the programs BALANCE and NETPATH do not account explicitly for H or O. However, evaporative concentration can be modeled by expanding the model to include mixing with pure water in addition to the mineral dissolution and precipitation and gas flux reactions. If evaporative concentration is indicated, the pure water component will receive a negative coefficient, corresponding to the subtraction of pure water from the system.

The amount of gaseous oxygen that has combined with pyrite in the overall oxidation reaction represented by the mass-balance model in Table 14.4 can be estimated by subtracting the amount associated with oxidation of other sulfides from the total O_2 coefficient. For the purpose of this discussion it is assumed that sphalerite and chalcocopyrite have oxidized by the following overall reactions:



The corresponding amount of O_2 consumed by reactions [21] and [22] is 0.0872 moles/kg H_2O , which leaves 3.45 moles/kg H_2O associated with pyrite oxidation. Dividing 3.45 by the moles of pyrite consumed (.982) gives a molar ratio of 3.51, which is in excellent agreement with the coefficient of O_2 in the following pyrite oxidation reaction:



Given that about 90% of the dissolved iron in water sample AMD-D was Fe(II), it is assumed that the consumption of oxygen by oxidation of Fe(II) from sulfides and silicate gangue minerals is negligible. Thus, nearly all of the oxygen consumed has contributed to the oxidation of reduced sulfur (in pyrite and other sulfide minerals) to sulfate.

TABLE 14.4—Reaction coefficients for mineral dissolution and precipitation, and gas fluxes for the formation of water sample AMD-D (data in Table 14.1), based on mass-balance computations using mineral formulas in Table 14.3.

	Reaction coefficient (mol/kg H_2O)	Formula weight (g/mole)	Reactive mass (g/kg H_2O)	Percent of total reactants (wt%)
Reactants				
Pyrite	.9816	120	117.8	
Chalcocopyrite	.0051	184	0.9	
Sphalerite	.0385	96	3.7	
Total Sulfides			122.4	48
Calcite	.0047	100	0.5	
Albite	.0119	263	3.1	
Sericite	.0111	389	4.3	
Chlorite	.0132	567	7.5	
Kaolinite	.0063	258	1.6	
Total Gangue			17.0	7
O_2 gas	3.5421	32	113.3	45
Total Reactants			252.7	100
Products				
Melanterite	.5759	152 ¹	87.5	
Silica (amorphous)	.1162	60 ¹	7.0	
CO_2 gas	.0047	40	0.2	
Total Products			94.7	37
Net Total (reactants-products)			158.0	63

¹Melanterite and amorphous silica formula weights without waters of hydration; H and O not included in mass balance.

Other examples

Examples of the application of inverse modeling to regional ground-water flow systems are provided by Denver (1989) and Plummer et al. (1990), and are discussed by Parkhurst and Plummer (1993) and Parkhurst (1997). Other examples of NETPATH applications, including the incorporation of stable isotope data, are given in the user's manual (Plummer et al., 1994). An application of BALANCE and WATEQ4F to an acid mine drainage problem at an abandoned and partially reclaimed coal mine is given by Cravotta (1994). Rowe and Brantley (1993) describe the application of NETPATH to reactions between acidic ground water and fresh volcanic rocks on the flank of the Poás Volcano, Costa Rica.

FORWARD MODELING—REACTION-PATH AND REACTION-TRANSPORT MODELS

Forward models generally describe geochemical and hydrogeologic systems with sets of initial and boundary conditions and march forward either with respect to time or reaction progress, resulting in a predicted future state. As applied to geochemical systems, the progress of a chemical reaction is often used instead of time as the progress variable in the absence of quantitative information on the rates of many geochemical processes.

There is a fundamental distinction between the forward geochemical models that have a spatial component and those that do not. In this section, we first describe models without a spatial component, and refer to them collectively as “reaction-path” models. Then, the discussion turns to models with a spatial component, referred to as “reactive-transport” models. Some additional capabilities of the forward models are also discussed in this section, including the abilities to compute sorption equilibria, to consider solid-solution/aqueous-solution interactions, and to incorporate kinetic rate expressions for mineral dissolution and precipitation.

Reaction-path models

Models describing the transfer of mass and the distribution of elements between aqueous solution, solids, and gasses by geochemical processes are often described as reaction-path models. The geochemical processes that are modeled include mineral dissolution and precipitation, fluid mixing, sorption, and ion exchange. The “path” refers to evolutionary changes in the composition and abundance of modeled phases, including the aqueous phase, through the course of the simulation. In most cases, it is the composition of the aqueous solution that is the frame of reference used to follow reaction progress in geochemical reaction-path models.

There are numerous examples in the geochemical literature of the application of reaction-path modeling to the genesis of hydrothermal ore deposits and accompanying wallrock alteration (e.g., Helgeson, 1970; Villas and Norton, 1977; Brimhall, 1980; Garven, 1982; Brimhall and Ghiorso, 1983; Janecky and Seyfried, 1984; Reed and Spycher, 1984; Bowers and Taylor, 1985; Spycher and Reed, 1989b; Plumlee et al., 1994, 1995) and to the formation of weathering products (e.g., Helgeson et al., 1969, 1970; Bladh, 1982). However, relatively few applications of reaction-path modeling have been made to environmental aspects of mineral deposits; contributions of this kind by Runnells et al. (1992) and by Parkhurst and Plummer (1993) are discussed later in this section.

Theoretical basis

Reaction-path models predict the results of hypothetical, irreversible water-rock-gas reactions applied to an initial solution, usually 1 kg of H_2O with known amounts of dissolved constituents. An initial analysis of aqueous speciation and mineral saturation is performed, and any supersaturated phases are either brought into equilibrium (saturation) or suppressed from the calculation if known to have slow kinetics relative to the time scale of interest (e.g., quartz at low temperature). The irreversible reaction products are then added to the initial solution in very small increments. A reaction progress variable ξ is defined most com-

monly as total moles of specific reactant(s) consumed. At each step of reaction progress, another speciation calculation is carried out, supersaturated phases are again brought to equilibrium, and the quantities of any minerals precipitated or dissolved are tallied. The reaction may be allowed to continue until either the aqueous solution comes to equilibrium with all reactants, or the reactants are consumed.

An important consideration in reaction-path modeling is whether to treat a system as open or closed. A closed-system model allows newly formed reaction products to participate as reactants and to be redissolved if the aqueous solution becomes undersaturated with respect to them at a later point of reaction progress. A variation of the closed-system model is a titration model, which can be used to simulate mineral dissolution or fluid mixing (Wolery and Daveler, 1992). In contrast, an open-system model assumes that the reaction products from each step of reaction progress are removed from contact with the aqueous solution and are not available for subsequent dissolution. A subset of open-system models is the situation where a system is in contact with a large external gas reservoir, such as would pertain to weathering at the earth's surface, in the hydrologically unsaturated zone, and in certain types of experimental conditions where gas fugacities are fixed (Delany and Wolery, 1984; Wolery and Daveler, 1992). The distinction between closed and open systems has important consequences for determining the compositional path that aqueous solutions follow during irreversible reactions. In general, fluid compositions resulting from mineral-solution reactions in a closed system follow phase boundaries on activity diagrams, whereas open systems allow solution compositions to cross activity boundaries between mineral stability, as illustrated in the following example.

Reaction-path models describing the titration of orthoclase ($KAlSi_3O_8$) into pure water are shown on Figure 14.4. Starting with 1 kg of pure water, the feldspar is titrated into the water a little at a time. In each increment, the additional reactant mineral is dissolved completely prior to the next reaction step, releasing the constituent cations (K^+ , Al^{3+} , and Si^{4+}) to the aqueous solution in their stoichiometric (molar) proportions within the feldspar ($K:Al:Si = 1:1:3$). After each increment of dissolution, the next step is to check for saturation with all mineral phases in the data base; if any phase becomes supersaturated in the newly created aqueous solution and is not suppressed in the calculation, then that phase precipitates from solution. Some examples of reaction-path calculations involving K-feldspar dissolution with quartz suppressed are shown on Figure 14.4 (from Helgeson, 1974, 1979). In an open system (path A'B'D' on Fig. 14.4), the first phase to become saturated is gibbsite, then kaolinite, and finally the solution comes to equilibrium with K-feldspar. In comparison, two closed-system models for K-feldspar dissolution yield different reaction paths (A'B'C'D' and ABCDE on Fig. 14.4), depending on initial water composition (see discussions by Helgeson, 1979, and by Parkhurst et al., 1980). Path A'B'C'D' indicates a solution composition that traverses the gibbsite field, precipitating gibbsite until reaching the kaolinite phase boundary. The aqueous solution composition then tracks along the gibbsite-kaolinite boundary, precipitating kaolinite and dissolving gibbsite, until all gibbsite is dissolved. Then, the closed-system model tracks across the kaolinite field until reaching equilibrium with K-feldspar. Path ABCDE differs from path A'B'C'D' in that a different starting composition leads to intersection of the K-mica stability field and a final stable assemblage of K-feldspar plus K-mica. In the exam-

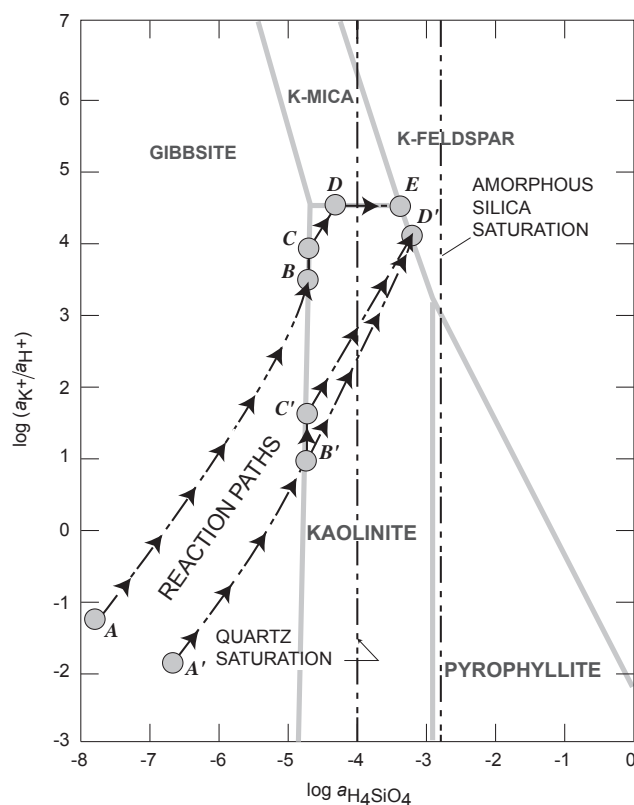


FIGURE 14.4—Equilibrium aqueous activity diagram for potassium versus silica at 25°C and 1 bar, showing a comparison of closed-system reaction paths (ABCDE and A'B'C'D') and an open-system path (A'B'D') for the dissolution of K-feldspar; after Helgeson (1974) and reproduced with permission from Manchester University Press.

ple shown on Figure 14.4, K-mica can be best thought of as a proxy for illite, hydromica or another similar phase that would be more likely to form than muscovite at the low temperature (25°C) of this simulation.

Input data and data base requirements

The necessary input data for a reaction-path model are a starting fluid composition and a set of reactants to be interacted irreversibly with that fluid. The reactants can take the form of a single mineral or gas, a group of minerals or gasses, a whole rock composition (e.g., volcanic glass), or another fluid composition. If a group of minerals is chosen, the user must define the relative kinetic rates of dissolution among these reactant phases. An arbitrary choice often made is to assume equal rates of dissolution based on volume percent, mole percent (e.g., Brimhall, 1980), or relative surface area in the reactant assemblage, however the rapidly accumulating data on low-temperature mineral dissolution kinetics (e.g., Petrovich, 1976, 1981a,b; Petrovich et al., 1976; Berner 1978, 1980, 1981; Berner and Holdren, 1979; Lasaga, 1981a,b; Aagard and Helgeson, 1982; Wood and Walther, 1983; Chou and Wollast, 1984, 1985; Wollast and Chou, 1985; Holdren

and Speyer, 1985a,b, 1986, 1987; Knauss and Wolery, 1986, 1988; Murphy and Helgeson, 1987, 1989; Murphy, 1989; Carroll-Webb and Walther, 1988; Dove and Crerar, 1990; Blum and Lasaga, 1991; Casey et al., 1991; Nagy et al., 1991; Rose, 1991; Nagy and Lasaga, 1992; Amrhein and Suarez, 1992; Murphy et al., 1992; Burch et al., 1993; Brady and Carroll, 1994; Brantley and Stillings, 1994; Oxburgh et al., 1994; Stillings and Brantley, 1995; Oelkers and Schott, 1995; White and Brantley, 1995) indicate that better approximations can and should be made for modeling weathering reactions. In using kinetic rate data from the literature it is important to realize that sample preparation techniques and fluid/mineral ratios can have a large influence on laboratory rates, and can explain in part the discrepancies of three orders of magnitude or more between rates observed in the laboratory and the field (e.g., Brantley and Velbel, 1993; Casey et al., 1993; Drever et al., 1994). Swoboda-Colberg and Drever (1993) and Velbel (1993) suggest that such discrepancies are due to physical differences involving spatially heterogeneous flow in field settings such that a small proportion of potentially available mineral surfaces actually participate in reactions with pore fluids at a given point in time.

Some of the more sophisticated reaction-path programs (e.g., CLOCK: Helgeson and Murphy, 1983; EQ6: Delany et al., 1986; Wolery and Daveler, 1992; KINDIS: Madé, 1991; Madé and Fritz, 1992) include kinetic rate laws for mineral dissolution and (or) precipitation. These expressions allow kinetic rates to change with solution composition and distance from equilibrium. Kinetic rate laws based on transition-state theory (Lasaga, 1981a,b) include terms for concentrations or activities of reactants (e.g., H^+) in the rate-limiting reaction that produce an activated complex, as well as a chemical-affinity or free-energy term (similar to the saturation index) that defines proximity to equilibrium. It is well known that mineral dissolution and precipitation reactions slow down near equilibrium, and this should be reflected in the kinetic rate expressions. In the absence of a rate expression based on transition-state theory, estimates of relative rates of mineral dissolution from experimental or field observations can also be used, providing better approximations than the relative amounts of minerals present in the starting assemblage. For most common sulfide minerals, empirical rate constants based on experimental studies are available (e.g., Wiersma and Rimstidt, 1984; McKibben and Barnes, 1986; Moses et al., 1987; Nicholson et al., 1988; Moses and Herman, 1991; Nicholson and Scharer, 1994; Rimstidt et al., 1994; see Nordstrom and Alpers, 1999). Sulfide minerals undergoing oxidation generally remain far from thermodynamic equilibrium, so it is less important to have a chemical affinity term in these rate expressions.

Data base requirements for reaction-path modeling are essentially the same as for aqueous speciation calculations, discussed previously. As with speciation modeling, the user must be diligent to use minerals and aqueous species for which data are available in the appropriate temperature range, and to use an appropriate expression for aqueous activity coefficients. For high ionic strength solutions ($I > 0.7$) it is generally recommended that a specific ion interaction (Pitzer) model be used. At least three computer programs are now available which incorporate the Pitzer equations into reaction-path modeling: EQ6 (Wolery and Daveler, 1992), PHRQPITZ (Plummer et al., 1988), and SOLMINEQ.88 (Kharaka et al., 1988). However, the Pitzer data bases are presently limited to a relatively small number of major ions, as discussed in the earlier section of this chapter on speciation modeling.

Output data and interpretation

The output from reaction-path modeling programs generally consists of predicted changes in solution composition and mineral assemblages as a function of reaction progress, including quantities of primary minerals dissolved and secondary minerals formed. If kinetic rate expressions are used, the time of reaction will also be computed.

Results from reaction-path modeling in terms of aqueous constituents and product-mineral abundances are commonly plotted as a function of reaction progress on a logarithmic scale (for example, see Brimhall, 1980; Brimhall and Ghiorso, 1983). Although results of the modeling are quantitative, interpretation in terms of comparison with field occurrences is often qualitative, and is considered successful if a certain sequence of reaction or weathering products is reproduced, with some agreement as to relative abundances of product phases. For simulation of laboratory experiments, one should demand much better agreement between a forward reaction-path model and actual observations, as the boundary conditions are much better defined, although equilibrium may be difficult to obtain depending on reaction kinetics.

A common technique used to visualize the results of such modeling is to trace the composition of the aqueous phase on activity-activity diagrams, which indicate the minerals predicted to dissolve or precipitate at different stages of the reaction path. Caution must be used with this approach, however, as two-dimensional representations can be misleading in systems with many chemical components and inspection of saturation indexes is required.

Available programs and their evolution

Figure 14.2 indicates the evolution of selected reaction-path modeling programs, and shows their relationship to other modeling programs, particularly the speciation programs with which they are intimately associated. The pioneering work on reaction-path modeling by Helgeson and coworkers (Helgeson, 1968; Helgeson et al., 1969, 1970), produced the PATHI (pronounced "path-one") program. During the 1970s, PATHI was modified by several different research groups, resulting in programs known as PATH+ and FASTPATH (not shown on Fig. 14.2).

A distinction can be made between reaction-path modeling programs in which the user must define the reaction path and those which are truly "path-finding." An example of a "user-defined" reaction-path modeling program is PHREEQE (Parkhurst et al., 1980), with which the user must indicate the stoichiometry of each phase to be dissolved or precipitated. The quantity of phases to be dissolved or precipitated with PHREEQE must also be specified, except in cases where the program is instructed to carry out sufficient reaction to reach a specified phase boundary, saturation, or supersaturation condition. In contrast, the "path-finding" modeling programs such as EQ6 (Wolery, 1979, 1992a), CHILLER (Reed and Spycher, 1984; Spycher and Reed, 1989a) and React (Bethke, 1992a, 1998) determine the identity and quantity of the phase(s) to be transferred into or out of solution by minimizing the Gibbs free energy of the system after each step of reaction progress. A useful computational tool which is available in some reaction-path modeling programs is an algorithm that automatically reverses and takes smaller progress variable steps if two or more potential product phases become supersaturated after a single increment of reaction progress.

Without this feature, one risks a situation where the computed reaction path could differ depending on the chosen step size for the progress variable, and risks violation of the phase rule. With a user-defined-path modeling program, one must manually control the step size so that only one additional phase becomes supersaturated at a time.

Applications of reaction-path modeling

Example: pyrite oxidation—An example of reaction-path modeling using the PHRQPITZ program (Plummer et al., 1988) is taken from Alpers and Nordstrom (1991), whose objective was to explore the origin of negative pH values observed in drip waters in underground mine workings of the Richmond mine at Iron Mountain (Nordstrom et al., 1991). In this example, pyrite is reacted with oxygen gas and initially pure water to yield aqueous ferrous iron, sulfate and hydrogen ions (see reaction [23]). In this simulation, all the iron remains ferrous; there is no oxidation of ferrous iron to ferric and subsequent oxidation of pyrite by ferric iron, as is thought to occur in nature. The reason for this simplification is the unavailability of Pitzer coefficients for ferric iron solutions. Results are plotted on Figure 14.5. A very small amount of reaction (0.0001 moles) is required to achieve a pH of 3.7, and a pH value of about 2 is reached after 0.01 moles of reaction, corresponding to only 1.2 grams of pyrite per kg of H₂O. Continued oxidative dissolution of pyrite leads to a pH value less than 1.0 after 0.17 moles of reaction, and finally to a pH value just below zero (-0.02) after 1.5485 moles of reaction [23], at which point the solution reaches saturation with respect to melanterite (Fe^{II}SO₄•7H₂O). The reaction continues, with essentially all of the iron going into melanterite:



A plot of pH versus the logarithm of the progress variable, in this case moles of pyrite oxidized, is shown on Figure 14.5b. The curvature on Figure 14.5b can be attributed to changes in the activity coefficient of H⁺ as the solutions become progressively non-ideal at higher sulfuric acid concentrations.

Other examples of reaction-path modeling—An example of reaction-path modeling applied to mining environments is the paper by Runnells et al. (1992), in which forward modeling was used to estimate ground-water compositions prior to mining by assuming equilibrium between water and various mineral assemblages. As stated earlier, a model is not useful if it cannot be tested. Thus, it is necessary to be able to confirm such predictions with field data for such an approach to be considered useful. However, in the absence of such data from mineralized but undisturbed areas, which are increasingly difficult to find, this sort of predictive effort can provide order-of-magnitude estimates for solubility constraints on metal compositions, provided that reasonable assumptions are used regarding the reactivity of the chosen phases.

Another example of forward modeling is the paper by Parkhurst and Plummer (1993), which used the PHREEQE model to predict *a priori* the evolution of water chemistry as an acid mine water is removed from contact with the atmosphere and migrates into the anoxic environment of a carbonate aquifer. The simulation

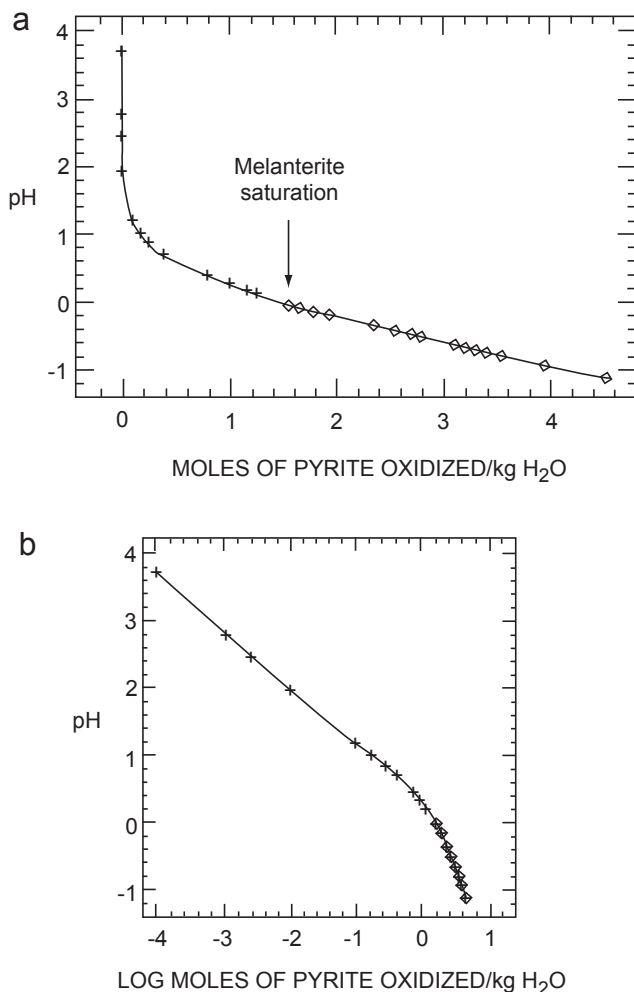


FIGURE 14.5—Forward simulation using program PHRQPITZ of pyrite oxidation, with melanterite precipitation at negative pH; from Alpers and Nordstrom (1991). (a) Linear horizontal scale; (b) Logarithmic horizontal scale, showing non-ideal solution behavior at negative pH values.

was purposely based on limited data from the Picher Pb-Zn mining area of northeastern Oklahoma and southeastern Kansas (Parkhurst, 1987; Playton et al., 1980) as a starting point for forward simulations, and was not intended to reproduce the exact chemical compositions found in those studies (Parkhurst and Plummer, 1993). Three different environments were simulated:

- 1) an oxic environment in which the mine waters were in contact with the mineralized zone (sphalerite, galena, pyrite, calcite, dolomite) and the atmosphere;
- 2) an anoxic environment in which contact with the atmosphere was cut off, but where sulfide oxidation continued with dissolved Fe^{3+} as the oxidant; and
- 3) the interaction of an anoxic mine water created in environment (2) with an unmineralized part of the carbonate aquifer (Parkhurst and Plummer, 1993).

With reaction progress from environment (1) to (3), the pH values rose from about 3 to about 6, and several minerals became super-saturated and were assumed to precipitate, in the following order:

gypsum, sphalerite, goethite, and smithsonite (ZnCO_3). The simulation was ended as the solution became saturated with dolomite, a constituent of the aquifer. As pointed out by the authors:

“...care must be taken not to over-estimate the value of these calculations. Many assumptions about equilibrium with phases and the amounts and relative rates of reactions were used to arrive at these results. Data provide the necessary information to test assumptions, but the most efficient use of that data would be to calculate saturation indices with a speciation code to determine which minerals are indeed in equilibrium and to calculate mass transfers using the mass-balance approach to determine the amounts and relative rates of reactions.” (Parkhurst and Plummer, 1993).

Reaction-path vs. mass-balance modeling

The choice of using reaction-path (forward) modeling rather than mass-balance (inverse) modeling should be based on one's objectives and the available data. If the system is sufficiently well constrained and has attained an approximate steady-state condition, and water chemistry data are available for at least two points along a flow path, then the mass-balance approach is preferred because it results in one or more exact solutions that provide possible explanations of the available data. However, many situations do not present sufficient data or knowledge of the system for this approach, or are sufficiently transient in nature that the mass-balance approach is inappropriate; in these cases the predictive, reaction-path approach can be a useful alternative. Table 14.5 provides a summary comparison between various aspects of the two approaches.

Combining reaction-path and mass-balance modeling

There are some advantages to combining the forward and inverse modeling approaches. An example is the study of the Madison aquifer in parts of Montana, South Dakota, and Wyoming (Plummer, 1985; Plummer et al., 1990; Parkhurst and Plummer, 1993), in which inverse modeling was used to determine the relative reaction rates of irreversible reactions, and then forward modeling was used to make predictions of various dissolved constituents, including dissolved Ca, Mg, inorganic C, pH, and CO_2 partial pressure. It was concluded that a relatively simple set of geochemical reactions, including dedolomitization and sulfate reduction, could explain the observed ranges in water composition and stable isotopes throughout the regional Madison aquifer system, if changes were allowed from place to place in relative rates and reaction extent (Plummer et al., 1990; Parkhurst and Plummer, 1993).

Example: Richmond Mine water

Another example combining the forward and inverse approaches is illustrated using the mass-balance example described in a previous section of this chapter for Richmond portal effluent at Iron Mountain, California. Using the results of the mass-balance calculations shown in Table 14.4, the PHREEQE program was used to simulate the formation of the mine water, starting from pure water. Rather than react all minerals at the same time, each mineral is reacted individually, so the contribution of each mineral to changes in pH and solution composition can be assessed. Results of the PHREEQE forward modeling are shown on Figure 14.6. First, the sulfide minerals are reacted with the appropriate amount of $\text{O}_{2(g)}$

TABLE 14.5—Comparison of features, inverse and forward modeling.

	Inverse modeling	Forward modeling
Theoretical basis	Mass balance, Stoichiometry, Consistency with saturation indices ensures thermodynamic reasonableness	Mass transfer, Irreversible thermodynamics
Role of kinetics	Implicit in choice of phases, No time scale	Can test assumed relative reaction rates, Computes time of reaction with rate laws, Simulates experiments
Input data (known or assumed)	Initial and final water compositions, Composition of possible reactants and products	Initial water composition only, Composition of reactants and products, Thermodynamic properties of products
Output	Proportions of reactants and products, accounting for observed changes in water chemistry along flow path	Predicts consequences of hypothesized reactions, Reaction paths
Applications	Can determine: geochemical processes in aquifers and surface waters, mixing proportions in ground waters	Designing experiments, Inaccessible systems, Ore deposit genesis, Predicts consequences of remedial alternatives

according to reaction coefficients in reactions [21], [22], and [23]. Reaction of 0.01 moles of pyrite per kg H₂O by reaction [23] results in a pH value of about 2.0; further reaction to a total of 0.1 moles results in a pH value of about 1.2. The full amount of pyrite (.982 moles) results in a pH value of about 0.5, which happens to be nearly identical to the actual pH of water sample 90WA103 (AMD-D, Tables 14.1 and 14.2). Additional reactions with sphalerite and chalcopyrite by reactions [21] and [22] have little effect on pH, as would be expected. Next, the gangue minerals are added to solution in the following arbitrary sequence: calcite, albite, sericite, chlorite, and kaolinite. As plotted on Figure 14.6, the total effect of all the gangue minerals is to raise pH by about 0.2 units, actually a large amount of neutralizing capacity given the logarithmic scale and the predicted pH value of about 0.5. Precipitation of amorphous silica has no effect on pH; the final step is precipitation of 0.576 moles of melanterite (Fe^{II}SO₄•7H₂O), which causes pH to drop by about 0.2 units because of the liberation of H⁺ ions from HSO₄⁻ and HFe^{II}SO₄⁺ aqueous complexes. The final computed pH value is 0.46, in excellent agreement with the measured value of 0.48.

The programs BALANCE and PHREEQE do not explicitly inventory moles of H and O, a deficiency corrected by PHREEQC (Parkhurst, 1995); however, in BALANCE and PHREEQE, the calculation of pH is made implicitly by charge and electron balance (Parkhurst et al., 1980, 1982). This means that the observed agreement in pH in the present example does not provide an independent confirmation of the validity of either the inverse or the forward modeling result. However it does give us some confidence in the robustness of these codes, and their ability to handle a very concentrated water composition without Pitzer parameters.

Surface chemistry models

A small, but increasing number of geochemical modeling programs have the capability to simulate the processes of adsorption and coprecipitation of inorganic aqueous species onto solid phases. A full review of the theory and application of sorption and coprecipitation modeling is beyond the scope of this chapter. The

interested reader is referred to reviews by Davis and Kent (1990) and by Dzombak and Morel (1990). The discussion in this chapter is limited to a brief summary of the capabilities and application of the modeling programs mentioned in the context of other modeling capabilities. More detail on this subject can be found in Smith (1999).

Available programs

The most widely used group of geochemical modeling programs with surface chemistry capabilities is the MINTEQ series. As indicated on Figure 14.2, and described in the earlier section on Aqueous Speciation Modeling, the original MINTEQ model-

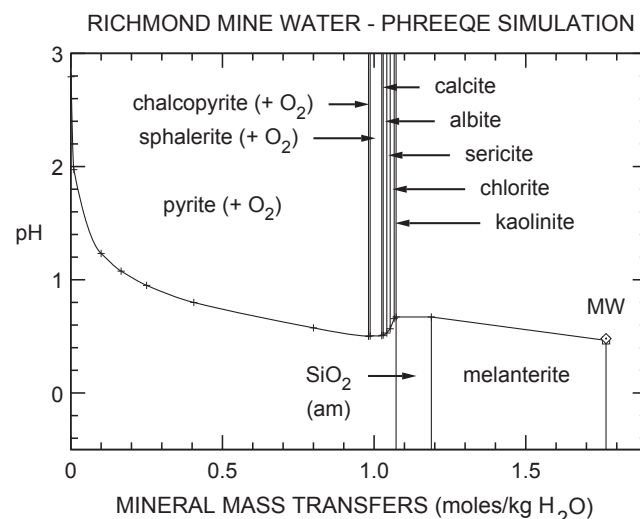


FIGURE 14.6—Forward simulation using program PHREEQE of mineral dissolution using reaction coefficients in Table 14.4; from Alpers and Nordstrom (1991).

ing program (Felmy et al., 1984) resulted from combination of the fundamental structure of the MINEQL program (Westall et al., 1976), which was in turn based on the sorption modeling capabilities of the REDEQL program of Morel and Morgan (1972), with the thermodynamic data base of WATEQ3 (Ball et al., 1981). The MINTEQA2 modeling program (Allison et al., 1991) has incorporated considerable changes from the original MINTEQ in terms of features and options available, the manner in which calculations are performed, and the thermodynamic data base.

The MINTEQA2 program has seven options regarding the modeling of surface reactions:

- 1) the activity K_d model,
- 2) the activity Langmuir model,
- 3) the activity Freundlich model,
- 4) the ion exchange model,
- 5) the constant capacitance model,
- 6) the triple-layer model, and
- 7) the diffuse-layer model (Allison et al., 1991).

The user defines surface properties for up to five minerals, each with up to two types of reactive sites. Reactions pertaining to each of the surface-reaction models are included with the aqueous speciation expressions, and the equilibrium distribution of aqueous species is determined among dissolved, sorbed, and solid phases. The surface complexes considered in the constant capacitance, diffuse-layer, and triple-layer models are analogous to complexes formed in aqueous solution, whereas the other four adsorption models neglect the electrostatic interactions of charged surfaces with solution composition (Allison et al., 1991).

Some examples of the application of MINTEQA2 to mining environments include the work of Webster et al. (1994) on transport of Zn, Cu, Fe, and As at the Leviathan mine, California, the work on arsenic sorption on ferrihydrite (Fuller et al., 1993; Waychunas et al., 1993), and the work of Stollenwerk (1994) simulating field and laboratory data on the interactions between acidic ground water and an alluvial aquifer near Globe, Arizona; see also Smith (1999).

Other geochemical modeling programs with sorption capabilities include HYDRAQL (Papelis et al., 1988), HYDRO-GEOCHEM (Yeh and Tripathi, 1989b) with its EQMOD subroutine (Siegel et al., 1992), and PHREEQC (Parkhurst, 1995), which includes a double-layer model based on Dzombak and Morel (1990) and a non-electrostatic model for surface-complexation reactions. The React program (Bethke, 1992a) has also been upgraded to include sorption modeling capabilities (Bethke, 1998).

Solid-solution/aqueous-solution modeling

There is no such thing in nature as a pure mineral. However, many phases approach a pure composition, and for the purposes of understanding the distribution of major elements in geologic systems, it is sufficient to approximate these solid phases as pure end members. For example, quartz is essentially SiO_2 , and in most applications one need not be concerned with trace amounts of Ti, Fe, Al, Li, and Na that may occur in it (Deer et al., 1966). However, there are numerous other minerals which display considerable variations in composition, and accounting for these variations can have an important effect on modeling some hydrogeochemical systems. The correct application of inverse models depends on knowledge of the possible compositions of solid phases

in the system, and compositional variations in minerals may correspond to significant shifts in both thermodynamic and kinetic properties, affecting the predictions of forward models. Therefore, solid solution effects have a potential impact on all types of geochemical modeling involving solid phases.

Some well known examples of minerals exhibiting a large degree of solid solution are silicates and aluminosilicates (feldspar, mica, amphibole, pyroxene, olivine), carbonates (Mg-rich calcite, ankerite, ferroan dolomite, siderite-rhodochrosite-magnesite), sulfates (e.g., barite-celestite and many others), sulfides (e.g., sphalerite), and sulfosalts (e.g., tennantite-tetrahedrite). As advances in analytical technology allow compositional information to be gathered from increasingly small volumes of material, we shall learn increasingly more about compositional variations in minerals at the microscopic and sub-microscopic scale. Thermodynamic principles for dealing with ideal and non-ideal solid solutions are relatively straightforward; however, there are large gaps in our ability to quantify non-ideality in specific binary and multi-component mineral systems, in many cases because of sparse experimental data.

Theoretical basis

Thermodynamic modeling of solid solutions among petrologists and mineralogists has focused on quantitative descriptions of departures from ideality. An ideal solution, whether gas, liquid, or solid, is one in which the different molecular species do not interact. Another way to express this is to say that an ideal solution obeys Raoult's law for all compositions (see Nordstrom and Munoz, 1994). The fundamental relationship of concentration to activity for solid phases can be expressed as:

$$a_i = X_i \cdot \lambda_i \quad [25]$$

where a_i represents the activity of the i^{th} component, X_i signifies the mole fraction of that component in the mineral, and λ_i is the rational activity coefficient. The partial molal Gibbs free energy, or chemical potential, of an ideal solid solution can be expressed as (Nordstrom and Munoz, 1994):

$$\bar{G}_{\text{ideal}} = \sum X_i \mu_i^0 + RT \sum X_i \ln X_i, \quad [26]$$

where μ_i^0 is the standard state chemical potential of the i^{th} component and the bar over G signifies a partial molal property. In non-ideal ("real") solutions, the departure from ideality, or excess Gibbs free energy is defined as $\bar{G}_{\text{excess}} = \bar{G}_{\text{real}} - \bar{G}_{\text{ideal}}$. The non-ideal component of the chemical potential is $\bar{G}_{\text{excess}} = RT \sum X_i \ln \lambda_i$, also known as \bar{G}^{XS} . The total free energy of the system can be expressed as the sum of the chemical potentials of all components in the system multiplied by their respective mole fractions, giving:

$$\bar{G}_{\text{real}} = \bar{G}_{\text{ideal}} + \bar{G}_{\text{excess}}$$

$$\begin{aligned} \bar{G}_{\text{real}} = \sum X_i \mu_i &= \sum X_i \mu_i^0 + RT \sum X_i \ln X_i \\ &+ RT \sum X_i \ln \lambda_i \end{aligned} \quad [27]$$

Several chemical models have been developed to compute solid-phase activity coefficients for binary and ternary mineral systems. Margules-type formulations (Thompson, 1967; Mukhopadhyay et al., 1993) have been used extensively in the petrologic literature. Within the context of ideal site-mixing, vacancies can be considered, as has been done for zeolites (Viani and Bruton, 1992). Other models for binary solutions include the regular solution model (Saxena, 1973, p. 11–12), the third-order Maclaurin model (Helgeson et al., 1970), the cubic Maclaurin model (Saxena, 1973, p. 16) and the Guggenheim polynomial model (Saxena, 1973, p. 14–15). All of the above solid-solution models are programmed in a general form into the EQ3/6 software package (Daveler and Wolery, 1992), which allows the user to select the appropriate model for any minerals for which the user provides appropriate fit parameters; a limited number of fit parameters, mostly for the ideal site-mixing model, are distributed with EQ3/6 (Daveler and Wolery, 1992).

A convenient formulation for solid-solution activity coefficients is the truncated Guggenheim series (sub-regular model) for the excess Gibbs free energy of mixing (Glynn, 1990):

$$\ln \lambda_i = X_{1-i}^2 [a_0 - a_1(3X_i - X_{1-i}) + \dots] \quad [28]$$

Equation [28] can be used to fit values of λ_i from solubility data for solid solutions. Glynn (1990) has compiled available mixing data for binary sulfate and carbonate mineral solid solutions at 25°C in terms of values for the fit parameters a_0 and a_1 . These data can be used for predictive modeling of mineral compositions likely to form from aqueous solutions of variable composition.

The literature on non-ideal mixing in silicate minerals formed at high temperatures is voluminous (e.g., reviews by Ghiorso, 1987; Ganguly and Saxena, 1987). However, these data generally involve phases that form at elevated temperature and pressure, and are not particularly relevant to geochemical modeling at surficial temperatures. Only phases that are likely to form at low temperatures (i.e., less than 100°C) are likely to play an important role in controlling the composition of non-hydrothermal solutions. Nevertheless, an understanding of solid-solution compositions among these minerals is of importance for the reasons stated above, i.e., proper use of mass-balance models and proper application of kinetic data for mineral dissolution and precipitation.

Available programs: Evolution and application

Glynn (1990, 1991b) developed the program MBSSAS to facilitate modeling of solid-solution/aqueous-solution interactions. This program allows the user to predict the thermodynamically stable composition of both solid and aqueous phases during hypothetical dissolution and precipitation reactions. In addition, MBSSAS can be used to construct phase diagrams and to calculate the stable intermediate compositions (i.e., miscibility and spinodal gaps) for binary series that are not stable at all compositions (Glynn, 1991b). Comparisons of modeling predictions with data generated from laboratory studies (Glynn and Reardon, 1990; Glynn et al., 1990) have shown that a non-equilibrium aqueous composition known as "stoichiometric saturation" is approached during the dissolution of relatively insoluble solid solutions that behave as single-component solids of invariant composition. For example, Mg-calcite, Sr-aragonite, and (Ba,Sr)SO₄ rarely achieve

thermodynamic equilibrium with the contacting aqueous solution in an observable time frame because of slow rates of solid diffusion and solid recrystallization kinetics. In contrast, thermodynamic equilibrium between the aqueous and solid phases is approached for more soluble solid solutions such as alkali halides (Glynn, 1991b).

Glynn and Parkhurst (1992) modified the PHREEQE reaction-path program to include solid-solution thermodynamics for any binary solid solution series. The resulting program allows the user to predict the composition of a solid solution forming in thermodynamic equilibrium with a given water composition, which itself may be evolving during reaction progress. Similar capabilities for prediction of the solid-solution composition of reaction products were incorporated into the EQ3/6 software package (Bourcier, 1986). A more recent version of EQ3/6 (Wolery, 1992a) gives the user a choice of several formulations to describe G^{XS} , as described earlier in this section.

In general, the application of solid-solution modeling to mining environments has been quite limited, however there are certain environments where the formation and dissolution of phases with variable composition can have important effects on water chemistry. For example, Alpers et al. (1994) have described a setting where the formation and dissolution of Zn-Cu-bearing melanterite [(Fe^{II},Zn,Cu)SO₄•7H₂O] appears to influence seasonal variations in the Zn/Cu ratio in effluent from an underground mine.

Another group of minerals, common in mining environments, that exhibits extensive solid solution is the alunite-jarosite group (Scott, 1987; Stoffregen and Alpers, 1987, 1992). The jarosite formula can be written as [K_xNa_y(H₃O)_{1-x-y}][Fe^{III}₃(SO₄)₂(OH)₆]. The mole fraction of hydronium (H₃O⁺) commonly ranges from 10 to 20% in jarosites formed at temperatures below 100°C (Kubisz, 1970; Ripmeester et al., 1986; Alpers et al., 1992b). Alpers et al. (1989) showed that the solubility of jarosite solid solutions with about 20 mole percent hydronium are consistent with an ideal solid solution between K and H₃O components. A value for the solubility product of jarosite solid solution with the composition [K_{0.77}Na_{0.03}(H₃O)_{0.20}][Fe^{III}₃(SO₄)₂(OH)₆] has been incorporated in the data base for WATEQ4F (Ball and Nordstrom, 1991); the saturation index for this phase should be evaluated along with that of the end members when dealing with mine waters for which data are available for Fe(II) and Fe(total). If jarosite is thought to be actively forming or recently formed, then the composition of the solid solution should be determined using chemical or X-ray diffraction methods (e.g., Alpers et al., 1992b) and a solubility product for the appropriate composition should be computed for comparison with the aqueous data. Use of the appropriate solid-solution composition can in some cases explain apparent supersaturation of water samples with respect to end-member compositions, where the solid solution represents the thermodynamically stable phase (e.g., Baron and Palmer, 1996).

Reaction-transport models

The coupling of hydrologic models with geochemical models results in models referred to as reaction-transport models. These models are fundamentally different than reaction-path models because they have a spatial component. The phenomena which can be simulated by reaction-transport modeling include advective

tion (the physical transport of fluid), molecular diffusion (the movement of dissolved species in response to concentration gradients), dispersion (the physical spreading of solutes caused by tortuous flow paths), decay (radioactive and biological), ion exchange, adsorption, oxidation-reduction, and mineral dissolution-precipitation. Space limitations preclude discussions of the theoretical basis of hydrologic transport modeling or the various strategies employed for improving the efficiency of numerical computation. The interested reader is referred to reviews and discussions by Rubin (1983), Cederberg (1985), Cederberg et al. (1985), Lichtner (1985), Yeh and Tripathi (1989a), Bahr (1990), Mangold and Tsang (1991), Apps (1992), and Dzombak and Ali (1993). The focus of this section is to describe the evolution of several reaction-transport modeling programs that are in current use and to discuss recent applications of this modeling approach to mining environments.

Available programs—their evolution and application

In several cases, existing geochemical models have been coupled explicitly with existing hydrologic models, resulting in a reaction-transport model. The mechanics of this coupling can be as straightforward as the calling of the chemical modeling program as a subroutine from the hydrologic program for each time increment and for each spatial node or element of the model. An example of this “brute force” method of coupling is the program DYNAMIX (Narasimhan et al., 1986; Liu, 1988; Liu and Narasimhan, 1989a,b), which coupled the saturated-unsaturated flow program TRUMP (Edwards, 1972) with the reaction-path program PHREEQE (Parkhurst et al., 1980). Many geochemical transport models, including TRUMP and DYNAMIX, take advantage of the fact that chemical transport and heat transport are described by equations of the same form (Narasimhan et al., 1986).

The evolution of selected reaction-transport modeling programs is outlined on Figure 14.7. An earlier attempt at explicit coupling involving the TRUMP and EQ3/6 programs resulted in the METASOM program (Cunningham, 1984; Ague and Brimhall, 1989). Both DYNAMIX and METASOM have been applied (Liu, 1988; Ague and Brimhall, 1989) to the problem of one-dimensional (vertical) transport and enrichment of copper in supergene weathering profiles, a setting which is similar to sulfide weathering in mining wastes. Another application of DYNAMIX to mining environments include a pseudo-three-dimensional model of ground-water contamination from a pyritic uranium mill tailings pile in Riverton, Wyoming (Narasimhan et al., 1986). DYNAMIX was also applied to selenium contamination at Kesterson Reservoir, California (Liu, 1988).

An approach to reaction-transport modeling based on the quasi-stationary-state approximation (Lichtner, 1985, 1988, 1992, 1993, 1994) has computational advantages over the explicit coupling techniques described earlier. Lichtner's approach makes use of the observation that most elements are much more concentrated in solid minerals than in the aqueous solution, which facilitates the solution of reaction-transport equations over geologic time spans. For very long time spans, Lichtner (1993) has shown that reaction-transport equations describing advection, diffusion, and dispersion approach asymptotically the pure advective local-equilibrium limit. The program MPATH (Lichtner, 1988, 1993) is based on the idea of multiple reaction paths, in which each reac-

tion path corresponds to a stationary state. Lichtner has applied MPATH to the problems of bauxite and laterite formation (Lichtner, 1988; Lichtner and Waber, 1992), uranium transport at a site that represents a natural analogue to a high-level nuclear waste depository (Lichtner and Waber, 1992), and supergene copper enrichment (Lichtner and Biino, 1992; Lichtner, 1994). This modeling approach was developed to simulate the geochemical evolution of weathering profiles over geologic time spans, rather than to determine geochemical processes in active weathering environments.

Two other reaction-transport modeling programs which make use of the PHREEQE program are PHREEQM (Appelo and Willemssen, 1987; Appelo et al., 1990, 1992; Appelo and Postma, 1993) and MST1D (Engesgaard, 1989; Engesgaard and Kipp, 1992). The PHREEQM modeling program uses a mixing cell approach, where the processes of advection and dispersion are simulated separately. In the PHREEQM code, advection is simulated by transferring water from one cell volume to the next at each time step. Ground-water velocity in the model is determined by an appropriate choice of cell size and time step. Dispersion and molecular diffusion are simulated by mixing the contents of adjacent cells at each time step, with chemical equilibration computed by the PHREEQE code between advection and dispersion steps (Appelo and Postma, 1993). In contrast, the MST1D code, which was developed by combining aspects of the three-dimensional transport program HST3D (Kipp, 1987) with PHREEQE, solves the transport equations (by a finite-difference approximation) without decoupling advection and dispersion, and iterates sequentially between the solution of the partial-differential transport equations and that of the algebraic chemical-reaction equations in the PHREEQE geochemical code. Glynn et al. (1991) compared the application of PHREEQM and MST1D to one-dimensional transport of acid mine drainage in an alluvial aquifer at Pinal Creek, a contaminant study site in the Globe-Miami mining district of Arizona.

Two other relatively new programs, MINTRAN and OTEQ, have coupled the MINTEQA2 program (Allison et al., 1991) to physically based flow models. The MINTRAN program (Walter et al., 1994a,b) resulted from coupling MINTEQA2 with PLUME2D, a two-dimensional flow model (Frind et al., 1990), for application to multicomponent reactive transport in ground water at mill-tailings environments. Frind and Molson (1994) describe the application of MINTRAN to a generic tailings impoundment with similarities to the Nordic deposit near Elliot Lake, Ontario, expanding on the work of Morin et al. (1988a,b) and Morin and Cherry (1988). The oxidation of pyrite and the diffusion of oxygen in waste dumps described in an algorithm by Davis et al. (1986) provided the basis for the numerical model PYROX (Wunderly et al., 1995, 1996). PYROX and MINTRAN have been coupled to produce the program MINTOX (Wunderly et al., 1995, 1996), a three-dimensional reaction-transport program that can be used to simulate pyrite oxidation, gas diffusion, and the formation of oxidation products in mining waste environments.

The OTEQ program (Runkel et al., 1996) combines one-dimensional in-stream solute transport with stream-bank storage from program OTIS (Runkel and Broshears, 1991) with MINTEQA2, resulting in a coupled reaction-transport code that can simulate redox chemistry and sorption processes. The OTEQ program has been applied to the simulation of solute transport during a pH-modification experiment in a stream affected by

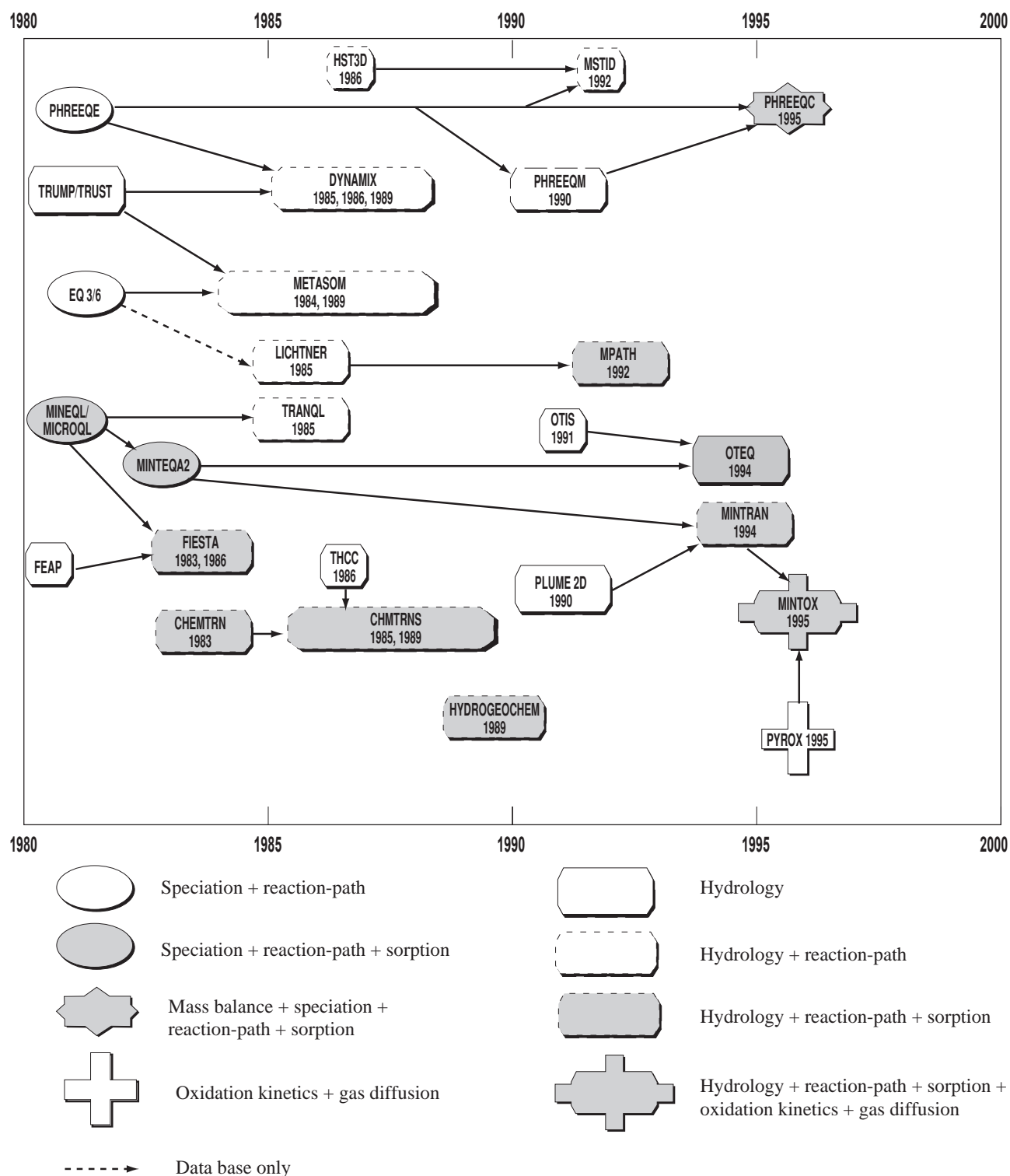


FIGURE 14.7—Evolution of selected coupled chemical-hydrologic modeling programs.

acid mine drainage in Colorado (Broshears et al., 1994, 1996; Kimball et al., 1994).

Other coupled chemical-hydrologic modeling programs include CHEMTRN (Miller and Benson, 1983), TRANQL (Cederberg, 1985), THCC (Carnahan, 1986), CHMTRNS (Noorishad et al., 1987), HYDROGEOCHEM (Yeh and Tripathi, 1989b) (Fig. 14.7). A comparison of features of these and other reaction-transport models was provided by Mangold and Tsang (1991).

Reaction-transport modeling is a rapidly evolving field of study, and the present review is far from complete. Many of the existing reaction-transport models are prone to problems with numerical dispersion and failure to converge, especially when modeling redox-sensitive reactions and sharp-front transport problems, which are poorly suited to finite-element and finite-difference approximations. Accordingly, the user should exercise considerable caution in the selection and application of existing reaction-transport programs for geochemical modeling, or in the development of new modeling programs.

UNCERTAINTIES AND LIMITATIONS OF GEOCHEMICAL MODELING

It is important to emphasize the critical assumptions that go into geochemical modeling, because careless application may lead to erroneous results and unreasonable models. For example, a central assumption in applying inverse modeling to ground-water compositions is that both initial and final water samples are along a single flow path. The best way to be assured of this would be to conduct a tracer injection test in which 100% of the tracer is recovered from the "final" well; however, this is not always practical because of limitations of budget and hydrogeologic settings. In the absence of such information, one must consider the apparent success of a mass-balance model to be qualitative or semi-quantitative at best, despite its exactness.

Another critical assumption with inverse modeling is that the chemistry of the system being modeled is in a steady-state condition. Transient behavior of either flow or chemistry, if not recognized, can cause erroneous results in mass-balance modeling. Consider, for example, a pyritic tailings impoundment overlying an permeable alluvial aquifer, with two monitoring wells (A and B) placed as shown on Figure 14.8. Depending on the hydrologic boundary conditions and in particular on the fluctuations of the water table, the flux rate of sulfide oxidation products to the ground water may vary considerably with time. For a constant water-table elevation, one might expect the fluxes to decrease with time exponentially as the reactant sulfides are consumed (Davis and Ritchie, 1986; Blowes, 1990). Therefore, if one were to attempt to use inverse modeling to derive the water-rock reactions affecting the ground-water composition between wells A and B, one must first determine that steady-state chemical conditions have been established. The transient nature of contaminant plumes and the other processes affecting hydrochemical transport (e.g., dispersion, diffusion) that are not considered in the mass-balance approach make the application of inverse modeling to this type of setting problematic. However, the mass-balance approach should be applicable in some special cases of this type of setting. For example a relatively permeable aquifer from which data are available over a long period of time could be shown to be in steady-state chemical condition if the travel time between sam-

pling points is short relative to the period for which data are available.

It must also be stressed that reactions hypothesized in mass-balance models must be feasible, both thermodynamically and kinetically. Thermodynamic feasibility can be established with saturation indices, by ensuring that only phases that are saturated or supersaturated are allowed to precipitate, and that only phases that are undersaturated are allowed to dissolve. It is also up to the user to determine independently whether or not there are any kinetic barriers to hypothesized reactions, including mineral precipitation and dissolution, ion exchange, and isotope exchange. Wherever possible, mass-balance modeling should be accompanied by detailed mineralogical and geochemical characterization of aquifer material.

Knowledge of the flow system and the effects of sampling on the system are important with regard to interpreting the chemistry of ground-water samples and using this type of data to determine boundary conditions for geochemical models, both inverse and forward. In some heterogeneous systems, especially fractured-rock aquifers, drilling and sampling cause drastic disruption of the natural flow system. Extensive well purging is often carried out with pumping rates substantially higher than natural flow rates, and the water sampled may represent water from the most hydraulically conductive zones or fractures and may not represent the bulk of water actually resident in the system before sampling.

Many of the limitations and uncertainties described with regard to inverse modeling also pertain to forward modeling. Assumptions are often made as to what are the reactive minerals, which minerals reach equilibrium and which do not, and what the relative reaction rates are. Detailed mineralogic characterization can provide valuable constraints on forward modeling (e.g., Lichtner and Waber, 1992), but even the most sophisticated of the models presently available will only approximate the complexity of the natural system. Forward modeling, by its very nature, puts much more responsibility on the user to make appropriate choices with regard to phases, components, and reaction equilibria. The major constraints on the usefulness and accuracy of the model come from the user's knowledge of hydrogeochemical processes.

Another important limitation, emphasized by Bethke (1992b), is that geochemical computations may be non-unique in the sense that a particular geochemical condition may be achieved by more than one possible equilibrium system. Computations that appear to be adequately specified may still contain ambiguities leading to non-unique solutions that are not obvious from code outputs. Also, models can be correct for incorrect reasons, i.e., two "wrongs" can sometimes appear to make a "right." Although a geochemical model may be based on sound principles, its application to real systems will usually result in large uncertainties because the real systems can only rarely be characterized in sufficient detail for the critical hydrogeochemical processes to be completely understood.

All of these limitations to geochemical modeling can be reduced to two main sources of uncertainty: (a) the input data (thermodynamic data, kinetic data, water compositions, mineral compositions, surface areas) and (b) the user's knowledge of hydrogeochemical processes, both in general and with specific reference to the real system being modeled. Future research in three areas will help to reduce these uncertainties. The first is to conduct basic research on thermodynamic, electrolyte, and kinetic properties of relevant geochemical substances and processes. The second is to carry out more research on applying the inverse

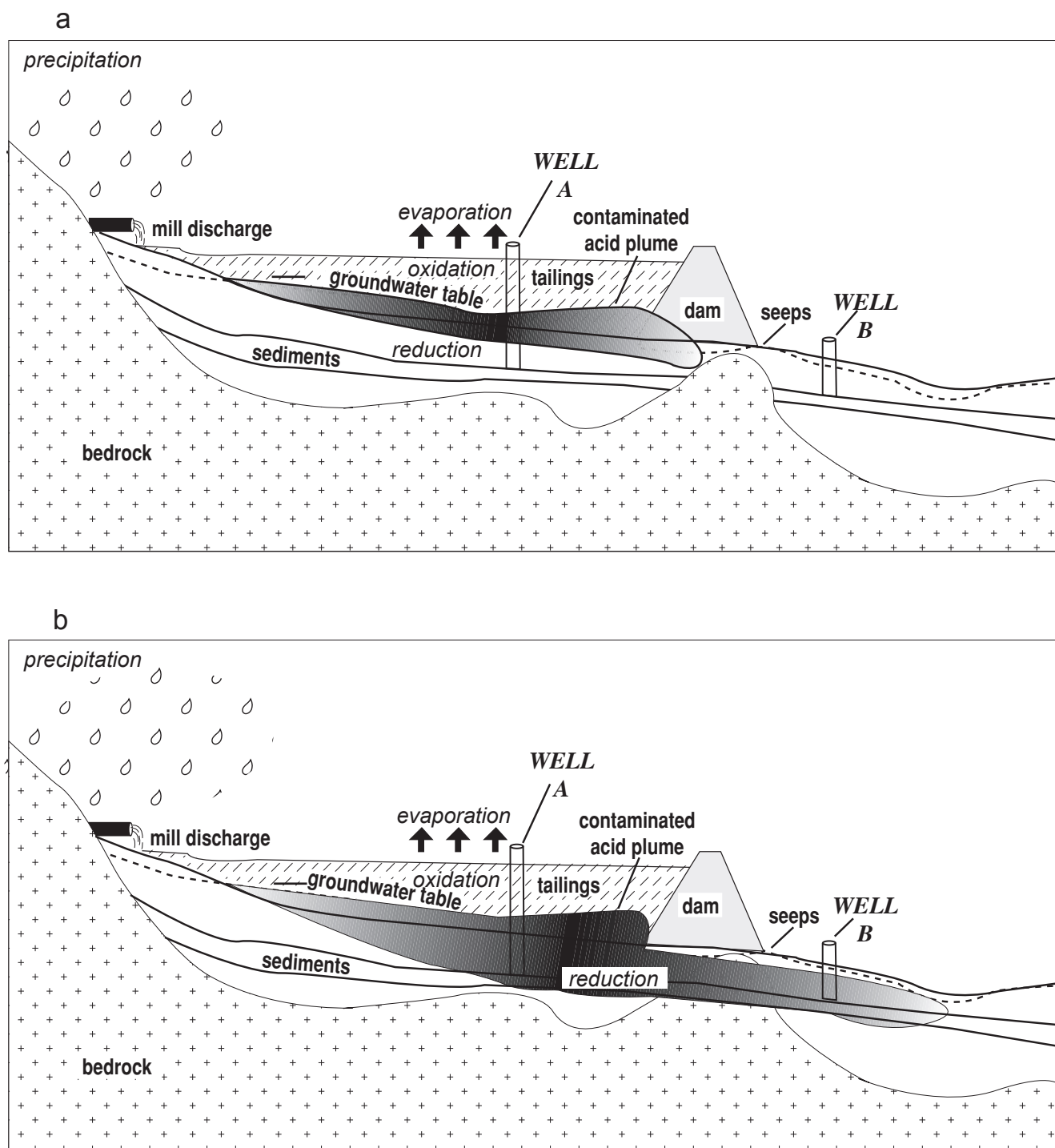


FIGURE 14.8—Schematic cross-section through a tailings impoundment at two points in time showing the evolution of a contaminant acid plume, to illustrate pitfalls of inverse modeling in transient systems.

modeling approach to water-rock interactions. The third is to apply systematic sensitivity analyses to modeling computations.

CONCLUSIONS

If used with proper caution and care, geochemical models can be powerful tools for interpreting the processes that affect water quality. However, as with any tool, the potential for misuse is high and it is the responsibility of the user to bring to each modeling application an adequate knowledge of the thermodynamic and kinetic behavior of phases to be modeled, as well as an appreciation of uncertainties in the input data.

Assumptions made in the construction of geochemical models must always be clear to users and clearly stated to readers of published results. For example, significant errors may result from the use of models that assume fully coupled aqueous redox conditions at low temperatures, where redox equilibrium is seldom attained. Anticipated improvements in modeling capabilities include the incorporation and quantification of redox disequilibrium (decoupled systems).

Inverse modeling of hydrochemical systems should be done where the data allow it; then forward modeling can be used to extend the analysis to parts of time and space where constraints are not available, i.e., to fill in the gaps. The inverse modeling is thus a type of calibration; if done properly, complementary forward modeling could provide a prediction of the inverse model's implications, which could be tested should more data become available.

There are numerous examples in the literature of the successful application of geochemical models to mining environments, several of which are mentioned and described in this chapter. Existing computer programs should be adequate for most mine drainage problems involving ground and surface waters. The aqueous models based on ion association (extended Debye-Hückel expressions) are adequate for mine waters with ionic strength less than about 1.0 for the speciated solution. The application of geochemical models to the formation of efflorescent sulfate salts from highly concentrated sulfate brines with ionic strengths greater than 1.0 is limited by the lack of specific-ion-interaction (Pitzer) parameters for Al, Fe(III), Cu, Zn, SO_4 and other constituents reaching high concentrations in some acid mine waters. However, the existing inverse and forward modeling programs are adequate for modeling the dissolution of such salts, allowing determination of their effects on water quality in various environments.

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