The Importance of Sensitivity Analysis in Predictive Geochemical Modeling of Mine Water

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Abstract

Geochemical modeling is often used as a tool in the prediction of mine water qualities. This paper discusses the importance of incorporating sensitivity analyses to improve estimation of the uncertainty in model predictions. Model examples, including case studies, are presented to demonstrate how small changes in an assumed input value can affect the model output. Modeling examples are based on PHREEQC, the equilibrium mass transfer code developed by the United States Geological Survey (USGS). This model is widely accepted by the regulatory and scientific community.

The examples presented describe a variety of sensitivity analyses related to a number of geochemical assumptions: equilibration with atmospheric carbon dioxide; inclusion of nitrogen species; uncertainty in thermodynamic parameters; charge balancing using anions affecting metal complexation; and redox potential. The latter is a critical parameter in geochemical modeling, but usually poorly constrained. Selection of redox conditions can have major ramifications in terms of modeling outcome.

Key Words: PHREEQC, uncertainty, pH, redox potential, Eh, aqueous, simulation

Introduction

Geochemical modeling is often used as a tool in the prediction of mine water qualities. George Box wrote "*essentially, all models are wrong, but some are useful*" (Box and Draper 1987). Incorporation of sensitivity analyses into modeling studies is essential to the development of meaningful mine water quality predictions. Sensitivity analysis is the study of how the variation (uncertainty) in the output of a mathematical model can be apportioned, qualitatively or quantitatively, to different sources of variation in the input of a model. Without an understanding of this sensitivity, interpretation of model results may be incomplete or even incorrect.

This paper focuses on the application of geochemical modeling to simulate the chemical processes occurring in mine water systems. Although biological reactions can be important in mine water systems, they are not considered here. The geochemical model used in this study is PHREEQC (Parkhurst and Appelo 1999), an equilibrium speciation and mass-transfer code developed by the United States Geological Survey (USGS). The model is designed to perform a wide variety of low-temperature aqueous geochemical calculations. The model has the ability to simulate mixing of waters, precipitation/dissolution of selected solids, redox reactions, atmospheric interaction, and adsorption of metals. PHREEQC is widely accepted by the regulatory and scientific community and is available free of charge from the USGS. Multiple thermodynamic databases of different origins and with different advantages/limitations are provided by the USGS (i.e. phreeqc.dat, minteq.dat, minteq.v4.dat, wateq4f.dat and llnl.dat).

Typically, geochemical modeling studies should include the following steps:

- **Study Definition** – Definition of the study objectives including the specific question(s) to be answered through geochemical modeling.
- **Conceptual Model Development** – Identification of the chemical reactions to be modeled and the key geochemical parameters likely controlling these reactions.
- **Data Compilation and Review** – Determination of the accuracy and completeness of information available to characterize the chemical properties of the system (aqueous and solid).

The above approach is used to define model assumptions and to select parameters for inclusion in sensitivity analyses. In particular, redox potential (Eh) and pH, often referred to as master geochemical variables, are controlling factors in many chemical reactions (e.g., mineral solubility and sorption) and therefore frequently included in sensitivity analyses. In most natural waters, Eh cannot be measured unambiguously (Appelo and Postma 1994), resulting in uncertainty in the redox values to be used in modeling. Difficulties in the measurement of redox potentials are generally attributed to a number of factors, including the presence of multiple redox species, a lack of equilibrium between redox species, and analytical difficulties and limitations associated with direct measurements of redox potential (Hem 1992). For this reason, the redox condition of waters is often inferred from the absence or presence of redox species, such as certain sulfur, nitrogen, or iron species. With respect to the assignment of pH values, the use of field-measured pH values is generally preferred to laboratory-measured values which may not reflect in-situ conditions due to geochemical reactions occurring between sample collection and laboratory determination of pH that change pH conditions (e.g., degassing of CO_2, mineral precipitation). However, field-measured pH values may not always be available.

This paper uses example models to demonstrate how small changes in an assumed input value can affect the model output. For the first example, a case study is presented in significant detail to demonstrate implementation of the steps listed above. For subsequent examples, only pertinent details regarding the model set-up and results are presented.

Geochemical Modeling Examples

Example 1 – redox potential sensitivity analysis

This example shows the effect of a change in assumed redox potential on predictions of copper mobility in a creek downgradient of a tailings storage facility (TSF) (Figure 1). Surface and groundwater quality at the site have been affected by discharge of acid rock drainage (ARD) from mine facilities. Cleanup activities are currently ongoing.

Figure 1. Site photograph showing creek and TSF.

The conceptual model for the study area is shown in Figure 2. Dissolved copper concentrations in the upper reaches of the creek (i.e. upstream of the TSF and downstream from a waste rock stockpile (WRS)) generally range from 20 to 40 µg/L. ARD from the WRS is captured, neutralized by lime addition in a water treatment plant, and then discharged to the creek upstream of the TSF. Dissolved copper

concentrations downstream of the TSF are lower (i.e. a few micrograms per liter). The observed decrease in dissolved copper concentrations downstream of the TSF is attributed to both 1) dilution from a clean water inflow; and 2) attenuation due to copper sorption onto iron (oxy)hydroxides. Although both mechanisms affecting copper concentrations occur year-round, dilution and sorption have been identified as the dominant controls on the reduction in copper concentrations in the spring and fall, respectively.

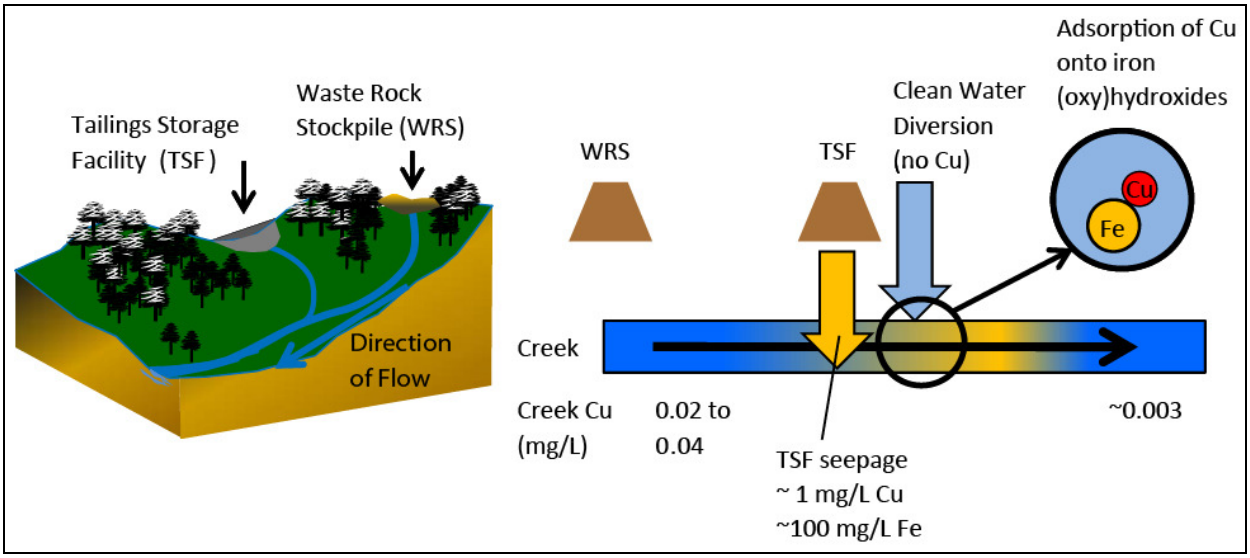

Figure 2. Site conceptual model for Example 1.

Discharge of ARD from the tailings impoundment is a source of iron loading to the creek. As tailings seepage containing dissolved iron discharges to the creek, both an increase in solution pH, due to mixing with the creek and clean water inflow, and a change to more oxidizing conditions, due to exposure to atmospheric oxygen, promote precipitation of iron (oxy)hydroxides. Metals and metalloids in the creek and/or tailings seepage (e.g., Cu, As and Co) are attenuated due to adsorption and/or co-precipitation with the iron (oxy)hydroxides.

Collection and treatment of tailings impoundment seepage is being considered. For constituents that behave conservatively in the creek, the beneficial effect of this alternative on downstream water quality is easily evaluated. Any constituent load removed due to capture and treatment of seepage will result in an equivalent load loss in the creek. The effect of collection and treatment of tailings seepage on copper concentrations in the creek, however, is not as straightforward. Iron loading from the tailings impoundment currently contributes to a net decline in copper concentrations in the lower reaches of the creek by acting as an adsorbent.

Geochemical modeling was conducted to evaluate the effect of tailings seepage collection on copper concentrations in the creek. For each inflow (i.e. the creek, tailings seepage and clean water diversion) a representative water quality was assigned. Solutions were mixed in proportion to their contribution to the total flow. Following mixing, geochemical controls on resultant water quality were evaluated. Precipitation of ferrihydrite [$Fe(OH)_3$] and adsorption onto this phase was simulated. The number of available ferrihydrite adsorption sites was calculated assuming 0.005 strong bonding sites and 0.2 weak bonding sites per mole of ferrihydrite precipitated. A specific surface area of 600 m^2/g was assumed. These three values represent default values developed by Dzombak and Morel (1990) and incorporated in PHREEQC as part of the standard thermodynamic database. Solution chemistries were assumed to be at equilibrium with atmospheric carbon dioxide (i.e. pCO_2 of $10^{-3.5}$ atm). Model simulations were conducted assuming a range of volumetric seepage collection as follows: 0% (base case); 50%; and, 90%. The

initial model simulations assumed Eh values of 200 mV and 500 mV for groundwater and surface water inflows, respectively (scenario A), based on typical values for groundwater and surface waters, respectively (Appelo and Postma 1994). Simulations were also conducted assuming a 100 mV increase in the Eh values, i.e. 300 mV and 600 mV for groundwater and surface water, respectively (scenario B). An increase in 100 mV was selected as representative of the range of uncertainty in the assumed values.

Good agreement between measured and predicted creek copper concentrations downstream of the TSF for the base case simulations indicates that the model accurately captures the geochemical processes occurring on site. Fall simulation model results for copper and iron are shown in Figure 3. Model results for the pure mixing simulation are shown as black bars. Model results with geochemical controls (i.e. mineral precipitation and adsorption) for the two redox scenarios are shown by the blue and green bars. The magnitude of copper adsorption predicted by the model is a function of a number of factors, including pH, number of adsorption sites and the concentration of other competing adsorption species (e.g., As). Sensitivity analysis simulations identified that the assumed redox values for the input solutions have an effect on model results with respect to both the amount of ferrihydrite precipitation and the affinity of copper for ferrihydrite. An increase in the initial redox value results in an increase in the amount of ferrihydrite precipitation (shown as a decline in the concentration of dissolved iron between the blue and green simulations). The reduction in dissolved copper is attributed to both an increase in the number of sorption sites and the form in which copper occurs in solution. For the original simulation (blue bars), copper in solution occurs primarily as Cu^{+} (pie chart for scenario A in Figure 3). A slight increase in oxidizing redox conditions results in an increase in the amount of Cu^{2+} (pie chart for scenario B in Figure 3), which is more readily sorbed on ferrihydrite.

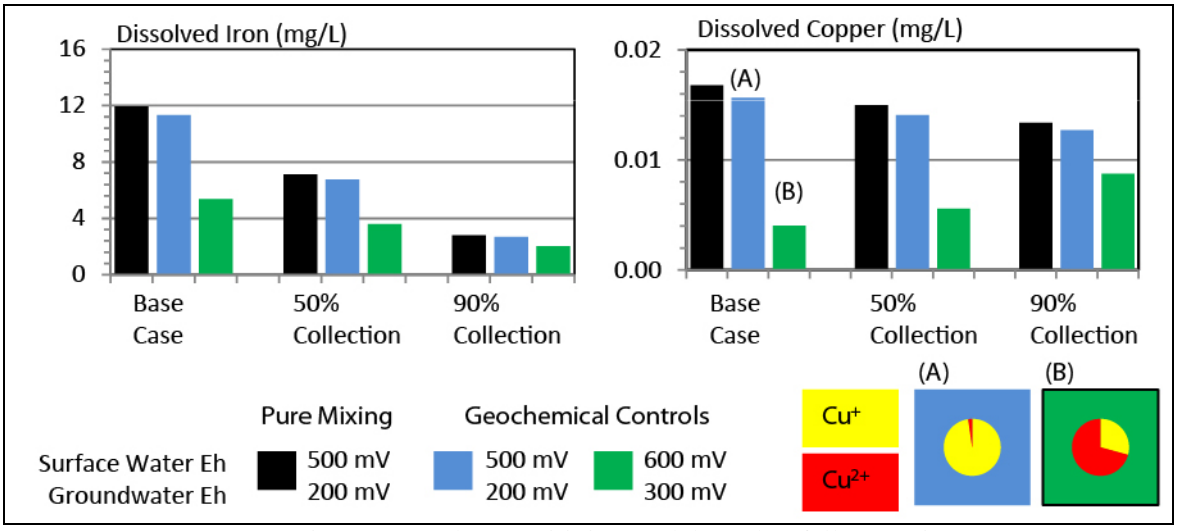

Figure 3. Redox sensitivity model results (fall scenario).

The results of the redox sensitivity simulation also indicate a different conclusion with respect to the effect of collection and treatment of tailings seepage on dissolved copper concentrations in the downgradient creek. For the scenario with the more oxidizing conditions (scenario B), a slight increase in dissolved copper concentrations is observed following collection of seepage as follows (green bars): 0.004 mg/L (base case); 0.006 mg/L (50 percent capture and treatment); and 0.009 mg/L (90 percent capture and treatment). These simulations predict an adverse effect on dissolved copper concentrations following collection and treatment of seepage, whereas the simulations of current conditions predict a beneficial effect, i.e. a reduction in dissolved copper concentrations.

The model study concluded that collection and treatment of tailings seepage is not predicted to have a significant impact on dissolved copper concentrations in the creek; however, there is the potential for small increases in dissolved copper concentrations following a reduction in iron loading. Model simulations were very sensitive to the assumed redox condition. Because actual redox conditions were poorly constrained and variable, the modeling results were, therefore, inconclusive. Because many of the chemical reactions that may control the transport of metals at mine sites (e.g., mineral precipitation and adsorption) are redox dependant, inclusion of a reasonable range of redox values in model simulations should be a priority.

Example 2 – inclusion of nitrogen species

Geochemical modeling may be used to predict the effectiveness of mine water treatment systems. In this example, geochemical modeling was conducted to evaluate the treatment of acidic waste rock seepage by an anoxic limestone drain. The assumed quality for waste rock seepage was based on the results of geochemical laboratory testing (i.e. static and kinetic testing results), a common practice in mine water quality predictions. Drill core is the most common material source for geochemical testing during the early stages of mine development. However, because testing of drill core cannot capture the potential for nitrogen release due to rinsing of residual products from blasting agents (e.g., ammonium nitrate/fuel oil (ANFO)), nitrogen concentrations are typically predicted independently. This example illustrates how inclusion of nitrate in the model simulation affected the model results due to its influence on redox potential.

The assumed seepage quality (indicative parameters only) and model results are shown in Table 1. Three simulations were conducted as follows:

- **Simulation 1** – seepage quality A equilibrated with an infinite amount of calcite; sorption onto ferrihydrite that precipitated from solution.
- **Simulation 2** - seepage quality A equilibrated with an infinite amount of calcite and atmospheric carbon dioxide (partial pressure of $10^{-3.5}$ atm); sorption onto ferrihydrite that precipitated from solution.
- **Simulation 3** - seepage quality B equilibrated with an infinite amount of calcite and atmospheric carbon dioxide; sorption onto ferrihydrite that precipitated from solution.

The only difference between seepage qualities A and B is the presence of dissolved nitrate nitrogen at 10 mg/L-N. Nitrate concentrations in mine waters are difficult to predict and dependent on a number of factors including the type of explosive, climatic conditions, and blast efficiency (Morin and Hutt 2009).

Table 1. Treatment evaluation model inputs and results.

Parameter (unit)	**Model Input**		**Model Results**		
	Seepage Quality (A)	**Seepage Quality (B)**	**Simulation 1**	**Simulation 2**	**Simulation 3**
Seepage Quality			A	A	B
pH (s.u.)	4.0	4.0	8.3	7.9	7.9
Eh (mV)	+200	+200	-250	-180	+400
SO_4 (mg/L)	1,150	1,150	1,150	1,150	1,150
Ca (mg/L)	300	300	308	313	320
Fe (mg/L)	10	10	9.8	9.9	0.0001
Cu (mg/L)	0.01	0.01	0.01	0.01	0.0001
As (mg/L)	0.20	0.20	0.19	0.20	0.0002
NO_3-N (mg/L)		10			10

Equilibration of acidic seepage with calcite results in an increase in pH and aqueous calcium concentrations. As shown in Table 1, model results for simulations 2 (no nitrate in waste rock seepage) and 3 (nitrate present in waste rock seepage) indicate significant differences (3 to 4 orders of magnitude) in the amount of ferrihydrite precipitation and subsequent attenuation of Cu and As due to sorption. The addition of the redox species nitrate in simulation 3 results in a large increase in the resultant redox value (Eh) and more favorable conditions for ferrihydrite precipitation and associated sorption. These results demonstrate the importance of understanding the variables that are controlling the resultant water chemistry, in particular pH and redox. In this simulation, equilibration with atmospheric carbon dioxide does not materially affect the model outcome in terms of predicted water quality (i.e. no significant differences in Simulation 1 and 2 model results). An example of a simulation in which carbon dioxide did materially affect the model outcome follows.

Example 3 – pit lake modeling – equilibration with atmospheric carbon dioxide

Geochemical modeling to predict pit lake water quality typically involves mixing of multiple solutions with variable water qualities. Following mixing, the potential for geochemical controls to affect resultant water quality is evaluated. Equilibrium with atmospheric carbon dioxide, at a partial pressure of $10^{-3.5}$ atmospheres, is often assumed.

This example illustrates the importance of assessing the partial pressure of carbon dioxide in all input solutions prior to mixing. Derivation of input water qualities by mathematical mixing of laboratory results from multiple samples may result in incompatible solution pH and alkalinity values. This may result in solutions with elevated values for the partial pressure of carbon dioxide (pCO_2).

Table 2 shows selected results for a simple pit lake model with four inflows: direct precipitation; groundwater; surface runoff; and pit wall runoff. Assumed water qualities for each inflow are shown (only indicative parameters presented). Two water qualities for pit wall runoff are included, with the assumed alkalinity value being the only difference between solutions A and B. A change in the assumed alkalinity results in a change in the partial pressure of carbon dioxide (a model calculated value). Model results for pure mixing and following equilibration with atmospheric carbon dioxide are shown. When equilibrium with atmospheric carbon dioxide is assumed, simulation A results in a higher final pH value than simulation B. Final pH values for the two simulations differ by more than 2 pH units (i.e. 5.2 versus 3.2 for simulations A and B, respectively). This difference is attributable to an unreasonably high pCO_2 value for simulation A pit wall runoff ($10^{2.0}$ atm), which is the result of an erroneous alkalinity concentration (5 mg/L) for a pH 3 water. This example illustrates how a very small change in an assumed input alkalinity concentration can have a significant impact on the model results.

Table 2. Pit lake model input and output water qualities for selected constituents.

Parameter (unit)	**Model Inputs**					**Model Results**			
	Rain	**Ground-water**	**Surface Runoff**	**Pit Wall Runoff (A)**	**Pit Wall Runoff (B)**	**Mix (A)**	**Mix (A) pCO_2 eqm.**	**Mix (B)**	**Mix (B) pCO_2 eqm.**
Mixing ratio (%)	4	5	30	61	61	-	-	-	-
pH (s.u.)	5.7	7.1	7.5	3.0	3.0	3.1	5.4	3.2	3.2
Alkalinity (mg/L)	0	100	7	5	0	10	10	0	0
SO_4 (mg/L)	0	142	31	754	754	476	476	476	476
Cu (mg/L)	0	0.02	0.003	8	8	5	5	5	5
pCO_2 (atm)	-	$10^{-2.1}$	$10^{-3.6}$	$10^{2.0}$	$10^{-2.1}$	$10^{1.8}$	$10^{-3.5}$	$10^{-2.4}$	$10^{-3.5}$

Example 4 – thermodynamic database uncertainty

Speciation modeling can be used in groundwater fate and transport studies to evaluate the potential for natural attenuation of a constituent due to mineral precipitation. The potential for mineral precipitation is assessed using the saturation index (SI) calculated according to Equation 1.

$$SI = \log (IAP/K_{sp}) \qquad (1)$$

where the SI is the ratio of the ion activity product (IAP) of a mineral and the solubility product (K_{sp}). An SI close to zero indicates that the water is at equilibrium with a particular mineral phase, suggesting that mineral precipitation may control aqueous concentrations. Analysis of the aquifer solids is required to confirm the presence of the mineral phase.

Speciation modeling was conducted to assess the potential for natural attenuation of cadmium due to precipitation of otavite [$CdCO_3$] in a groundwater plume downgradient of a mine facility. Figure 4 shows groundwater laboratory and field-measured pH values and cadmium concentrations for samples collected from a monitoring well over a time period of approximately 15 years. Solubility curves for otavite using the solubility products included in the MINTEQ (log K -13.7) and PHREEQC (log K -12.1) databases are superimposed on this figure. This figure shows the effect of uncertainty in thermodynamic data on model results. If a log K value of -12.1 is assumed, the model results indicate equilibrium with respect to otavite; however, if a log K value of -13.7 is assumed, the model results indicate supersaturation with respect to otavite. Although the literature reports a wide range of values for the solubility product of otavite, a recent literature review by Stipp et al. (1993) suggests a log K value of –12.1. This is consistent with the value adopted by the PHREEQC database. When a log K value of -12.1 is assumed, the groundwater modeling results suggest that precipitation of otavite is the principal control on dissolved cadmium concentrations in the groundwater.

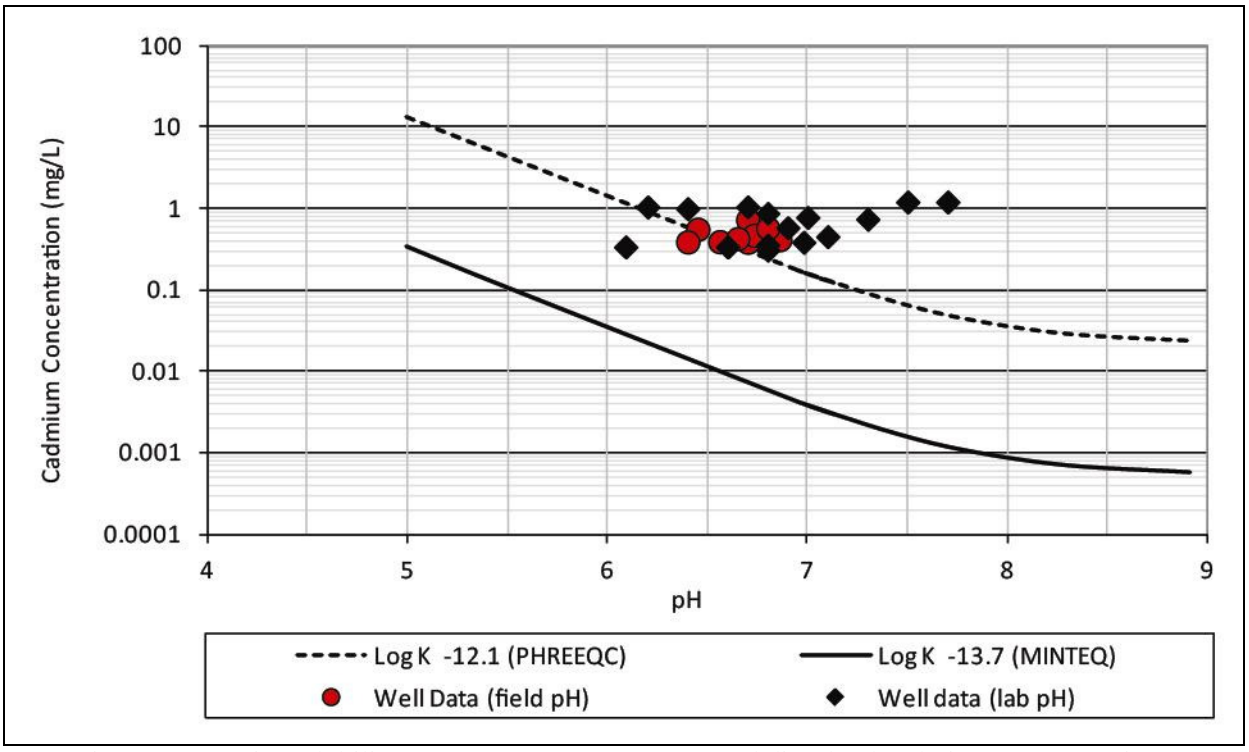

Figure 4. Otavite solubility curves, pH measurements and dissolved cadmium concentrations.

Figure 4 also illustrates the importance of using field-measured pH values (preferably measured using a flow-through cell) in geochemical modeling. In general, use of the higher, laboratory-measured pH

values would result in the conclusion that groundwater is supersaturated with respect to otavite. Higher laboratory-measured pH values are likely attributable to degassing of carbon dioxide after sample collection.

Example 5 – selection of ions for charge balance

Natural waters are always electrically neutral (i.e. always have balancing concentrations of cations and anions when reported in units of equivalents per unit volume or mass). Geochemical modeling codes, such as PHREEQC, must have input solutions that are electrically neutral to achieve numerical stability in solving the simultaneous equations that are used in the calculations. To attain electroneutrality for all model input solutions, charge-balance deficits are adjusted by instructing the program to automatically add (or subtract) the amount of a specified anion or cation necessary to achieve electroneutrality. In selecting the anion or cation to be added, the modeler must ensure that addition of the ion does not materially affect the outcome of the geochemical model. Because chloride and potassium are "inert", conservative ions, and K/Cl-bearing salts generally are very soluble, chloride and potassium are often selected for use in charge balancing. However, as the next example will illustrate, this approach may not always be appropriate. The addition of an ion to a solution changes its chemical speciation, which may affect the reactive chemistry.

Geochemical modeling was conducted to estimate the amount of mercury sorption onto a defined amount of hydrous ferric oxide. The initial solution chemistry is shown in Table 3. The initial charge balance error for this solution was 16%, indicating an anion deficit. The solution was charge balanced by the addition of sulfate (simulation A) or chloride (simulation B) and equilibrated with 1 g of hydrous ferric oxide (Hfo). The number of available adsorption sites was calculated assuming the default conditions of 0.005 strong bonding sites and 0.2 weak bonding sites per mole of Hfo with a specific surface area of 600 m^2/g.

Table 3. Charge balance example simulation results.

Parameter (unit)	**Model Input**	**Model Output**	
		Simulation A – SO_4 charge balance	Simulation B – Cl charge balance
pH (s.u.)	7.0	7.2	7.2
Eh (mV)	500	430	470
Alkalinity (mg/L)	100	108	108
Ca (mg/L)	100	98	98
Cl (mg/L)	1.0	1.0	85
Hg (mg/L)	2.0	0.03	0.15
K (mg/L)	2.0	2.0	2.0
Mg (mg/L)	50	46	47
Na (mg/L)	20	20	20
SO_4 (mg/L)	270	360	248
charge balance error (%)	16	0	0

Model results are shown in Table 3. For simulation A, adsorption results in a decrease in aqueous mercury concentrations from 2 mg/L to 0.03 mg/L. For simulation B, mercury adsorption is predicted to be less effective than in simulation A, resulting in a final dissolved mercury concentration of 0.15 mg/L. Mercury speciation results for simulations A and B are shown in Figure 5. In simulation B, the addition of chloride results in the formation of mercury chloride complexes that inhibit adsorption of mercury. The addition of chloride to correct the charge balance error, therefore, materially affects the model outcome.

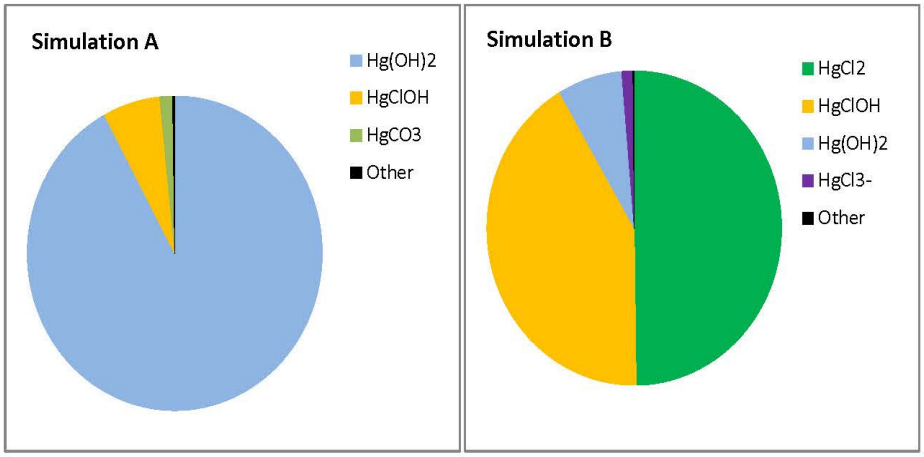

Figure 5. Mercury speciation results (Example 5 - Simulations A and B)

Summary and Conclusions

The model examples presented in this paper demonstrate how a small change in an assumed input value can affect the model output. Sensitivity analyses are an important component of any modeling study to identify and understand 1) which variables affect the modeled system and the predicted outcomes, and 2) how they affect the model result.

- **Redox Potential and pH -** Redox potential and pH are controlling factors in many chemical reactions and therefore should be included in sensitivity analyses. Small changes in redox potential may affect both adsorption (example 1) and mineral solubility reactions. The redox potential of solutions during chemical reactions will be affected by the presence of oxidized species in solution (e.g., addition of nitrate – example 2). Due to the inherent difficulties in measuring Eh in natural waters, measurement of a redox couple, in particular a couple for the parameter of interest (e.g., As^{3+} and As^{5+}), is an alternative methodology to estimate Eh values. Sensitivity analyses may also be conducted over a range of reasonable Eh values for groundwater or surface water systems (Appelo and Postma 1994).
- **Atmospheric Gases** – Equilibration with atmospheric gases will affect model results (example 3). It is recommended that model results with and without geochemical controls be evaluated. The partial pressure of gases in input solutions should be reviewed to ensure they are within expected and reasonable ranges.
- **Thermodynamic Databases** – Interpretation and application of geochemical model results should consider the degree of uncertainty in the thermodynamic database (example 4). In acidic mine environments, where metal concentrations may be elevated and uncommon mineral phases present, verification of the thermodynamic database is important. The USGS has published numerous papers that provide thermodynamic data for metals of interest in mine water systems including arsenic, chromium and aluminum (e.g., Nordstrom et. al. 1990; Nordstrom and Archer 2003; Ball and Nordstrom 1998; Nordstrom and Ball 1986). The selection of geochemically-credible mineral phases is fundamental to the evaluation of the potential for secondary mineral precipitation to limit metals mobility at a mine site. Nordstrom and Alpers (1999) provide guidance on likely mineral solubility controls in mine waters.
- **Charge Balance** – The selection of a parameter for use in charge balancing may affect the chemical behavior of ions in solution. This paper demonstrated the effect of an increase in chloride concentrations on the affinity of mercury for an adsorbent (example 5). Although not demonstrated in this paper, complexation reactions may also affect mineral solubility.

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Acronyms

Hfo	hydrous ferric oxide
IAP	ion activity product
K_{sp}	solubility product
SI	saturation index
TSF	tailings storage facility
USGS	United States Geological Survey