

A Calibrated Predictive Geochemical Model of Leaching and Attenuation Reactions in a Mine Pit Lake

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ABSTRACT: A geochemical model was developed to predict future water quality of the Cove pit lake in support of site closure and regulatory permitting. The terminal, groundwater-fed Cove pit lake began filling in 2001, and water-quality samples from the 15-year filling period were used to calibrate the pit-lake model and evaluate accuracy of the predictions.

Inputs to the pit-lake model included geochemical characterization results and a calibrated groundwater flow model. Modeling included the processes of mineral dissolution and precipitation, gas exchange, and adsorption.

The results of the geochemical model assess long-term chemogenetic effects on water quality and, overall, closely match observed chemistry for a variety of constituents. This work highlights the applicability of various geochemical datasets to predictive modeling, evaluates discrepancies between observed and predicted water quality, and presents geochemical modeling techniques used to achieve predictions that are both representative of observed water quality and useful for evaluating future pit-lake chemistry.

1 INTRODUCTION

The McCoy-Cove mine is a non-operational gold mining complex located along the Battle Mountain-Eureka Trend in central Nevada. The mine is composed of the McCoy and Cove open pits and associated underground workings. The Cove pit has partially filled to form the Cove pit lake following the cessation of mining and dewatering operations at the site. Regulatory requirements stipulated predictive geochemical modeling of the pit lake to evaluate the potential for water-quality degradation and for use in ongoing permitting and closure activities.

In compliance with regulatory guidance, water-quality monitoring has been conducted at the Cove pit lake during the 15-year filling period. These water-quality data provide a benchmark for the calibration of a pit-lake geochemical model. In addition to water-quality observations, a number of geochemical testing procedures were previously utilized to characterize Cove pit wall rocks. These include solid-phase rock chemistry tests, Meteoric Water Mobility Procedure (MWMP) tests, acid-base accounting (ABA) tests, and humidity-cell tests. Using the geochemical code PHREEQC, the geochemical model incorporated the water balance from a calibrated groundwater flow model, empirical solute-loading derived from the geochemical characterization testing, and the chemogenetic processes of mineral dissolution and precipitation, adsorption, and gas exchange. The geochemical model was then calibrated to the observed chemistry from water-quality monitoring reports.

2 BACKGROUND

The Cove pit has been the subject of multiple previous studies that included hydrological (Hanna & Streiff 1994; Itasca 2016), geological/mineralogical (Johnston 2003; Johnston et al. 2008), and geochemical (HCI 2002) publications and reports. These studies were used to provide background information on the Cove pit.

2.1 *Mining Operations*

Mining operations in the Cove pit began in 1988 using a combination of underground and open-pit methods. Dewatering began in 1989 using a combination of dewatering wells and sumps (Hanna & Streiff 1994). Operations continued through 2001 when the Cove mine was put into care-and-maintenance status, which continues to the present.

2.2 *Geology of the Cove Pit*

The ultimate pit surface (UPS) of the Cove pit is composed of the Triassic Augusta Mountain Formation, an intermixed sequence of limestone, dolostone, conglomerate, and sandstone. The Augusta Mountain Formation is further subdivided into the Home Station, Panther Canyon, and Smelser Pass Members. The Home Station Member is a massively bedded limestone with minor lenses of sandstone and conglomerate. The Panther Canyon Member, which was the major ore host in the Cove deposit, has been further subdivided into the lower dolostone submember and the upper transitional submember. The lower dolostone submember is a uniformly bedded dolostone, and the upper transitional submember coarsens upward from a dolostone, through silty and sandy dolostone and sandstone, to an upper conglomerate. The uppermost member of the Augusta Mountain Formation, the Smelser Pass Member, is a microcrystalline limestone. Subsequent to deposition of sedimentary rocks, the area was subjected to Tertiary volcanism, which included emplacement of Eocene dikes and sills followed by deposition of the Tuff of Cove Mine (Johnston 2003; Johnston et al. 2008).

2.3 *Regional Hydrogeology and Water Quality*

Two distinct aquifers transmit groundwater flow within the area immediately surrounding the Cove pit, an alluvial aquifer and a regional carbonate bedrock aquifer. In general, the geochemical characteristics of both aquifers are similar, although the regional carbonate bedrock aquifer displays greater average concentrations of total dissolved solids (TDS), alkalinity, sulfate, and a number of major (e.g. Ca, Mg, Mn, and Na) and trace (e.g. As, Sb, B, Cd, Tl, and Zn) dissolved constituents.

Observed water quality in the Cove pit lake is generally acceptable, with an average pH value of 7.9 standard units (s.u.) and an average TDS of 1,540 mg/L in 2015. The dominant solutes in pit-lake waters, in order of decreasing concentrations, are SO₄, alkalinity, Ca, Na, Cl, Mg, and K. The majority of constituents have shown a decreasing trend over the 15-year infilling period of the pit lake (to date). Constituents that have shown an increase in average concentration include alkalinity, Al, As, B, Cr, F, pH, K, Na, and Tl. Fluoride is the only one of these constituents that currently exceeds the associated NDEP Profile III reference value; although, a screening-level ecological risk assessment (ERM 2016) indicates that current and predicted F concentrations do not pose a risk to wildlife or livestock.

3 GEOCHEMICAL CHARACTERIZATION

The Cove pit UPS was characterized to satisfy initial permitting requirements, and in association with previous water-quality studies (e.g. HCI 2002). Characterization methods included both static and kinetic geochemical tests.

3.1 *Static Geochemical Testing Procedures*

Geochemical characterization of the Cove UPS has included MWMP tests, ABA procedures, and solid-phase rock chemistry tests. Meteoric Water Mobility Procedure tests are intended to quantify the release of solutes stored in a rock sample following interaction with meteoric water. The results of MWMP tests for the Cove pit were used to supplement the kinetic testing results by providing information on the release of Cl, F, and NO₃, as these parameters were not included in humidity-cell tests (see below).

Acid-base accounting (ABA) procedures are used to evaluate the balance between acid-generation potential (AGP) and acid-neutralization potential (ANP) within the UPS and are indicative of the potential net production of acid by the weathering of wallrock material. The results of ABA procedures for Cove pit wallrock indicate that the UPS is overall net acid-neutralizing but that some UPS materials (e.g. portions of the Panther Canyon Member) can be acid generating. The specific results of ABA tests (together with the kinetic testing results discussed below) were used to calibrate a site-specific pyrite-oxidation model that was subsequently used to predict the mass of oxidized rock inundated by the pit lake at different times.

Solid-phase rock analyses that employed acid-digestion and inductively coupled plasma spectroscopy were used to define the total amount of each chemical constituent available within the Cove UPS. These results were used to set an upper limit on the total amount of each constituent that could be released from the UPS through leaching reactions.

3.2 *Kinetic Geochemical Testing Procedures*

In addition to static geochemical testing procedures, the temporal variation in leachate chemistry was examined using humidity-cell tests. Humidity-cell tests consist of sequential flushing of a reaction vessel set up to promote continuous oxidation of rock materials, thereby evaluating the variance in leachate chemistry over prolonged periods of time. The results of humidity-cell tests were used to calculate an empirical solute-loading rate for each parameter included in the predictive geochemical model. These solute-loading rates represent the pseudo-steady state, long-term loading of constituents due to ongoing sulfide-oxidation and other mineral dissolution reactions in the UPS. A total of 32 humidity-cell tests were conducted for the Cove pit.

3.3 *Lithochemical Model*

A previous study of the Cove pit indicated that the lithologies exposed in the UPS are variably altered (Johnston et al. 2008), which has affected the geochemical characteristics of the various geologic units exposed in the UPS. The influence of alteration on acid-generation and leaching characteristics was apparent from the characterization testing; therefore, the geologic map of the Cove pit was used in conjunction with previous studies and geochemical characterization results to create a lithochemical model of the Cove UPS. This lithochemical model identified and mapped the distribution within the UPS of six distinct lithochemical rock types for utilization in the predictive geochemical model: 1) Intrusive-Unaltered, 2) Limestone-Clay, 3) Limestone-Carbonaceous, 4) Limestone-Unaltered, 5) Panther Canyon-Sulfide, and 6) Panther Canyon-Oxide. Each of these lithochemical rock types will be at least partially inundated by the pit lake during filling.

4 PREDICTIVE MODELING METHODS

The chemical composition of the Cove pit lake will be controlled by a variety of factors over the time period that the lake is approaching geochemical and hydrogeologic equilibrium. These factors include groundwater seepage into the lake, evapoconcentration, solute-loading from the UPS, gas exchange with the atmosphere, mineral dissolution and precipitation, and adsorption. Each of these processes was incorporated into the predictive geochemical model.

4.1 Water Sources

The balance between meteoric precipitation and evaporation at the Cove pit is typical of the arid conditions that are found throughout much of Nevada, with evaporation rates that are greater than meteoric precipitation rates. The Cove pit hydrogeologic groundwater flow model (HCI 2002, Itasca 2016a) indicated a net evaporation rate of 1.02 m/yr. The volume of water evaporated from the pit lake in each annual model time step was calculated as the product of this evaporation rate and the surface area of the pit lake. Evapoconcentration was applied in the PHREEQC model by removing the corresponding fraction of pure deionized water (pH=7, TDS=0).

The quantity of water in the pit lake, as well as groundwater inflow into the pit lake, was taken from the calibrated hydrogeologic groundwater flow model. This groundwater flow model was calibrated to the observed pit-lake stage elevation as well as water levels measured in groundwater wells in the area (Itasca 2016b). In order to obtain an estimate of the range of potential groundwater inflow compositions, regional groundwater chemistry was statistically analyzed to obtain three representative compositions for each aquifer. These three compositions were the average composition (mean concentration for each parameter), and the 10th and 90th percentiles (of the concentrations for each parameter) for groundwater compositions in both the alluvial and carbonate bedrock aquifers. The average groundwater composition was used as the input for the base-case prediction, whereas the 10th and 90th percentiles, respectively, represent lower and upper bounds for predicted values. These three compositions were paired with the water quantity from the flow model to define the overall solute loading from influent bedrock and alluvial groundwater in each time step in the model.

4.2 Solute Loading

The release of solutes stored in the weathered UPS has the potential to impact the water quality of the Cove pit lake. For example, stored solutes can accumulate as a result of sulfide-oxidation reactions during mining when the water table was depressed due to dewatering operations and possibly prior to mining in the zone above the pre-mining water table.

To simulate solute release in the predictive water-quality model, empirical solute-loading rates were calculated using the results of humidity-cell tests. The release of solutes from the humidity-cell tests varied through time. Release rates at the onset of testing were typically elevated, while additional reaction products (solute) that had accumulated in the sample prior to testing were being flushed from the sample. This process was simulated in the pit-lake water-quality model by calculating long-term, pseudo-steady-state solute-release rates from the humidity-cell tests (mass of solute per kg of oxidized rock per unit time) for each rock type and then applying those rates to the predicted oxidized mass for the respective rock type at the time it is inundated by the pit lake.

The predicted oxidized mass of each rock type through time was estimated using a modified approach to the Davis-Ritchie model of pyrite oxidation (Davis & Ritchie 1986, 1987, Davis et al. 1986). This model of pyrite oxidation is based on the diffusion of oxygen gas (O_2) through wall rock. The Cove pit-lake study utilized a propriety modified version of the original Davis-Ritchie model, developed by Liu et al. (2002). Additional research on pyrite oxidation has formulated rate laws governing the oxidation reaction (Jerz & Rimstidt 2004). Calculations using the method of Jerz & Rimstidt (2004) indicated that pyrite-oxidation rates may be appreciable at an O_2 concentration of approximately 0.01% of the mean atmospheric value.

The Cove pit pyrite-oxidation model was used to estimate the O_2 concentration profile through the wall rock throughout time. The predicted O_2 concentration profile was used to predict the thickness of the zone of active oxidation (i.e. greater than 0.01% of atmospheric oxygen). This thickness of the zone of oxidation was paired with the density of the UPS to derive an estimate of the rock mass actively undergoing oxidation for each lithochemical rock type of the Cove UPS throughout the modeling period.

The mass of each constituent released in each time step was then calculated according to Equation 1. The mass of solute released in each time step (S_t) from rock type n is calculated as the product of the rock mass in the oxidizing zone (M), the calculated solute-release rate (S_r), the amount of time over which the solutes had been accumulating (t , 1-year time-step duration),

and a surface area proportionality constant (C_{SA} , a scalar that relates the reactive surface area of rock in humidity-cell tests to the reactive surface area of rock in the UPS; a value of 0.25 was used in the predictive water-quality model and is discussed in more detail in Itasca 2016b). The total solute release was then summed for each of the n rock types present in the UPS.

$$S_t = \sum_1^n S_r * M * t * C_{SA} \quad (1)$$

4.3 Gas and Solid-Mineral Equilibrium Phases

The exchange of gases (carbon dioxide [CO_2] and O_2) between the atmosphere and water is a process known to affect pit-lake water quality. Pit lakes that exhibit (or are anticipated to exhibit) seasonal mixing will have enhanced gas exchange relative to stratified pit lakes or pits that are backfilled with tailings or waste rock. Pit lakes that have enhanced gas exchange with the atmosphere tend to have greater O_2 concentrations and oxidation-reduction (redox) potential, and as a result display decreased solubility for metals commonly bound in oxyhydroxides, such as Mn and Fe (Eary 1999). Enhanced CO_2 exchange with the atmosphere tends to increase pH, due to CO_2 degassing. Degassing occurs as pit-lake waters move closer to equilibrium with CO_2 concentrations in the atmosphere (values of approximately $10^{-3.5}$ atm), and farther from equilibrium with groundwater CO_2 (values of approximately $10^{-1.5}$ to 10^{-3} atm).

Although limnological modeling of the Cove pit-lake has not been performed, observations from the surface, middle, and bottom of the lake for constituents known to be dependent on the redox potential of pit-lake waters (i.e. Fe, Mn, and As) indicate that the pit lake experiences turnover at least once per year.

The PHREEQC geochemical model simulates equilibrium reactions between the bulk pit-lake solution and the specific set of equilibrium phases defined in the model inputs. The inclusion of these phases in the model was based on observations from analogous pit lakes, experimental results, literature review, and theoretical considerations. Equilibrium phases were designated for a number of constituents in the pit lake, including Al (gibbsite), Ba (barite), Ca (calcite, dolomite, and gypsum), Cd (otavite), Cu (malachite), F (fluorite), Fe (ferrihydrite), Mn (rhodochrosite), Pb (cerussite), Sr (strontianite), and Zn (smithsonite). All of these mineral equilibrium phases, with the exception of dolomite, have been noted as a likely equilibrium control in pit lakes (Eary 1999) and were allowed to precipitate in the model. Dolomite was allowed only to dissolve in the predictive model to simulate the reaction of acid-neutralizing rock types (primarily Limestone-Unaltered) with leachate derived from acid-producing rock types (Intrusive-Unaltered, Panther Canyon-Sulfide). The presence of dolomite available for reaction with acidic leachate is supported by Johnston et al. (2008), who noted the dolomite component of the Cove UPS.

4.4 Adsorption

Adsorption of species onto precipitated Fe and Mn oxyhydroxides is a process hypothesized to control the concentrations of metals (e.g. Cd, Cr, Pb, and Zn) and metalloids (e.g. As, Se, and Tl) in pit-lake environments (Davison 1993, Eary 1999, López et al. 2010), and that has been indicated by previous pit-lake modeling studies (Tempel et al. 2000, Castendyk & Webster-Brown 2007, Newman 2014). Adsorption of species to precipitated ferrihydrite in the predictive geochemical model was simulated using the diffuse double layer model (DLM) provided by Dzombak & Morel (1990). Due to incomplete thermodynamic data, adsorption to Mn oxyhydroxide phases (e.g. manganite and birnessite) was not included in the predictive model, although adsorption is known to occur on these solid species (Tonkin et al. 2004).

In order to evaluate the sensitivity of predicted water quality to adsorption, a predictive simulation was also completed using the base-case water chemistry (mean concentration for each constituent) and assuming no precipitation of (or subsequent adsorption to) ferrihydrite.

5 PREDICTIVE MODELING RESULTS

The water quality of the Cove pit was simulated for 100 years beyond the present, for a total of approximately 115 years of pit-lake infilling. In general, the predicted water quality of the Cove pit lake is similar to that of influent groundwater, with additional controls imparted from solute loading, mineral precipitation, evapoconcentration, and adsorption.

5.1 Pit-Lake Chemogenesis

Pit-lake water-quality predictions indicate an initial influx of chemical constituents to the juvenile pit lake as the UPS is flushed of accumulated solutes. Figures 1-4, respectively, display the predicted concentrations of Ca, SO₄, Na, and As throughout the simulation period. Figures 1-2 illustrate the flushing of solutes accumulated by sulfide-oxidation and mineral dissolution reactions in the UPS. Calcium concentrations in the simulated pit lake are initially high, followed by a decreasing trend as the initial pit lake is diluted by influent groundwater. These trends are reflected in the pit-lake monitoring data and are similar for SO₄ (Fig. 2). Calcium continues to follow a decreasing trend throughout the simulation period due to precipitation of calcite, whereas SO₄ shows a slight increasing trend as a result of evapoconcentration. Constituents with similar trends that were also predicted to be involved in mineral precipitation reactions include Al (gibbsite), Ba (barite), Cu (malachite), F (fluorite), and Fe (ferrihydrite).

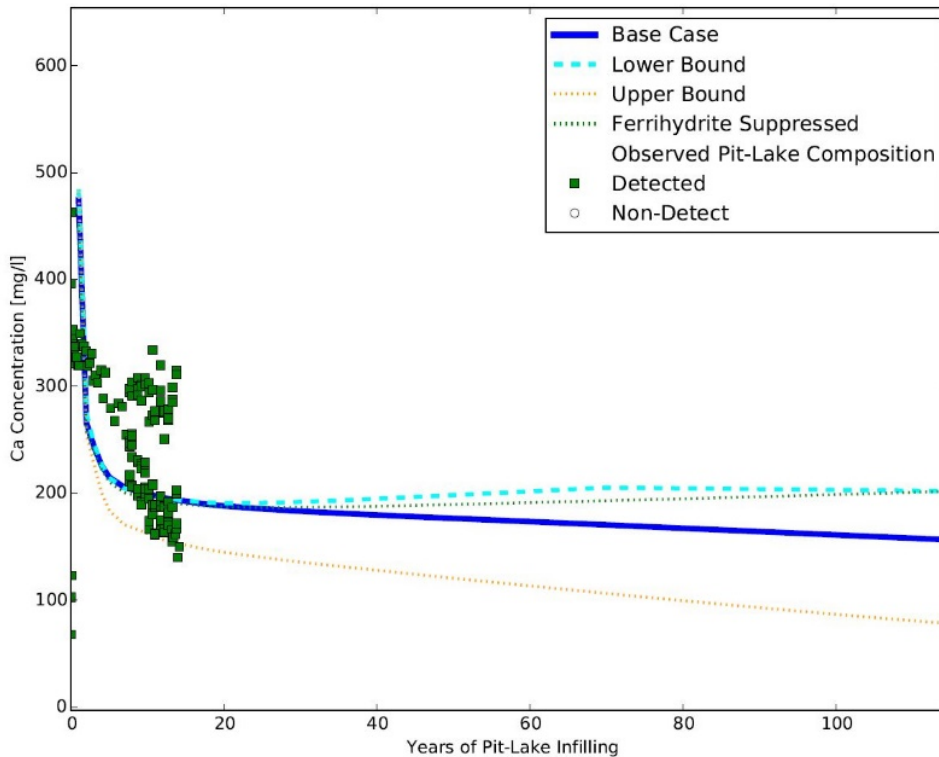


Figure 1. Calcium predictive water-quality model results (lines) and observations (points).

The long-term evapoconcentration trend in the pit lake is exemplified by Na in Figure 3. This constituent is originally derived from leaching of the UPS and influent groundwater and is not predicted to participate in subsequent chemical reactions, such as mineral precipitation or adsorption (although some ion exchange in clay minerals may occur). The increasing trend in predicted Na concentrations primarily reflects evapoconcentration of the pit lake and is similar to the trend observed in the pit-lake monitoring data. Other constituents displaying only long-term evapoconcentration trends (and not being affected by mineral equilibria) include Ag, B, Cl, Hg, K, Li, Mg, Mn, Mo, N, P, and U.

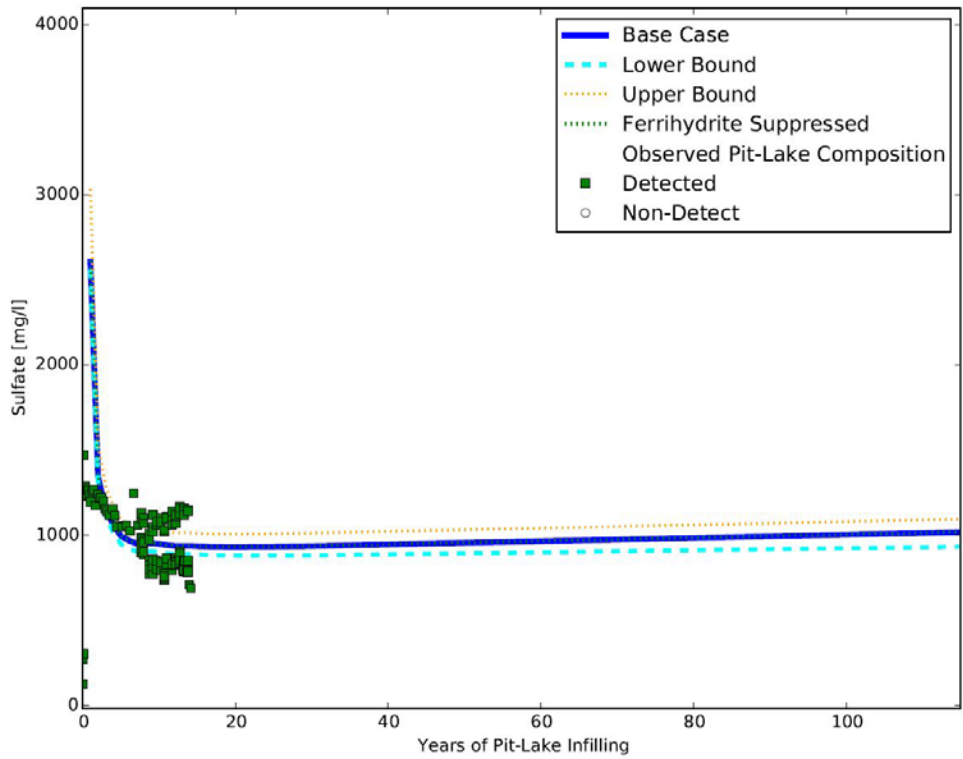


Figure 2. Sulfate predictive water-quality model results (lines) and observations (points).

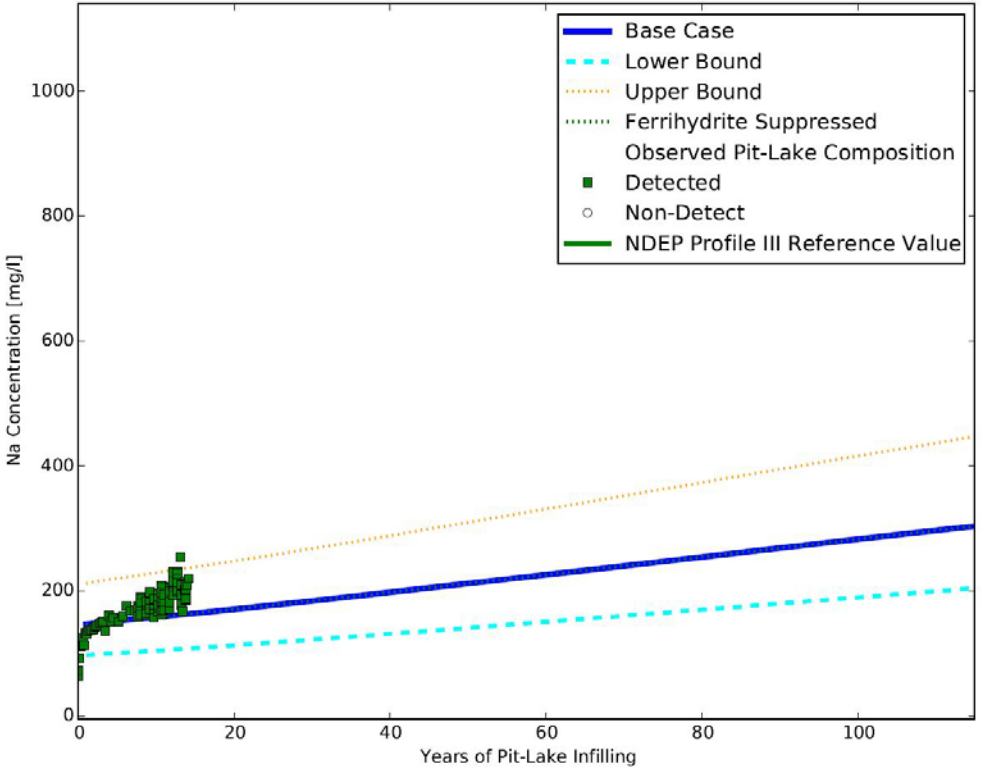


Figure 3. Sodium predictive water-quality model results (lines) and observations (points).

The effect of adsorption in the simulated pit lake is illustrated by the predicted As concentrations in Figure 4. Predicted As concentrations are temporally stable throughout the simulation period (with the exception of the simulation with ferrihydrite suppressed) and are generally less than the observed concentrations. Predictions indicated that approximately 90% of the As present in the pit lake would be adsorbed. Significantly greater concentrations of As in the simulation with ferrihydrite suppressed indicate the sensitivity of the model results to adsorption reactions. Other constituents markedly affected by adsorption include Be, Cd, Cr, Cu, Pb, Ni, V, and Zn.

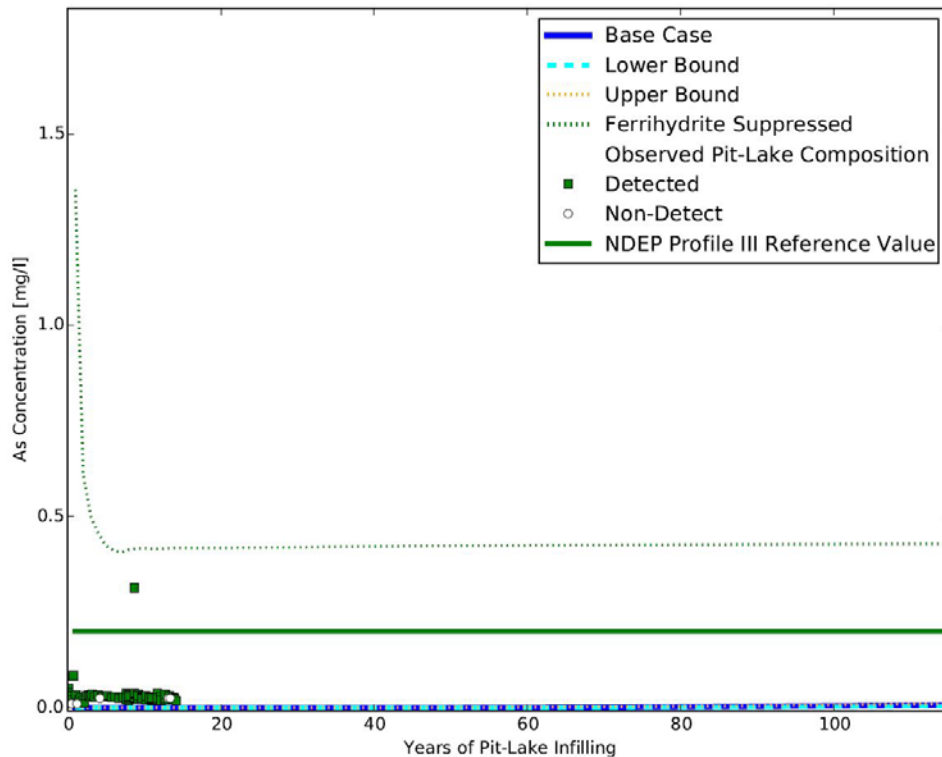


Figure 4. Arsenic predictive water-quality model results (lines) and observations (points).

5.2 Comparison of Predicted and Observed Pit-Lake Chemistry

In general, the geochemical model reasonably represents the observed concentrations of parameters monitored throughout the initial approximately 15-year period of infilling from 2001 through 2015. Figure 5 provides a comparison of the predicted concentrations of parameters included in the pit-lake water-quality model for the base-case scenario with the average observed concentrations from 2015.

Figure 5 illustrates that a number of major and minor constituents were predicted relatively accurately by the geochemical model; these constituents lie near the 1:1 line on Figure 5, which represents predicted concentrations that are equal to the average pit-lake concentrations from 2015. These constituents include alkalinity, B, Ca, Cr, Cl, K, Mg, Mo, Na, pH, Sr, SO₄, and Zn. Constituents that were moderately overpredicted by the model (plotted close to but above the 1:1 line) include Cd and Mn. Constituents that were moderately underpredicted by the model (plotted close to but below the 1:1 line) include Ag, Ba, Li, Ni, Se, and U.

Many of the apparent discrepancies between the predicted and observed concentrations illustrated in Figure 5 are attributable to the use of detection limits to represent concentrations for non-detects in the observed pit-lake water quality (Al, Be, Cu, Fe, P, Pb, Sn, and V); however, there were several notable discrepancies between predicted and observed water quality. Concentrations of NO₂-NO₃, Sb, and Tl were overpredicted by the model and As concentrations were underpredicted.

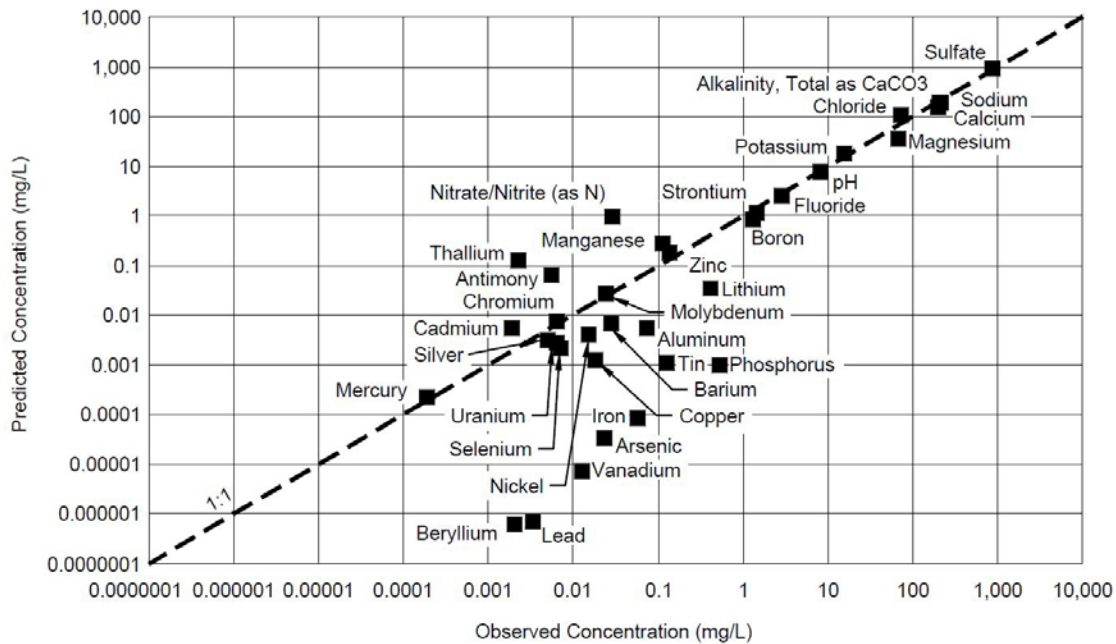


Figure 5. Comparison of predicted and observed (average from 2015) pit-lake chemistry.

5.3 Discrepancies Between Predicted and Observed Concentrations

Possible causative factors for the discrepancies between the observed and predicted concentrations include propagation of detection limit errors, thermodynamic database considerations, and inadequate geochemical characterization data.

5.3.1 Detection Limits

As described above, most of the apparent discrepancies occur for solutes that are below detection limits in the pit lake. Solute concentrations that were not detected during the humidity-cell tests were assigned concentrations of zero for use in calculating the solute-loading rate. However, influent groundwater chemistry was calculated using one-half the detection limit for non-detect samples; therefore, the addition of constituents from influent groundwater may overrepresent loading of these constituents to the pit lake.

5.3.2 Thermodynamic Considerations

Several of the parameters noted to be underpredicted were also noted to display similar differences between predicted and observed concentrations in predictive modeling performed by Eary & Schafer (2009) of a Post-Betze proto-pit-lake test. Specifically, Eary & Schafer (2009) noted significant underprediction of As, Cu, Fe, and Pb. These researchers hypothesized that detection-limit errors and a lack of appropriate thermodynamic data for the incorporation of trace elements into solid minerals were likely causes of noted discrepancies (Eary & Schafer 2009). A lack of, or incomplete, thermodynamic data is the most likely cause for the discrepancy between predictions and observations of Sb and Tl in the Cove pit lake. The thermodynamic database used in the predictive geochemical model (minteq.V4) does not contain appropriate thermodynamic data for adsorption of Tl. Addition of these thermodynamic data to the database may have reduced the predicted Tl concentrations; however, the default database was used. Tempel et al. (2000) cited a similar cause for the overprediction of As in a modeling study of the Gatchell pit lake (the thermodynamic data in that study did not include arsenic sorption data). Although the thermodynamic database used in the Cove model does contain data for the adsorption of Sb, there are a limited number of surface species compared to those for constituents such as As. An expanded thermodynamic database including data from the literature (e.g. Xi et al. 2011) may have resulted in additional Sb adsorption and an improved representation of the measured pit-lake concentrations.

Discrepancies between As predictions and observations in the Cove model may also be linked to adsorption behavior. The simulation that suppressed ferrihydrite precipitation (and as-

sociated As sorption) resulted in predicted arsenic concentrations that were 0.392 mg/L greater than those observed in the pit lake, whereas the predictions that included ferrihydrite precipitation (and sorption) underpredicted arsenic concentrations by 0.024 mg/L. This indicates that, although As sorption to ferrihydrite is probably occurring in the Cove pit lake, the extent of this reaction may be overrepresented by the PHREEQC model when ferrihydrite precipitation and sorption is included. Nonetheless, the most representative prediction of the measured As concentrations was achieved by including the processes of ferrihydrite precipitation and sorption.

One study quantitatively addressed arsenic adsorption in pit-lake predictions in the Dexter pit lake (northeastern Nevada). That study modeled ferrihydrite precipitation and adsorption over several seasonal mixing events (Newman 2014) and indicated that the precipitation of ferrihydrite, and subsequent adsorption of As, tended to underestimate Fe and As concentrations in the bulk pit lake. Calibration of these processes, based on the observed hydrodynamic structure and observed Fe and As concentrations, was required to more accurately simulate the Fe and As concentrations in the Dexter pit lake; however, the details necessary for that type of calibration are not currently available for the Cove pit lake.

Additional research on the speciation of aqueous As indicates that a number of species have poorly constrained thermodynamic data (Nordstrom & Archer 2003; Helz & Tossell 2008). Nordstrom & Archer (2003) provided a comprehensive review and update to thermodynamic data for a variety of As species. Helz & Tossell (2008), however, indicated that these updated thermodynamic data may be applicable only under redox conditions containing small amounts of dissolved sulfide. Stratified pit lakes are known to display elevated dissolved sulfide in hypolimnion waters (Martin & Pedersen 2002); therefore, the thermodynamic database used for the predictive geochemical model may not accurately describe the speciation of aqueous As (Helz & Tossell 2008), which in turn affects adsorption behavior (Plant et al. 2003).

In addition to sorption, the mechanism of coprecipitation can remove metals and metalloids from solution. The thermodynamic database used did not include data that would enable simulation of coprecipitation of constituents like Sb and Tl with equilibrium precipitates such as ferrihydrite.

5.3.3 *Geochemical Characterization Data*

Geochemical characterization data quality may be an additional source of error in the predictive geochemical model. Humidity-cell testing was conducted on all of the parameters included in the model, with the exceptions of Cl, F, and NO₂-NO₃. For these parameters, the solute-loading rates were approximated from the results of the MWMP tests. Comparison of SO₄ release from both humidity-cell tests and MWMP tests indicated that MWMP releases were approximately 30 times greater. The MWMP releases for Cl, F, and NO₂-NO₃ were therefore adjusted by this empirical factor to approximate the humidity-cell release rates. Close agreement between predicted and observed concentrations for Cl and F (Fig. 5) indicate that this approach resulted in a close match for these constituents, but not for NO₂-NO₃, which was overpredicted by the geochemical model. This approach highlights a useful way to circumvent gaps in geochemical characterization data, although empirical adjustments may not always be practical or justified.

In addition to the lack of data for several parameters, the original ABA characterization underrepresented the sulfur content and associated acid-generating behavior of several Cove pit samples. A variety of ABA methods have been used to characterize waste rock for mining operations (e.g. Sobek et al. 1978). The method used in the original Cove pit UPS characterization (total sulfur by peroxide oxidation) did not account for the entire AGP of six of the 32 Cove humidity-cell samples. These six samples were observed to produce more sulfur than was indicated by the method to be originally present in the sample. To account for this experimental error, the total original sulfur present in each sample, which was an input to the pyrite-oxidation model, was adjusted to be 1.5 times the amount that was released over the entire testing period. The scalar of 1.5 was chosen to be environmentally conservative (i.e. tend towards overestimation of AGP), based on the SO₄ production rate trends during the testing period. Without the applied adjustments, the net effect of these errors would likely cause underprediction of total sulfur available for release and overprediction of the mass of oxidized rock available for leaching, which in turn would underpredict leaching of sulfur (as SO₄) from the UPS relative to the other constituents.

6 CONCLUSIONS

The Cove pit lake represents a novel opportunity to compare the results of a predictive geochemical model to a pit-lake water-quality dataset of relatively long duration. Additionally, geochemical characterization data for the Cove UPS allow an empirical model for solute loading to the pit lake to be constructed. The combination of solute loading, groundwater inflow, and aqueous geochemical processes were used in a predictive model to assess long-term water quality and to guide regulatory decisions.

The predicted concentrations of most of the major and minor constituents are similar to the measured concentrations after approximately 15 years of infilling. Predicted concentrations of trace constituents (i.e. less than approximately 0.1 mg/L) were generally representative of the measured concentrations, but were not as similar as for the major and minor constituents. Many of the apparent discrepancies between predicted and measured concentrations were attributable to the use of detection limits to represent concentrations that were below detection limits in some or all of the pit-lake samples. Some of the discrepancies between predicted and measured concentrations were more noteworthy; concentrations of NO₂-NO₃, Sb, and Tl were overpredicted by the model and As concentrations were underpredicted, primarily as a result of limits associated with the thermodynamic database used in the model.

Sensitivity evaluations generally represented the ranges of concentrations measured in the pit lake, and the model predictions were useful from a regulatory standpoint to assess the need (or, in this case, the lack thereof) for preventative actions in the pit lake. It is important to note that long-term predictions of water quality inherently contain uncertainty related to ranges in groundwater chemistry, geochemical characteristics of host rock, and climate.

Although data deficiencies and non-ideal historical methodologies likely hindered the predictive performance of the predictive geochemical model, this work highlights several approaches for addressing these hurdles. Specifically empirical corrections, while simple, may be appropriate where data are inadequate. Finally, this work highlights the inherent uncertainties in geochemical modeling that arise from incomplete or inaccurate thermodynamic datasets.

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