Predicting sulfate mineral solubilities in concentrated water

By:
C.J. Ptacek & D.W. Blowes
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Authors: Ptacek, C.J. and Blowes, D.W.

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Current Status: Migration of acid and metals from mine environments is a severe problem in Canada and the world. The oxidation of sulfide minerals leads to the release of acid, sulfate, and dissolved metals. Formation of secondary sulfate phases is an important control on the concentrations of dissolved metals, and long-term environmental geochemistry of mine waste sites. This review provides a description of current efforts at predicting the solubility of environmentally relevant sulfate phases in concentrated waters. Recent advances in the Pitzer ion-interaction model for predicting sulfate mineral solubility, in particular metal sulfate solubility, are described.

Next Steps: Develop detailed user-friendly computer code for predicting metal sulfate mineral solubilities based on the Pitzer ion-interaction model, with a particular emphasis on metal-rich acidic waters typical of those found at mine waste sites.
Abstract

Surface and subsurface waters at many sites, including industrial, mining, metallurgical, and radioactive waste sites, frequently contain elevated concentrations of dissolved solids. Prediction of the fate of environmentally significant metals and other dissolved constituents in concentrated waters typically requires consideration of mineral solubility controls. These predictions, however, have been limited because of the absence of a comprehensive geochemical model for application to concentrated waters. The introduction of the ion-interaction model in the early 1980’s provided a major advance in the prediction of sulfate mineral solubility controls in concentrated natural waters. Since its introduction, continuous improvements to the ion-interaction model have been made. This review provides a summary of the many improvements made over the past two decades. The emphasis is on the predictive capability of the ion-interaction model to describe sulfate mineral solubility in a variety of water types, including those that occur at mine sites, radioactive waste sites, and in natural settings. A summary of the model development is provided, recent improvements are described, and the capability of the model for predicting sulfate mineral solubility in complex field settings is assessed.
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Editors:
Charles N. Alpers  U.S. Geological Survey, Sacramento, California
John L. Jambor  Leslie Research and Consulting and
                 Department of Earth and Ocean Sciences,
                 University of British Columbia, Vancouver

FRONT-COVER PHOTOGRAPH: Mclanterite [(Fe++,Zn, Ca)SO₄·7H₂O]
stalagmites (blue and blue-green) from the Mattie deposit, Richmond tunnel,
Iron Mountain, California. Yellow and brown minerals are products
of mclanterite oxidation and dehydration. Field of view is 10 x 7 cm.

BACK-COVER PHOTOGRAPHS: a. Mclanterite stalactite (blue-green,
with orange, Fe²⁺-rich water inside) from the Mattie deposit, Richmond
tunnel, Iron Mountain, California. Photo copyright: Bud Eagle 1992. Field of
view: 3 x 8 cm.  b. Copiapite stalagmite (yellow) with halotrichite needles
(white) from the Richmond Mine, Iron Mountain, California. Field of view: 25
x 40 cm.  c. Voltaite from the Richmond Mine, Iron Mountain, California.
Canadian Museum of Nature specimen CMNOC 3525. Photo courtesy of
George Robinson. Width of specimen: 8 mm.  d. Coquimbite (pale purple)
with copiapite, and voltaite from the Richmond mine, Iron-Mountain,
California. Canadian Museum of Nature specimen CMNOC 3526. Photo
courtesy of George Robinson. Width of specimen as viewed is 2 cm.

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Blacksburg, Virginia

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Predicting Sulfate-Mineral Solubility in Concentrated Waters

Carol Ptacek
National Water Research Institute, Environment Canada
Burlington, Ontario, Canada L7R 4A6
Department of Earth Sciences, University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

David Blowes
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

INTRODUCTION

Sulfate minerals participate in a variety of mineral-water reactions with waters containing elevated concentrations of dissolved solids. Reliable prediction of sulfate-mineral solubility in concentrated waters is required for a multitude of geological, hydrogeological, industrial, and meteorological applications. Precipitation of pure sulfate minerals or sulfate-bearing solid solutions can limit concentrations of dissolved metals, radionuclides, and other cations at waste-disposal sites, in marine and other naturally occurring saline waters, in industrial waters, and in smog. Formation of these solids can control the major-ion geochemistry of water and, in turn, influence the behavior of trace constituents.

One of the most widely used and robust approaches for predicting mineral solubility in concentrated waters is the Pitzer ion-interaction approach as first introduced by Pitzer (1973), as applied to geological systems by Harvie and Weare (1980) and Harvie et al. (1980), and as summarized by Weare (1987). Clegg and Whitfield (1991) and Pitzer (1979a,b; 1991) provided further comprehensive discussions on the developments and application of the ion-interaction approach to predict mineral solubility in natural waters. This chapter focuses on the application of the ion-interaction approach, or its variations, for predicting sulfate-mineral solubility in a variety of geochemical settings. Included are a summary of the Pitzer approach as applied to predictions of mineral solubility, a summary of the available constants for modeling sulfate-mineral solubility, and examples of applications for natural and contaminated sites. The discussion focuses on recent additions to earlier models developed for application to near-Earth-surface temperature and pressure conditions. Applications outside this temperature and pressure range are described only briefly.

BACKGROUND

Compositions of concentrated waters

The majority of concentrated waters in nature form as a result of solar evaporation of marine and continentally-derived waters. The evaporation of seawater leads to predictable sequences of mineral formation, including precipitation of several common sulfate minerals (e.g. gypsum, mirabilite,thenardite, epsomite; Table 1; see chapter by Spencer, this volume). Evaporation of continentally-derived waters leads to waters of more variable composition (e.g. Jones et al. 1977; Monnin and Schott 1984; Domagalski et al. 1990). Entrapment of evaporative brines is thought to be the principal mechanism leading to the formation of subsurface brines (Landes 1960). Saline waters can form through other
mechanisms, including the dissolution of evaporite deposits, mineral alteration, and hydrothermal and magmatic processes. Different combinations of these processes can lead to brines of differing composition (e.g. Gavrieli et al. 1995). The quantitative prediction of sulfate-mineral solubility in natural brines has been a focus of research for many decades.

Among other concentrated waters are industrial waters, such as those used in metallurgical processes, and wastewaters, such as landfill leachates and waters associated with mining activities. In these waters, the formation and dissolution of sulfate minerals have the potential to influence the chemical composition of the water and its surrounding solids. Prediction of sulfate-mineral solubility in industrial waters has received widespread attention. Numerous studies have focused on quantification of sulfate-mineral solubility in industrial settings over a wide range in temperature and pressure. Quantification of sulfate-mineral solubility in wastewaters, mine waters, mine-waste leachate, and in other environmental settings has received less attention. For example, concentrated mine waters commonly develop in mine workings and in mine-waste and refinery-waste containment facilities. Very high concentrations of dissolved constituents form through a combination of reactions involving mineral alteration and evaporation. Oxidation of sulfide minerals, especially the Fe-bearing sulfides pyrite (FeS₂) and pyrrhotite (Fe₁₋₂S) leads to elevated concentrations of dissolved Fe(II), Fe(III), SO₄, and H₂S in mine workings and subsurface pore waters. Large volumes of water containing high concentrations of metals, sulfate, and acid, in excess of 900,000 mg/L total dissolved solids, have been reported (Nordstrom and Alpers 1999). Management of such mine sites requires prediction of the solubility of sulfate minerals. Development of a comprehensive geochemical model for the extreme concentrations observed at many mine and metallurgical sites is a relatively new area of study.

**Modeling approaches**

**Ion-association approach.** The first comprehensive ion-association model for application to natural waters was developed in the early 1960s (e.g. Garrels and Thompson 1962). Models based on the ion-association approach have been widely applied to predict sulfate-mineral solubility in a variety of settings. The original models were generally limited

to applications at 25°C and waters of low ionic strength (typically <0.1 m). Enhancement of the early versions of the ion-association model to extend its applicability to broader salinity and temperature ranges has been described thoroughly (Parkhurst et al. 1985; Ball and Nordstrom 1987; Allison et al. 1990; Millero and Hawke 1992). For example, the addition of various extensions of the Debye–Hückel equation to cover a wider concentration range, and inclusion of a large number of ion-association constants have provided reliable calculations to ionic strengths of up to 1 m and a broader temperature range (e.g. Ball and Nordstrom 1987; Parkhurst 1990; Nordstrom et al. 1996; Liu and Millero 1999). Robust models based on the ion-association approach have been developed for specific applications, such as precipitation calculations in seawater (see Millero and Hawke 1992). Ion-association models developed for natural systems incorporate experimental data for a large number of ion pairs, activity correction equations for single ions and ion pairs over the temperature and concentration range of interest, and mineral-solubility data as a function of temperature (Parkhurst et al. 1985; Ball and Nordstrom 1987; Allison et al. 1990). Models based on the ion-pair approach have not been developed extensively for solutions containing complex mixtures of electrolytes to very high concentrations.

**Pitzer ion-interaction approach.** The most widely accepted approach for prediction of ion activities and mineral solubilities in complex concentrated electrolyte mixtures is based on the Pitzer ion-interaction formalism (Pitzer 1973, 1974, 1975; Pitzer and Mayorga 1973; Pitzer and Kim 1974). Models based on the Pitzer approach have been developed for application to a variety of geochemical systems, from acidic to basic, dilute to concentrated, over a range in temperature, total pressure, and partial pressures of component gases (Pitzer 1982, 1991; Clegg and Whitfield 1991). The earliest geochemical applications of Pitzer-based models involved mostly calculations of ion-activity and mineral-solubility relations in waters containing seawater-type components. Whitfield (1975) applied Pitzer’s equations to calculate ion activities in seawater. Harvie et al. (1980), Harvie and Weare (1980), and Harvie et al. (1982, 1984) applied Pitzer’s equations to calculate ion activities and mineral precipitation sequences in evaporating seawater.

![Figure 1](image-url)

**Figure 1.** Comparison of results from the ion-pair model (PHREEQE) and the ion-interaction model (PHRQPITZ) for predicting gypsum solubility in NaCl and Na₂SO₄ solutions. Symbols represent experimental data.

A comparison of two widely used computer codes, one based on the ion-pair approach (PHREEQE, Parkhurst et al. 1985), and the other the ion-interaction approach (PHRQPITZ, Plummer et al. 1988), indicates better agreement between experimental
solubility data and the ion-interaction model than between the experimental data and the ion-pair model (Fig. 1). Although enhancements to the ion-pair model by modifying ion-association constants and incorporating extended versions of the Deby–Hückel equation have yielded improved agreement between experimental data and ion-pair model predictions at higher concentrations (e.g. Nordstrom and Ball 1984; Parkhurst 1990), the majority of model calculations for concentrated solutions of complex composition typically rely on the Pitzer formulism for calculating ion activities.

Models based on the ion-interaction approach have been developed extensively for a variety of industrial and geochemical applications. A number of excellent reviews on the original development of the Pitzer ion-interaction approach, and database compilations dedicated to predicting the geochemical behavior of the main components present in seawater, are available (e.g. Weare 1987; Plummer et al. 1988; Clegg and Whitfield 1991; Pabalan and Pitzer 1991). For predictions of the solubility of minerals in non-seawater systems, and for trace components in seawater-type waters, the application of Pitzer-based models requires special consideration to determine whether the geochemical database incorporated in the model (interaction parameters, mineral-solubility constants, etc.) accurately encompasses the composition of the water to be modeled. This review summarizes recent additions to the earlier work on developing Pitzer-based models, with a particular emphasis on recently evaluated ion-interaction parameters and the application of ion-interaction models to field settings.

**Combined or “hybrid” model.** The Pitzer ion-interaction equations, in their original form, assume complete dissociation of all ions, and represent the interaction between ions solely with ion-interaction equations with parameters derived from experimental data. It became apparent early in the development of models based on the ion-interaction approach that the assumption of complete dissociation provided an inadequate description of the chemical behavior of some electrolyte solutions over a broad range of concentration, temperature, and pressure. Introduction of association constants for strongly associated species provided a large improvement to the original “strict” Pitzer approach (e.g. Millero and Schreiber 1982; Harvie et al. 1984; Readon and Beckie 1987; Read and Clegg 1997). Many applications require the introduction of ion pairs or association constants to provide reliable predictions of mineral solubility in concentrated solutions. Models which include both association constants and ion-interaction equations have been dubbed “combined” or “hybrid” models, or modified Pitzer models.

An alternative to including ion-association and stability constants directly into an ion-interaction model is the approach taken by Millero and coworkers. Here, stability constants are corrected using ionic strength-dependent equations based on the ion-interaction formulism (e.g. Millero and Hawke 1992). The approach described by Millero and Hawke (1992) is particularly well-suited to the description of trace constituents in waters covering a range of concentration but with a similar matrix.

**MODEL DESCRIPTION**

**Summary of model formulation**

Development of specific models based on the Pitzer formulism to predict mineral solubility in natural waters requires ion-interaction parameters and mineral free-energy data. Binary and ternary interaction coefficients, obtained from solution properties for all binary and ternary combinations of ions in the water from which the solid is precipitating or dissolving, are required. Higher order interaction coefficients are generally not required. The interactions between binary and ternary combinations of ions are estimated through statistical regression of experimental data. For example, the equilibrium reaction for dissolution of a simple divalent metal sulfate:

\[
\text{MSO}_4 \rightleftharpoons \text{M}^{2+} + \text{SO}_4^{2-}
\]

is described by the mass-action expression:

\[
K_w = a_w m_w = m_w m_{\text{SO}_4}^2 \gamma_w \gamma_{\text{SO}_4}^2
\]

where \(a\) represents the activity, \(m\) the molality (mol/kg solvent), and \(\gamma\) the single-ion activity coefficient. To calculate concentrations of dissolved species \(m\) in equilibrium with a phase (or solubility), estimates of \(\gamma\) are required. Values of \(\gamma\) depend strongly on the solution composition and concentration, and are defined for cations and anions as (Harvie and Weare 1980; Plummer et al. 1988):

\[
\ln \gamma_w = z_w^2 F + \sum_z m_z (2B_{wz} + ZC_{\text{wz}}) + \sum_z m_z (2\Phi_{wz} + \sum_z \mu_{wz} w_{wz}) + \sum_z \mu_z \ln \sum_z m_z \mu_{wz} c_w
\]

and

\[
\ln \gamma_x = z_x^2 F + \sum_z m_z (2B_{xz} + ZC_{\text{xz}}) + \sum_z m_z (2\Phi_{xz} + \sum_z \mu_{xz} w_{xz}) + \sum_z \mu_z \ln \sum_z m_z \mu_{xz} c_x
\]

where the subscripts \(w\) and \(x\) represent cations and \(w\) and \(x\) represent anions. The summation index \(z\) represents the sum over all cations in the system, and the double summation \(w < z < x\) represents the sum over all distinguishable pairs of dissolved cations. Similar definitions for \(a\) and \(a < a\) apply for anions in the system. The quantity \(F\) includes the Debye–Hückel term and other terms as follows:

\[
F = -\frac{\sqrt{F}}{1 + b F} \left[ F \ln (1 + b F) \right] + \sum_z \sum_z \mu_z m_z B_{wz} + \sum_z \mu_z m_z \Phi_{wz} + \sum_z \mu_z m_z \mu_{wz}
\]

where \(b = 1.2\) at 25°C, \(I\) is the ionic strength, and \(A^4\) is defined as:

\[
A^4 = \frac{1}{3} (2\pi N a_a/1000)^4 (e^3 / DK I)^4
\]

In Equation (6), \(N_a\) is Avogadro's number, \(e\) is the density of water, and \(D\) is Boltzmann's constant, and \(K_D\) is the dielectric constant of water.

For salts containing monovalent ions, the terms \(B_{\text{BX}}^* B_{\text{BX}}^* \) and \(B_{\text{AX}}^* B_{\text{AX}}^* \) are defined as:

\[
B_{\text{BX}}^* = B_{\text{BX}}^* + B_{\text{BX}}^* e^{-\alpha \sqrt{I}} \quad (7)
\]

\[
B_{\text{AX}}^* = B_{\text{AX}}^* + B_{\text{AX}}^* (\alpha \sqrt{I}) \quad (8)
\]

\[
B_{\text{AX}}^* = B_{\text{AX}}^* (\alpha \sqrt{I}) / I \quad (9)
\]
The variable CMX is also required to define the solution chemistry for single-salt systems and is given by:

$$C_{CMX} = C_{CMX}^{bulk} / \left(2 \sqrt{\mu_{x}} \right)$$

The coefficient $Z$ in Equations (3) and (4) is:

$$Z = \sum m_i x_i$$

The parameters $\beta^{(0)}, \beta^{(1)}, \beta^{(2)},$ and $\gamma^{(1)}$ that define the variables $B$ and $C$ in Equations (12)-(15) are determined from statistical fits of experimental data, usually osmotic coefficient data, obtained for binary solutions.

For solutions containing more complex mixtures of electrolytes, the additional parameters required are $\Phi$, to describe cation–cation and anion–anion interactions, and $\Psi$, to describe cation–anion–anion and anion–anion–cation interactions. Values of $\Phi$ are calculated using:

$$\Phi^s = \theta^s + \theta^p(I) + \theta^g(I)$$

$$\Phi^b = \theta^b + \theta^p(I)$$

$$\Phi^g = \theta^g(I)$$

where $\theta$ is the only adjustable parameter and is determined empirically from experimental data collected for solutions of more complex composition. $\theta^s$, $\theta^p$, and $\theta^g$ are defined in Pitzer (1973) and Harvie and Weare (1980). More recent modifications of the original Pitzer's solubility equations have been developed to improve predictions in highly concentrated solutions (e.g., Rard and Clegg 1997).

Values of $\Phi$ and $\Psi$ required to calculate mixing in ternary systems are generally obtained from the same two-salt mixtures so that the parameters are internally consistent. Binary and ternary interaction parameters are usually derived from isopiestic data at concentrations above about 0.1 m, and at lower concentrations from other data types, such as freezing-point depression or electrochemical cell data. Commonly, solubility products and mineral free-energy values are adjusted so that they are compatible with a given solution-chemistry model (see Pitzer 1979b, 1991, 1993; Fabalan and Pitzer 1991). As an independent check, mineral free-energy values are often compared to values obtained from independent thermodynamic methods. The resulting solubility products may or may not be consistent with values obtained using alternative solution-chemistry models, such as the conventional ion-association model. The ion-interaction parameters are also temperature dependent, allowing for reliable calculation of solubility relations versus temperature (Sylveste and Pitzer 1976, 1977; Fabalan and Pitzer 1987; see Fig. 2).

**Internal consistency of model data sets**

A fundamental requirement in the development of a robust ion-interaction model is consistency or compatibility of ion-interaction parameters and other thermodynamic constants. The development of a set of ion-interaction parameters for a specific system requires binary interaction parameters for all binary combinations of ions, and ternary interaction coefficients for all ternary combinations of ions. If an extra charged species is included, as in the modified or hybrid approach, then all binary and ternary combinations of parameters. Once a set of interaction parameters is developed for all binary and ternary combinations, then the model is usually further developed for predicting mineral solubility by adjusting mineral free-energy data until the difference between predicted concentrations and experimental concentrations is minimized through, for example, linear least-squares regression. Weighting coefficients are commonly utilized to accommodate different expected or actual degrees of precision in the regression analysis (see Harvie et al. 1984). The final model should be an "internally consistent" set of equations and data which can be used as a combined package to predict mineral solubility within that system. This condition of internal consistency is the same as that required in the development of an ion-association model, as described in detail by Nordstrom and Muñoz (1994).

A generalized ion-interaction model, intended to describe most of the constituents typically encountered in natural waters and waste sites, requires that all of the binary interaction parameters are evaluated using the same form of Pitzer's equations (e.g., original equations versus extended equations, completely dissociated form versus incorporation of association constants, etc.), that all ternary interaction coefficients are determined using a consistent set of binary interaction coefficients, and that all mineral solubilities are estimated using mineral free-energy values in a manner that is consistent with the aqueous model. Improvements in the techniques of parameter calculation, such as the ridge regression technique to avoid intercorrelated parameters (van Cappellen 1991), and the use of methods for simultaneously representing different data types (e.g., Muliandy et al. 1998), and utilization of empirically extended versions of Pitzer's equations (e.g., Rard and Clegg 1997), need to be applied in a consistent fashion.

Archer and Rard (1993) provided a concise description of the complexities involved with the development of internally consistent data-sets within the framework of the ion-interaction formalism. In the example system described, Archer and Rard (1993) described a case for which the tabulated standard-state properties were adjusted to bring agreement between calculated and observed phase behavior (a common practice); it was concluded that adjustments made to the standard-state properties may have compensated for errors in the excess properties.

Constants and fitting parameters assembled for specific modeling efforts cannot simply be combined with those assembled for other applications unless a systematic evaluation of the data compatibility has been performed. This incompatibility of model databases and formulations has been an important limitation in applying the ion-interaction approach to complex field sites. The following sections focus on various models assembled.
to apply the Pitzer’s equations to predict mineral solubility in natural waters, the compatibility of these models, and what might be needed to make the models more compatible.

Table 2. Summary of aqueous systems studied involving sulfate-mineral solubilities in waters of bulk seawater-type composition.

<table>
<thead>
<tr>
<th>System</th>
<th>Sulfate Compounds</th>
<th>T Range °C</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-K-Mg-Ca-Cl-SO₄</td>
<td>alkali-earth phases in Table 1</td>
<td>25°C</td>
<td>Harvie and Weare (1980), Harvie et al. (1982, 1984)</td>
</tr>
<tr>
<td>Na-K-Mg-Cl-Cl₂SO₄</td>
<td>mirabilite, thenardite, gypsum, anhydrite, glauberite</td>
<td>25 to 250°C</td>
<td>Møller (1988)</td>
</tr>
<tr>
<td>Na-Cl-Cl₂SO₄</td>
<td>anhydrite, gypsum</td>
<td>to 200°C</td>
<td>Monnin (1990)</td>
</tr>
<tr>
<td>Ca-Na-Cl₂SO₄</td>
<td>gypsum, anhydrite</td>
<td>0 to 250°C</td>
<td>Raj and Atkinson (1990)</td>
</tr>
<tr>
<td>Na-K-Cl₂SO₄</td>
<td>mirabilite, thenardite, arcanite, epsomite, picromerite</td>
<td>-60 to 25°C</td>
<td>Spencer et al. (1990)</td>
</tr>
<tr>
<td>Na-K-H₂O-Cl₂SO₄</td>
<td>gypsum, anhydrite</td>
<td>0 to 100°C</td>
<td>He and Morse (1993)</td>
</tr>
<tr>
<td>Na-Cl₂SO₄</td>
<td>thenardite, mirabilite</td>
<td>0 to 100°C</td>
<td>Marliacy et al. (1998)</td>
</tr>
<tr>
<td>Na-K-Mg-Ca-Cl₂SO₄-H₂O</td>
<td>mirabilite, thenardite, epsomite, arcanite, gypsum, + others</td>
<td>-60 to 25°C</td>
<td>Marion and Farren (1999)</td>
</tr>
</tbody>
</table>

1 P = 1 bar, except for Monnin (1990), which is 1 kbar

MODEL DEVELOPMENT TO PREDICT SULFATE-MINERAL SOLUBILITY

Sulfate-mineral formation in the system Na-Ca=Mg-K-Cl-SO₄-H₂O

Much effort has been focused on the prediction of sulfate-mineral solubility both in seawater-type mixtures and in waters containing the major ions observed in seawater (Table 2). In papers by Harvie et al. (1980), Harvie and Weare (1980), and Harvie et al. (1982, 1984), as summarized by Weare (1987), the Pitzer approach was applied to predict ion activities and mineral solubilities in waters containing the major constituents in seawater. These papers described the development of a comprehensive model (referred to as the Harvie-Møller-Weare or HMW model) for the formation of evaporite minerals, including sulfate minerals, from concentrated solutions. Prediction of the solubility of the common sulfate minerals (e.g. anhydrite, alabandite, biotite, epsomite, gypsum, glauberite, hexahydrite, kainite, kieserite, leonite, mirabilite, picromerite, polyhalite, syngenite, and thenardite) over a range in concentration in the binary, ternary, and through the full six-component Na-Ca=Mg-K-Cl-SO₄ system was described in detail.

The initial efforts of Harvie and coworkers were expanded to predict mineral solubilities at higher temperature in the work of Pabalan and Pitzer (1987), Møller (1988), Greenberg and Møller (1989), and Møller et al. (1998). In these papers, the ion activities and mineral solubilities were described for the mixed Na-Ca-K-Cl-SO₄-H₂O system to 350°C.

Predicting Sulfate-Mineral Solubility in Concentrated Waters

Pabalan and Pitzer (1987) and Pitzer (1991) provided sulfate-mineral solubility relations for several binary and ternary sulfate mixtures, and reported the corresponding ion-interaction parameters. Data for mirabilite and thenardite solubility at 0 and 35°C were presented. Also given were data for arcanite solubility between 0 and 225°C, and the solubility of the MgSO₄ minerals epsomite, hexahydrite, and kieserite between 0 and 200°C, with the corresponding derived ion-interaction parameters. Solubility isotherms for NaCl and Na₂SO₄ mixtures, for KCl and K₂SO₄ mixtures, and for MgCl₂ and MgSO₄ were provided for several temperatures.

Monnin (1990) expanded the efforts of Møller (1988) to include the influence of pressure to 1 kbar, and presented solubility isotherms for gypsum and anhydrite at various pressures. Monnin used density and compressibility data to estimate P dependence in the interaction parameters. Monnin determined that the introduction of ion pairs was necessary to predict relations at higher T and P conditions. This is in contrast to the approach of Harvie and Weare (1980), who found that the assumption of complete dissociation provided a reliable representation of sulfate-mineral solubility in the simplified seawater system. The expansion of Monnin (1990) allows the ion-interaction approach to be applied to higher pressure systems, such as those that occur in deep oceanic basins and in the crustal subsurface. Others also expanded the original HMW model to include a larger temperature and pressure range for specific applications, such as was done by He and Morse (1993) to describe halite, gypsum, and anhydrite solubility in oil-field brines.

The original parameterization of the Na-K-Mg-Cl-Ca-SO₄-H₂O system by Harvie and Weare (1980) was expanded by Spencer et al. (1990) to include temperatures to -60°C for prediction of mineral-solubility relations during seawater freezing. The focus of the Spencer et al. parameterization was mainly on chloride minerals, but included sulfates such as mirabilite and thenardite. Spencer et al. recommended that the sulfate portion of their model not be extended below -37°C, and be limited to waters with low SO₄ concentrations. Marion and others (Marion and Farren 1999; Morse and Marion 1999) revised and expanded the Spencer et al. model to improve the parameterization for Na and Mg sulfate phases, and to add several sulfate solids not previously included in the Spencer et al. model. This latter contribution allows for prediction of sulfate-mineral formation to temperatures as low as -37°C, and to lower temperatures if concentrations of SO₄ are also limited to low values. This limitation at very low temperatures is attributed to the lack of experimental data from which constants can be derived, and not to deficiencies in the modeling approach.

More recent work, such as that by Archer and Rand (1998) on the MgSO₄-H₂O system from 298.15 to 440 K and the solubility of MgSO₄·7H₂O at 25°C, which used modified versions of the original Pitzer’s equations, and include a MgSO₄ ion pair to represent this system. Marliacy et al. (1998) provided a consistent approach for parameterization of the NaSO₄ + NaCl system between 273.15 K and 373.15 K which allows simultaneous representation of molar dissolution enthalpies and solubility data for halite, thenardite, and mirabilite in binary and ternary systems. Solubility isotherms provided for Na₃SO₄ + NaCl mixtures at 303.15 and 373.15 K indicate good agreement between predicted and experimental data. The crystalization enthalpies were further considered in this system for application to materials that are mirabilite-based and have latent heat storage (Marliacy et al. 2000). Other studies, such as that described by Pavicevic et al. (1999) on the Na₂HPO₄-NaSO₄ system at 298.15 K, allow calculations to be performed in other industrially important mixtures.

Geochemical interpretations and predictions involving sulfate minerals in various settings commonly integrate geochemical models with physical flow and solute-transport equations. These integrated models require estimation of various solute-transport and weathering processes.
as density. Pitzer's equations can be used to estimate solution densities (e.g. Monnin 1989; Obst et al. 1997) and mutual diffusion coefficients (Albright et al. 1998). These models require data on binary and ternary mixtures, from which physical properties of more complex mixtures can be calculated, similar to the approach used to calculate ion activities in complex mixtures through Equations (3) and (4). Systematic measurements and compilations of partial molal density and diffusion-coefficient data for concentrated binary and ternary electrolyte mixtures are required. For calculation of physical properties involving sulfate waters, these compilations must also include data for mixtures containing sulfate (e.g. Albright et al. 1998 and references within), and evaluation of the interaction model parameters for use with Pitzer's equations. Integration of these physical properties with solute-transport equations is an important step in predicting sulfate-mineral solubility in non-static systems.

Table 3. Summary of aqueous systems studied for sulfate minerals containing trace components in seawater and continental waters.

<table>
<thead>
<tr>
<th>System</th>
<th>Phases</th>
<th>T Range</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr–Na–Cl</td>
<td>celestine</td>
<td></td>
<td>Reardon and Armstrong (1987)</td>
</tr>
<tr>
<td>Ba–Na–Cl–SO₄</td>
<td>barite</td>
<td>25 to 300°C</td>
<td>Raju and Atkinson (1988)</td>
</tr>
<tr>
<td>Ca–K–Mg–Na–Sr–Cl–SO₄</td>
<td>celestine, barite</td>
<td></td>
<td>Monnin and Gallinier (1988)</td>
</tr>
<tr>
<td>Sr–Na–Cl–SO₄</td>
<td>celestine, barite</td>
<td>25 to 100°C</td>
<td>Raju and Atkinson (1989)</td>
</tr>
<tr>
<td>Ba–Na–Sr–SO₄</td>
<td>celestine, barite</td>
<td>25°C</td>
<td>Felmy et al. (1990)</td>
</tr>
<tr>
<td>Fe(II)–Na–Cl–SO₄</td>
<td>mirabilite, melanterite, mixed Fe(II)Na phase</td>
<td>25°C</td>
<td>Ptacek (1992)</td>
</tr>
<tr>
<td>Na–K–Ca–Mg–Ba–Sr–Cl–SO₄</td>
<td>barite, celestine</td>
<td>to 200°C</td>
<td>Monnin (1999)</td>
</tr>
</tbody>
</table>

1 P = 1 bar, except for Monnin (1999), which is 1 kbar.

Formation of Ba, Sr, and Rb sulfates

Reardon and Armstrong (1987) presented experimental data and ion-interaction parameters derived to describe celestine solubility in water, seawater, and NaCl solutions over a range in temperature (Table 3). Monnin and Gallinier (1988) evaluated the solubility of celestine in the system Ba–Ca–K–Mg–Na–Sr–Cl–SO₄–H₂O and observed good agreement between predicted solubility values using Pitzer's equations and celestine solubility in NaCl solutions, but less satisfactory agreement for celestine solubility in Na₂SO₄ solutions. Felmy et al. (1990) reported new solubility studies for barite and celestine in Na₂SO₄ solutions, and interpreted the data using Pitzer's equations.

Phase equilibria in the system K₂SO₄–Rb₂SO₄–H₂O system at 25°C were described by Kalinkin and Rumyantsev (1996). This system involves formation of continuous solid solutions. To address this problem, Kalinkin and Rumyantsev (1996) combined solid-solution theory (see chapter by Glynn, this volume) with Pitzer's equations. Problems encountered during their analysis were described in detail. The need to quantify the formation of solid solutions in concentrated solutions is apparent (Gamejager 1993). Although there have been some outstanding advances in this area (e.g. Königsberger et al. 1999), general deficiency in predictive capabilities is evident when existing ion-interaction models are applied to solid solutions or systems with multiple closely related phases.

Barite and celestine solubility in the Na–K–Ca–Mg–Ba–Sr–Cl–SO₄–H₂O system to 200°C and 1 kbar was parameterized by Monnin (1999). The results were compared to measured mineral solubility in pure water to 1 kbar, and in NaCl solutions to 300 bars. Activity coefficients of Ba²⁺ and SO₄²⁻ in seawater were also calculated for temperature, pressure, and salinity values observed in the ocean, and were compared to published values. Again, inclusion of the BaSO₄ ion pair was necessary to provide agreement to experimental data. Monnin (1999) provided a thorough review of previous studies on barite and celestine solubility, including studies that had focused on concentrated solutions (see chapter by Hanor, this volume).

Boerlage et al. (1999) compared the application of a model based on Pitzer's equations with other models for calculating the saturation state for BaSO₄ in a reverse-osmosis system. It was observed that at higher ionic strengths, the Pitzer approach was more reliable than the models typically used in water-treatment applications.

Formation of metal sulfates

The majority of the early effort on metal-sulfate systems has been dedicated to predicting the solution properties of metal-sulfate binary mixtures (e.g. see Pitzer 1974), with less attention focused on the metal-sulfate ternary mixtures and the formation of metal-sulfate solids. Binary interaction parameters are available for most common metal-sulfate mixtures, with the exception of questionable parameters for Fe(III)–SO₄ mixing, and no parameters for Fe(II)–SO₄ mixing. Osmotic coefficient data for Fe(II)–SO₄ are inconsistent with data for other metal-sulfate mixtures (see Fig. 3). The trends in osmotic coefficient data for FeCl₂ solutions are consistent with those for other metal chlorides, but the experimental data for Fe(II) by Oykova and Balarew (1974) deviate from the trends of other metal-sulfate solutions, and from more recent data by Nikonov et al. (1989). Fe(III) hydrolizes strongly, and parameterization for this system is complex.

In a series of papers by Reardon and others (Reardon and Beckie 1987; Reardon 1988, 1989; Baes et al. 1993), interaction parameters were evaluated for various metal-sulfate mixtures (Table 4). Reardon and Beckie (1987) provided solubility products for melanterite (FeSO₄·7H₂O) and szomolnokite (FeSO₄·H₂O) over the temperature range 0 to 100°C. Here the binary interaction parameters for FeSO₄ mixing were derived from the osmotic coefficient data of Oykova and Balarew (1974). Reardon (1988) expanded the concentration range for the binary parameters for Al–SO₄ mixing, from which a solubility product for Al₂(SO₄)₃·17H₂O (alunogen) was obtained. Reardon (1988) then provided solubility isotherms for mixing in the ternary systems between Al₂(SO₄)₃ and CuSO₄, FeSO₄, MgSO₄, NiSO₄ or CaSO₄ (e.g. Fig. 4). In most cases, the experimental solubilities for these systems were closely predicted using ternary interaction parameters set.
Predicting Sulfate-Mineral Solubility in Concentrated Waters

Table 4. Summary of aqueous systems studied involving Mg-sulfate and metal-sulfate solubilities in acidic solutions.

<table>
<thead>
<tr>
<th>System</th>
<th>Phases</th>
<th>P,T Range</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–HSO₄–SO₄</td>
<td>melaniterite, szomolnokite</td>
<td>0-90°C</td>
<td>Reardon and Beckie (1987)</td>
</tr>
<tr>
<td>Al–Cu–SO₄, Al–NH₄–SO₄</td>
<td>chalcantite, alunogen, morenosite, halotrichite, epsonite, pickeringite, gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al–Mg–SO₄, Al–Ca–SO₄</td>
<td>chalcantite</td>
<td>25°C</td>
<td>Baes et al. (1993)</td>
</tr>
<tr>
<td>Cu–HSO₄–SO₄</td>
<td>nickelite</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>Pb–Na–SO₄</td>
<td></td>
<td>60°C</td>
<td></td>
</tr>
<tr>
<td>Mg–HSO₄–SO₄</td>
<td>MgSO₄·7H₂O, MgSO₄·5H₂O, MgSO₄·H₂O</td>
<td>25°C</td>
<td>Reardon and Clegg (1999)</td>
</tr>
<tr>
<td>Ba–HSO₄–SO₄</td>
<td></td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>Ra–HSO₄–SO₄</td>
<td></td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>K–Cu–Ni–SO₄</td>
<td>K₃SO₄·NiSO₄·6H₂O, cyanochroite</td>
<td>25°C, 1 bar</td>
<td>Christov (1999)</td>
</tr>
</tbody>
</table>

The temperature dependence of three hydrates of NiSO₄ were provided by Reardon (1989), together with newly derived ion-interaction parameters. Baes et al. (1993) obtained binary interaction coefficients for the CuSO₄ mixture and a solubility product for CuSO₄·5H₂O at 25°C.


Ion-interaction parameters and solubility products for mixing in the ternary systems Fe(II)–Na–SO₄ and Fe(II)–Cl–SO₄ were evaluated by Piteck (1992) (see Fig. 5). Also evaluated were the solubility products for melaniterite, mirabilite, and a mixed Fe,Na hydrated sulfate phase at other temperatures. These studies were conducted to provide interaction parameters for Fe(II) mixing in solutions containing Na, SO₄, and Cl, and to predict the solubility of siderite in brines and mine drainage waters.

Christov (1999) summarized solubility data for a study which included measurements in the system K–Ni–SO₄ and K–Cu–SO₄. The study described previously determined Pitzer parameters for the binary systems CO₃–H₂O, CaCO₃–H₂O, and MgCO₃–H₂O.
were calculated for $K_2SO_4$, $NiSO_4\cdot 7H_2O$, $CuSO_4\cdot 5H_2O$, and the double salts $K_2SO_4\cdot NiSO_4\cdot 6H_2O$ and $K_2SO_4\cdot CuSO_4\cdot 6H_2O$ Christov (1999) attributed the small difference between $K_0^a$ and the values that had been obtained in previous studies to small differences in measured saturation concentrations used in the calculations, not to errors in the ion-interaction parameters. For the mixing in these ternary systems, $K_2SO_4\cdot NiSO_4\cdot 6H_2O$ is stable for $mK_2SO_4 > 0.8m$, and $K_2SO_4\cdot CuSO_4\cdot 6H_2O$ is stable for $mK_2SO_4 > -0.2m$ (Fig. 6). At lower concentrations of $K_2SO_4$, the single hydrates of Ni and Cu are stable. In addition to the double sulfates, Christov determined the free energy of mixing for $K_2SO_4(Ni,Cu)SO_4\cdot 6H_2O$, which is expected to form in solutions containing both Ni and Cu. The solubility of this latter phase is described well with the Pitzer approach assuming regular mixing, which is consistent with the similarity in unit-cell parameters of the co-crystallizing isostructural double salts. The efforts of Herbert and Mönig (1997) to include Cd and Zn in the HMW model were described by van Gaans (1998); these authors investigated the interaction of Cd and Zn with Cl and SO$_4$.

Formation of sulfates in acid systems

Prediction of equilibria reactions in systems containing elevated concentrations of acid is important for a variety of applications (Tables 4 and 5). These include industrial and metallurgical applications in which acid is added for manufacturing, ore extraction, and other purposes (see Paine et al. 1997, 1998; Schuiling and van Gaans 1997).
environmental geochemistry of mine-waste sites where elevated concentrations of acid and
metals are common (e.g., Blows and Jambor 1990; Blows et al. 1991; Pateck and Blows
1994; Ridley et al. 1997, 1999; Nordstrom and Alpers 1999; Nordstrom et al. 2000), and
the formation of acid-sulfate aerosols where highly evaporative conditions lead to extreme
concentrations of dissolved acid and the formation of acid-sulfate solids (e.g., Clegg et al.
1998). Although ion-interaction models have been developed for specific applications,
much of the information is directly transferable to other systems.

Prediction of sulfate-mineral solubility in acidic solutions requires, foremost,
interaction parameters for describing the pure acid solutions prior to the addition of other
acids or dissolved salts. The aqueous properties of H₂SO₄ using Pitzer’s equations were
first represented by assuming complete dissociation of H₂SO₄. Later, the inclusion of the
bisulfate species HSO₄⁻ improved the predictions for this system (e.g., Reardon and Beckie
1987). These contributions provide reliable predictions up to 6 m H₂SO₄. Hovey et al.
(1993) and Clegg et al. (1994) introduced a molar fraction-based version of the ion-
interaction equations and introduced an ionic-strength-dependent third virial coefficient
which further improved predictions in the H₂SO₄ system. The Clegg et al. (1994) approach
seems to be widely used to predict the chemistry of formation of atmospheric aerosols,
wherein very high concentrations of acid are common. Hachimi et al. (1996) derived
parameters for the H₂SO₄ system between 0 and 27 mol kg⁻¹.

The previously described studies by Reardon and Beckie (1987), Reardon (1989), and
Baes et al. (1993) also included parameterization and mineral solubilities for solutions
containing H₂SO₄. Parameterization of the system FeSO₄-H₂SO₄-H₂O between 0 and
90°C approaches 6 m H₂SO₄. Solubility isotherms were presented for several temperature
increments. Reardon (1989) provided an analysis of mixing in the system NiSO₄-H₂SO₄-H₂O
mostly at 25°C, and concentrations of NiSO₄ were closely predicted to 6 m H₂SO₄. In the parameterization of the CuSO₄-H₂SO₄-H₂O at 25°C, Baes et al. (1993)
established solubility relations for CuSO₄-5H₂O versus H₂SO₄ up to a concentration
of 6 m H₂SO₄. Baes et al. (1993) also gave a useful discussion of the role of parameter
covariance on the predicted solution concentrations.

In a series of papers focusing on application to the processing of uranium ore, Paige
H₂SO₄ ranged between 0 and 6.19 mol kg⁻¹. The parameterization by Paige et al. relied
on that of the H₂SO₄ system by Reardon and Beckie (1987). In this case, the HSO₄⁻ species
was incorporated into the data analysis, but ion pairs were not.

Hovey et al. (1993) described the thermodynamics of Na₂SO₄(aq) between 0 and
100°C for mixtures containing H₂SO₄ and Na₂SO₄. Hovey et al. (1993) included new
experimental data for this system, and modeled data presented by Rard (1992). The
analysis by Hovey et al. (1993) explicitly considered the formation of the HSO₄⁻ species,
and provided a molar ratio-based analysis to 6 m and a molarity-based analysis to 15 m.
Rard (1997) and Rard and Clegg (1999) provided experimental data and analysis with the
Pitzer model for MgSO₄ mixtures with H₂SO₄ at 298.15 K. Their analysis included the formation of a Mg₂SO₄⁻ ion pair, and the HSO₄⁻ species. Solubility curves for
MgSO₄-7H₂O, MgSO₄-5H₂O, and MgSO₄-2H₂O as a function of H₂SO₄ concentration were
provided.

Formation of sulfate minerals in solution and temperature ranges representing
conditions in atmospheric aerosols was described by Potokuchi and Wexler (1995),
Massucci et al. (1996), Clegg et al. (1996, 1998), and Pierrot et al. (1997), among others.
The formation of numerous sulfate phases containing H⁺, NH₄⁺, Na⁺, NO₃⁻, Cl⁻, and
others, was quantified. Complex solubility diagrams were provided over a range of
solution-composition and temperature conditions, similar to the original diagrams for
mineral stability as had been depicted by Harvie et al. (1984). Information related to these
studies can likely be used to predict mineral solubility in other acidic systems.

Formation of sulfates in basic systems

The application of the Pitzer approach to predict sulfate precipitation from basic waters
has received less attention than in other systems. Harvie et al. (1984) gave solubility
predictions for mirabilite, thenardite, aracnate, and other mixed sulfate and carbonate
compounds in the system N-K-Mg-Ca-Cl-SO₄-H₂O at 25°C. Solubility curves for SO₄²⁻
and CaOH, KOH, NaHCO₃, and Na₂CO₃ solutions were provided. Pitzer (1991)
summarized the solubility relations of thenardite in NaOH, NaCl, and Na₂SO₄ mixed
solutions at various temperatures. Duchesne and Reardon (1995) derived interaction
coefficients for predicting the solubility of portlandite in concentrated solutions, and
included solubility isotherms for mixtures containing Ca(OH)₂ with CaSO₄, K₂SO₄, or
Na₂SO₄. The solubility of gypsum was closely described in these mixtures, including the
transitions to Ca(OH)₂ at lower SO₄²⁻ concentrations.

APPLICATION OF THE ION-INTERACTION APPROACH
TO FIELD SETTINGS

Various model formulations based on the ion-interaction approach have been
developed and applied to predict mineral saturation indices, equilibrium concentrations,
and sequences of mineral precipitation and dissolution in field systems. These applications
include comparison of precipitation sequences for evaporating seawater (Harvie et al. 1984;-
Brentley et al. 1984), evaporation of continental lake waters (Morrin and Schott 1984;-
Fleming and Weare 1986), mineral stability in subsurface brines (Langmuir and Melchor
1985), and mineral stability in stratified ocean brines (e.g., Morrin and Ramboz 1996;-
De Lange et al. 1990; van Cappellen et al. 1998). An ion-interaction model has been used
to predict the aqueous geochemistry and mineral solubility controls in acid mine waters
(Blows et al. 1991; Pateck and Blows 1994; Nordstrom et al. 2000) and acid waste
ponds (van Gaans and Schulling 1997). Most of the above applications involve either the
direct formation of sulfate minerals, or address the indirect influence of elevated
concentrations of dissolved sulfate ions on ion activities.

In a geological context, the application of the Pitzer model has relied mainly
on the original parameterization of the Na₂K-Mg-Ca-Cl-SO₄-H₂O system as developed
by Harvie and Weare (1980) and Harvie et al. (1984), which is referred to as the HMW
model. This development was incorporated into the geochemical computer code
PHRPITZ (Plummer et al. 1988), which is based on the earlier computer code
PHREEQE (Parkhurst et al. 1985). The introduction of PHRPITZ made calculations
involving the HMW model easily accessible, and the result has been widespread use
of the HMW model by the geochemical community. A variety of ion-interaction models,
including the HMW model for 25°C, the TEQUIL geothermal model by Moller et al. (1998),
the freezing model by Spencer et al. (1990), the aerosol models by Clegg and others
(e.g., Clegg et al. 1998), are also available for use online or can be downloaded from the internet
(e.g., http://geotherm.ucsd.edu; and http://www.hpc1.uea.ac.uk/~e770/aim.html). Over the past
decade, the original HMW model and variations have been applied to numerous cases
of field settings.

In the applications of geochemical models, mineral solubility relations are typically
expressed in terms of the saturation state of a water with respect to a specific mineral. The
degree of saturation is expressed as a saturation index (see Plummer et al. 1988), or a
normalized saturation index (e.g., Fleming and Weare 1986). In PHRPITZ, the saturation

index, \( SI \), is defined as \( SI = \log IAP - \log K \), where \( SI = 0 \) represents equilibrium conditions, \( SI < 0 \) undersaturated conditions, and \( SI > 0 \) supersaturated conditions. The solubility constant \( K \) is usually corrected for deviation from temperature from standard conditions, and the ion-activity product (IAP) is calculated for the appropriate temperature and pressure conditions; therefore, the degree of saturation is corrected accordingly.

Results of the applications

Prediction of sulfate-mineral solubilities in waters containing the major seawater components. Harvie et al. (1980) applied Pitzer’s equations to calculate the sequence of mineral formation from evaporating seawater. The calculations were consistent with observed precipitation sequences in seawater.

Another early application of Pitzer’s equations to calculate solubility relations for sulfate minerals was that by Krumgalz and Millero (1982, 1983). In this application, the Harvie and Weare (1980) formulation of the Pitzer model was used to calculate saturation indices for Dead Sea water, and mixtures of Dead Sea water and Mediterranean water, to assess the degree of gypsum saturation and the likelihood of gypsum precipitation under mixing conditions. It was concluded that the Dead Sea waters are supersaturated with respect to gypsum, that gypsum precipitation is limited by kinetic factors, and that supersaturation of the Dead Sea water with respect to gypsum is consistent with other experimental data. Later applications of this model included calculations to determine the maximum extent that the Dead Sea could evaporate before the activity of water in the overlying atmosphere would exceed the activity of water in the evaporated Dead Sea water (Krumgalz et al. 2000).

The ion-interaction model was applied to a modern marine evaporite at Boca de Virrili, Peru (Brantley et al. 1984). The estuary has a pronounced horizontal salinity gradient that has formed in response to evaporative losses, with salinity values ranging from marine composition at its mouth, to brines of approximately 330,000 ppm total dissolved solids (TDS) in the innermost waters. Application of a revised version of the Harvie and Weare (1980) model, assuming a fractional crystallization pathway, yielded close agreement between predicted and observed concentrations of the major ions. Predicted locations of calcite, gypsum, and halite precipitation also agreed closely with field observations.

The geochemistry of alkaline earth sulfates in the slightly acidic, Ca-rich brines of the Palo Duro Basin of Texas was investigated by Langmuir and Melchior (1985) to evaluate mineral stabilities at a potential repository for highly radioactive wastes. An ion-interaction model was applied to calculate saturation indices for gypsum, anhydrite, celestine, barite, and \( RaSO_4 \). The calculations indicated that the brines in this basin are at saturation with respect to gypsum (SI between -0.11 and +0.07), celestine (SI between -0.19 and +0.22), and anhydrite (SI between -0.18 and -0.02), and are near saturation with respect to barite at several locations (SI between -0.65 and +0.34) except one. The brines are strongly undersaturated with respect to pure \( RaSO_4 \), consistent with the expectations of a Ra-Ba solid-solution control on Ra concentrations.

De Lange et al. (1990) described sulfate-related equilibria in hypersaline anoxic brines of the Tyro and Bannock basins of the eastern Mediterranean. The Bannock brines are probably formed from recent dissolution of underlying late-stage evaporites into seawater. Pitzer’s equations were used to calculate gypsum, dolomite, and barite SI values. Near-saturated conditions were observed in the Tyro and Bannock basins, with the saturation state being exceeded as a result of mixing of two brine types. The predicted precipitation of gypsum is consistent with observations of freshly precipitated gypsum in the Bannock Basin. There is no obvious evidence for substantial amounts of gypsum precipitation in the Tyro brines. Supersaturation was predicted for barite at the interface between brine types where stagnation of waters occurs. At the time of the calculations, however, there was only limited information for predicting barite saturation indices in complex brines using Pitzer’s equations.

Marion and Farren (1999) applied the extended version of the Spencer et al. (1990) model (the FREZCHEM model) to predict mineral precipitation sequences during evaporation and freezing of seawater. Marion and Farren (1999) specifically expanded the Spencer et al. model to improve sulfate mineral stability relations and to incorporate additional sulfate solids. The predicted sequences of mineral formation, and the predicted concentrations of dissolved ions agree remarkably well with experimental data (Fig. 7). This example illustrates the benefit of continuously improving the model parameterization and evaluation process.

Saturation indices for anhydrite were calculated by Moulin and Ramboz (1996) for the pore waters and sediment pore waters of the Red Sea deeps. Changes in pressure were observed to have the same magnitude of effect as temperature on the calculated saturation indices for anhydrite.
Yechiel and Ronen (1997) described sequential precipitation of gypsum, halite, carnallite, and possibly sylvinite and bischofite in newly exposed sediments of the Dead Sea. The presence of these minerals was verified by SEM, and their depth of occurrence was inferred from saturation indices, calculated using PHRQPITZ.

From the above examples, it can be concluded that the ion-interaction approach has been well-developed for many geochemical applications involving the formation of sulfate minerals formed with the major ions Na and Ca, and to a certain extent, the trace components Ba and Sr.

**Prediction of sulfate-mineral solubilities in deep subsurface brines.** As part of a study on the geochemical evolution in the Culebra Dolomite Formation, New Mexico, Siegel and Anderholm (1994) calculated saturation indices for common evaporite minerals using PHRQPITZ and compared the results with mineralogical observations. Calculated saturation indices for gypsum were 0.001±0.09 for 30 water samples, consistent with the ubiquitous presence of gypsum and the rapid approach to equilibrium typically observed for this mineral. With the exception of one sample, the waters were undersaturated with respect to anhydrite.

He and Morse (1993) gave a summary of ion-interaction parameters that were derived to describe the solubility of halite, gypsum, and anhydrite in Na–K–H–Ca–Mg–Cl–OH–SO₄–H₂O solutions over a range of temperature and pressure. Comparisons were provided for predicted solubilities and experimental data for the temperature range 25–200°C and the pressure range 1-1000 bar, and example calculations were performed to show scale formation in oil-field settings.

The potential for scale formation and corrosion from geothermal waters in geothermal plants was addressed by Pátzay et al. (1998), who gave experimental data for CaCO₃ and CaSO₄ mixtures, CaSO₄ solubility in NaCl solutions at elevated temperature, and temperature- and pressure-dependent Pitzer parameters. Specific applications to a geothermal plant included data such as the bubble point and partial pressures of various gases.

**Prediction of sulfate-mineral solubilities in continental lakes and shallow groundwaters.** Donovan and Rose (1994) applied PHRQPITZ to calculate saturation indices for lake water and groundwater collected from an area of evaporative groundwater-dominated lakes in the North American Plains. These lakes are basic, ranging between pH 8.5 to 10.3, and exhibit a large range in salinity, from 1000 to 264,000 ppm TDS. The precipitation of carbonate minerals limits Ca²⁺ activity, preventing the formation of gypsum. As a result, high concentrations of SO₄ and other dissolved constituents develop. Many of the lakes approach saturation with respect to mirabilite, occasionally biséilde, and non-sulfate phases. Calculated reaction sequences using the ion-interaction model indicate that evaporation of water with a composition consistent with shallow groundwater, and to a lesser extent groundwater derived from intermediate depths, is the most probable source for both the final composition of the lakes in this region and for the observed massive accumulations of mirabilite-and carbonates.

**Prediction of sulfate-mineral solubilities in acid waters.** Blowes et al. (1991) applied a modified version of the HMW model to a mine drainage site in eastern Canada. Oxidation of sulfide-rich tailings at this site has led to the development of high concentrations of sulfate (up to 100 g/L) and ferrous iron (up to 50 g/L), and to pH values as low as 0.5 in the pore waters of the tailings. Blowes et al. (1991) added the temperature-dependent interaction parameters for the Fe(II)–H₂SO₄–H₂O system presented by Reardon and Beckie (1987) to PHRQPITZ and provided saturation indices for a number of minerals, including gypsum and melanterite (Fig. 8). The saturation indices for gypsum...
varied between -0.0487 and 0.0601. Gypsum was observed to be present throughout the depth of the tailings. Saturation indices for melanterite ranged from -1.0228 at the base of the impoundment, to -0.2916 at 50 cm below the impoundment surface. Saturation-index values for melanterite reached a maximum at the depth of a cimented hardpan layer, 30 to 50 cm below the impoundment surface. Mineralogical study indicated that the hardpan layer was composed of tailings cemented by secondary precipitates, principally melanterite and gypsum. The melanterite was crystalline and ranged in color from clear to pale green. Energy-dispersion analyses indicated that samples that had crystallized in situ in the tailings were almost pure FeSO₄. As interaction parameters were not available for the Fe(III)-H₂SO₄-H₂O system, Blowes et al. (1991) estimated Fe(III) activities through field-measured Pt-electrode Eh values and the Nernst equation. Calculations indicated the pore water to be undersaturated with respect to Fe(OH)₃ near the impoundment surface. As the pH increased toward the hardpan layer, the water became supersaturated with respect to Fe(OH)₃·H₂O. Saturation indices calculated for jarosite indicated supersaturated conditions throughout the impoundment. Jarosite and goethite were detected in samples of the tailings materials, but accumulations of Fe(III)-bearing minerals were small. Blowes et al. (1991) also applied the ion-association model MINTEQA2 (Allison et al. 1990), for which the database was updated with the association constants from WATEQ4F (Ball and Nordstrom 1987) to include constants for acidic waters. The saturation indices calculated for gypsum using MINTEQA2 indicated consistently highly supersaturated conditions, suggesting that this model does not reliably describe mineral solubility relations in mine drainage waters at high concentrations of dissolved solids.

Schuilirig and van Gaans (1997) described geochemical reactions that occur in an acidic discharge pond at a TiO₂ plant at Armysanks, Crimea, Ukraine. Waste acid and fine-grained "phosphogypsum" have been discharged into an isolated bay since 1969. The pH in the pond has slowly decreased to 0.85 over the course of the pond's operation. The acid was initially neutralized by contact with underlying carbonate-rich muds, but the formation of a hardpan has prevented further neutralization of the acid, and concentrations of acid have slowly increased due to evaporation. Precipitation of natrojarosite occurs as the water is concentrated from evaporation. Calcium from the underlying carbonate sediments reacts to form gypsum. As occurs at many base-metal processing sites that utilize jarsite to control Fe (Dutricz and Jambor, this volume), the jarsite at Armysanks incorporating many trace metals, including V, Cr, and Ni. PHRQIPITZ was applied to describe the geochemical evolution of this acid pond through a series of titration calculations (van Gaans and Schuilirig 1997). The predicted changes in geochemistry agreed closely with the observed chemistry for various periods in the history of the pond.

One of the issues surrounding application of the Pitzer approach to concentrated waters relates to the thermodynamic treatment of acid. It would be convenient for field scientists to have a method to relate measured conventional hydrogen-ion activity (determined as pH) to the hydrogen-ion activity used in the various Pitzer-type models (see Harvie et al. 1984). Nordstrom et al. (2000) described geochemical reactions at the Iron Mountain mine site in California, where the combination of sulfide-mineral oxidation, the resulting elevated temperatures (35-48°C), and evaporation has led to hundreds of grams per liter of sulfate and Fe, and high concentrations of acid (pH < 2), to remain dissolved in the mine waters. Nordstrom et al. (2000) developed pH-electrode calibration curves using PHRQIPITZ and standard H₂SO₄ solutions (Fig. 9) to provide an internally consistent approach for defining pH and to separate HSO₄⁻ and SO₄²⁻ species at the Iron Mountain site. Among other efforts directed at the measurement of pH in concentrated waters are those by Harvie et al. (1984), Knauss et al. (1990, 1991), Mesmer (1991), Pateck (1992), and Dorta-Rodriguez et al. (1997). These efforts assist in the specification of pH-sensitive constituents often required to model sulfate-mineral solubility in natural waters.
Predicting Sulfate-Mineral Solubility in Concentrated Waters


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Predicting Sulfate-Mineral Solubility in Concentrated Waters


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Stable Isotope Systematics of Sulfate Minerals

Robert R. Seal, II
U.S. Geological Survey
934 National Center
Reston, Virginia 20192

Charles N. Alpers
U.S. Geological Survey
6000 J Street
Sacramento, California 95819

Robert O. Rye
U.S. Geological Survey
963 Denver Federal Center
Denver, Colorado 80225

INTRODUCTION

Stable isotope studies of sulfate minerals are especially useful for unraveling the geochemical history of geological systems. All sulfate minerals can yield sulfur and oxygen isotopic data. Hydrous sulfate minerals, such as gypsum, also yield oxygen and hydrogen isotopes for the water of hydration, and more complex sulfate minerals, such as alunite and jarosite also yield oxygen and hydrogen isotopic data from hydroxyl sites. Applications of stable isotopic data can be divided into two broad categories: geochemistry and tracer studies. The equilibrium partitioning of stable isotopes between two substances, such as the isotopes of sulfur between barite and pyrite, is a function of temperature. Studies can also use stable isotopes as a tracer to fingerprint various sources of hydrogen, oxygen, and sulfur, and to identify physical and chemical processes such as evaporation of water, mixing of waters, and reduction of sulfate to sulfide.

Studies of sulfate minerals range from low-temperature surficial processes associated with the evaporation of seawater to form evaporite deposits to high-temperature magmatic-hydrothermal processes associated with the formation of base- and precious-metal deposits. Studies have been conducted on scales from submicroscopic chemical processes associated with the weathering of pyrite to global processes affecting the sulfur budget of the oceans. Sulfate isotope studies provide important information to investigations of energy and mineral resources, environmental geochemistry, paleoclimates, oceanography (past and present), sedimentary, igneous, and metamorphic processes, Earth systems, geomicrobiology, and hydrology.

One of the most important aspects of understanding and interpreting the stable isotope characteristics of sulfate minerals is the complex interplay between equilibrium and kinetic chemical and isotopic processes. With few exceptions, sulfate minerals are precipitated from water or have extensively interacted with water at some time in their history. Because of this nearly ubiquitous association with water, the kinetics of isotopic exchange reactions among dissolved species and solids are fundamental in dictating the isotopic composition of sulfate minerals. In general, the heavier isotope of sulfur is enriched in the higher oxidation state, such that under equilibrium conditions, sulfate minerals (e.g., barite, anhydrite) are expected to be enriched in the heavy isotope relative to disulfide minerals (e.g., pyrite, marcasite), which in turn are expected to be enriched relative to monosulfide minerals (e.g., 1529-6466/00/0040-0012$05.00).