USE OF GEOCHEMICAL MODELING IN THE INTERPRETATION OF

WATER QUALITY AND OVERBURDEN CHEMICAL ANALYSIS[1]

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Abstract.--This paper contains concepts and examples of how geochemistry can be used to interpret chemical analysis from monitoring wells, soil leachates, and overburden to predict the water quality resulting from mining and reclamation activities. The processes involving the major chemistry are described by thermodynamic models calibrated to the steady-state conditions of the undisturbed groundwater/soil system. The behavior of trace metals are interpreted as a function of the major chemistry.

INTRODUCTION

One very important aspect of reclamation of surface mining activities is the quality of impacted surface and ground water. Evaluation of the impacts on the chemical character of ground and surface water for the reclamation plan is, in a major part, a geochemical problem. The geochemical basis for evaluation of the water quality is the premise that a pre-mining chemical steady state (quasi-equilibrium) existed between the ground water and the soil and rock minerals in contact with the water under conditions of restricted free oxygen. Mining activities disturb this steady state by exposing the mineral/water system to the atmosphere or by the introduction of water with a different chemical character into the system. Reactions between the minerals and water occur, consuming the oxygen from the atmosphere and changing the composition of the water.

Changes in the pH and redox conditions (Eh) by the chemical reactions depend upon the buffering capacity of the water with respect to pH and Eh. The buffering capacity is a measure of the mineral content available to maintain given pH and Eh conditions. For example, calcite in the soils commonly buffers the ground water at a near neutral pH. Generally, sulfide minerals or organic material maintains reducing redox conditions. In well buffered systems, the pH and Eh will revert back to pre-mining conditions after reclamation. Poorly buffered components and many ionic components in the ground water may be irreversibly changed by the mining activities.

Geochemical analysis of water quality must distinguish between major and trace components. The aqueous concentrations of major components are primarily determined by precipitation and dissolution reactions; whereas, the concentrations of trace elements are often controlled by sorption. The major chemistry affects the sorption mechanisms by providing sorptive substrates and determining the aqueous species of the trace elements.

This paper will show, by examples, how the data from monitoring wells, column leach tests, bulk analysis and soil extracts can be used to evaluate the geochemical reactions of the mineral/water system and predict the effects on the water quality. The examples are from evaluations of water quality done for larger investigations of mining reclamation. Common to the various examples is the use of the geochemical computer code, PHREEQE (Parkhurst et al., 1982), to calculate the equilibrium between the minerals and water from chemical thermodynamic data. The chemical reactions-- precipitation and dissolution--between the minerals and water that control the chemical steady state of the major elements can be deduced from the calculations by PHREEQE. Once these reactions are defined, the effects on the ground water at any set of geochemical conditions created by mining or reclamation can be predicted.

GEOCHEMICAL COMPUTER CODE, PHREEQE

The precipitation and dissolution reactions of the major components in the minerals and water are controlled by thermodynamic principles. The thermodynamic computer code, PHREEQE, is based upon a speciation-solubility model that calculates the distribution of aqueous species at given pH and Eh conditions. For example, the distribution of iron species may include

Fe^{+2}, Fe^{+3}, $Fe(OH)_2$, $Fe(OH)_2^+$, $Fe(OH)_3$, $FeSO_4$, $Fe(SO_4)^+$, $FeCl^{+2}$, and $FeH_3SiO_4^{+2}$ (see example of PHREEQE results in Appendix A). The chemical activities of the various species are calculated by thermodynamic distribution constants for each species. Activity coefficients (gamma) are determined for each species as a function of ionic strength and are the proportionality factor between concentration and chemical activity.

The degree of mineral equilibrium is calculated by PHREEQE from the distribution of aqueous species and is expressed as a saturation index. The saturation index (SI) is defined as the logarithm of the ratio of the ion activity product (IAP) of the component ions of the mineral in solution to the equilibrium solubility product (K_{eq}) of the mineral. For example, assuming the chemical activity of water is 1.0, the SI of $Fe(OH)_3$ is calculated according to the following equations:

$$Fe(OH)_3 + 3H^+ = Fe^{+3} + 3H_2O \qquad (1)$$
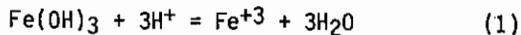
$$IAP = \{a_{Fe^{+3}}\}/\{a_{H^+}\}^3 \qquad (2)$$

$$SI = \log \{IAP/K_{eq}\} \qquad (3)$$

where K_{eq} is the thermodynamic solubility product of Equation 1. A SI of zero indicates equilibrium, a SI of less than zero indicates undersaturation, and a SI of greater than zero indicates supersaturation. Ideally, precipitation will occur under supersaturated conditions and dissolution will occur under conditions of undersaturation.

Natural systems are typically characterized by quasi-equilibrium, steady-state conditions rather than true chemical equilibrium. Chemical equilibrium is rarely achieved because the flux of components in and out of the system is faster than rates of chemical reactions. As equilibrium is approached, the rates of mineral precipitation and dissolution become very slow (Lerman, 1979). Oftentimes, however, equilibrium is closely approached and constant chemical conditions are maintained.

In PHREEQE calculations, conditions of apparent disequilibrium are reflected by non-zero saturation indexes of the minerals controlling the chemical character of the water. Besides slow reaction rates, non-zero saturation indexes may indicate differences between the thermodynamic data of the idealized minerals used in the PHREEQE data base and the non-idealized mineral actually forming in the natural system. Thermodynamic models are calibrated to the conditions of the natural system by calculating the steady-state saturation indexes characteristic to undisturbed waters. These saturation indexes are bounding conditions for predictive calculations with PHREEQE.

PHREEQE has the capability to calculate the quantities of minerals removed and added to the water and the resulting water quality at the specified saturation indexes for the minerals

system. The chemical components of the water quality that are predicted by PHREEQE are those which are determined by thermodynamic functions. This generally includes the concentrations of major elements and the pH and Eh. The major elements include those that are part of the soil-forming minerals or play a role in determining the pH and Eh of the system. The major elements often include Na, K, Ca, Mg, Al, Si, Fe, and Mn, as well as the anions. Alternatively, trace components do not play a role in defining the chemical environment but rather their behavior is a function of the major chemistry of the system.

The concentrations of the trace components are generally determined by sorption rather than precipitation/dissolution reactions. There are, however, exceptions to this generality. Commonly, the concentrations of uranium and elements that occur predominately as anionic species, such as selenium, vanadium, and molybdenum, are controlled by precipitation reactions. For trace components whose concentrations are not controlled by precipitation reactions, PHREEQE can aid in the evaluation of sorption by (1) calculating the predominant aqueous species and (2) calculating the quantity of substrates precipitating. The sorption behavior varies for different aqueous species. In addition, the most effective substrates for sorption are the freshly precipitated minerals, especially oxides and hydroxides.

GEOCHEMICAL MODELS

General

Chemical analysis of ground water from monitoring wells and analysis of soil leachate are commonly available for reclamation evaluations. These data represent perturbed systems from the mining activities. The chemical character of ground water reflects the in-situ perturbations on the mineral/water steady-state system. The chemical character of the water leachate of soils simulates the seepage from spoils or overburden. Leaching with acid or other reagents can be used to selectively remove precipitated phases of the soil. From analysis of ground water, soil leachate, the bulk mineralogy of the soils, and geochemical modeling can be used to define the mineral/water steady-state system. This analysis can be extended by further geochemical modeling to predict the geochemical character of the ground water or seepage resulting from the geohydrologic conditions of various reclamation designs.

Batch leaching by acid is useful to study the precipitation of water insoluble minerals, such as oxides, hydroxides, and carbonates. Acid leaching also removes the trace components incorporated into these precipitates. These mineral often precipitate as water flows from an acidic environment into a ground-water system well buffered at a near neutral pH.

Leaching of soil packed in columns is often used to determine the changes in the chemical character of the seepage as a function of pore volumes of water introduced into the system. The pore volume is calculated from the particle density, a measured weight, and bulk density. Water introduced into the packed column dissolves the soluble salts and initiates chemical reactions. The changing composition of the column effluent with increasing pore volumes of water indicates variation in the quantity of a soluble component in the solid phase or an alteration in the chemical parameters controlling the reactions between the solid and aqueous phases. The chemical character of soil leachate differs from the chemical character of ground water and seepage because (1) the flow rates of the column experiments are too rapid to allow for the chemical steady-state characteristic of the ground water and (2) oxygen is unlimited in the laboratory setting, in contrast to a restricted oxygen supply in the subsurface.

Slow kinetics of geochemical reactions between ground water and soil minerals are common because the reactions are generally incongruent, i.e., solid-solid reactions. The dissolution of a chemically unstable solid phase produces supersaturated conditions in the aqueous phase with respect to a more stable solid phase, which subsequently precipitates. Exchange of elements between the aqueous and solid phases is controlled by diffusion. The rates of reactions involving minerals with crystal lattices more complex than simple ionic salts are typically slower than the reaction rates of simple ionic salts.

Procedure

The procedure for a generic application of geochemical modeling to reclamation and water quality investigations combines the conceptual model developed from general information available in the literature with the quantitative model generated by thermodynamic calculations. Initially, the conceptual model serves as a guide for the quantitative model and is later modified in accordance with the quantitative results. The steps involved are as follows:

1. Determine qualitatively the mineralogy of the overburden from the geology of the site or by soil analysis.

2. From the literature, determine the minerals that are present in the overburden which are known to commonly control the steady-state chemical character of the ground water (Lindsay, 1979).

3. From general geochemical principles, speculate on the reactions that are likely to occur between the minerals and the ground water when in contact with the atmosphere.

4. Choose thermodynamic data for the important minerals and aqueous species to use in PHREEQE.

5. Use PHREEQE to calculate the saturation indexes of important minerals in undisturbed ground waters to (1) verify the minerals that control the steady-state ground water composition and (2) determine the degree of mineral equilibrium that characterizes the steady-state system.

6. Use PHREEQE to calculate saturation indexes of important minerals in soil leach data and post-mining ground water. Compare the saturation indexes in the pre- and post-mining waters to document the reactions that are occurring in the perturbed system.

7. Use the saturation indexes characteristic of the minerals in the pre-mining steady state and the reactions that lead to the perturbed system to predict the resulting ground water character under various sets of conditions associated with reclamation options.

Data Requirements

The data required for the geochemical model include analysis of ground water and the solid phases. Within the major chemistry of the water character, various elements determine the ionic strength, the pH, and the Eh. The elements comprising the ionic strength and pH of the ground water are almost always required. Eh measurements and the elements involved in the determination of Eh are required when an element of concern is dependent upon Eh. The trace components required in the analysis are those of concern in the water quality.

Except for very simple problems where the major chemistry is dominated by elements that are independent of pH and Eh, such as sodium, potassium, and chloride, some of the elements involved with ionic strength, pH, and Eh are interrelated. For example, in seepage from soils containing sulfide minerals, the concentration of iron often contributes significantly to ionic strength, and the reactions which determine the iron concentration are a function of pH and Eh.

Almost universally, pH measurements are required. They are easily done with a glass electrode specific to pH measurements. To model the changes in pH as a function of environmental conditions, the concentrations of elements involved in the pH buffer must be known. Commonly, pH is buffered by carbonate minerals, such as calcite. Modeling the pH equilibria of a calcite system requires analysis of calcium and carbonate or bicarbonate and other elements that compete with the carbonate for calcium, such as sulfate. In systems where calcite is absent, the pH may be buffered by the aluminosilicate minerals. A model of the pH-aluminosilicate relationship requires aluminum and silicon analysis.

Measurements of Eh are generally considered more difficult than pH measurements and are oftentimes not taken. The concepts of Eh and the limitations of Eh measurements have been reviewed by many researchers (Stumm and Morgan, 1970; Langmuir, 1971; and Lindburg and Runnells, 1984). Problems exist in the techniques of measurement, as well as in the interpretation of Eh relative to equilibria among the electroactive elements in the water. Eh measurements cannot be applied to thermodynamic models as rigorously as can be done with pH. In order for Eh measurements to be reproducible and interpretable, the electron transfer must be rapid and reversible, the electroactive species must be present in significantly high concentrations, and other dissolved species must not interfere at the electrode surface (Stumm and Morgan, 1970).

Despite the potential difficulties, Eh measurements have been related to iron equilibria in acid-mine drainage (Nordstrom et al., 1979) and sulfur equilibria in a pyrite rich aquifer (Boulegue and Michard, 1979). Qualitatively, changes in Eh measured along the flow path of an aquifer have been related to the decrease in the concentrations of electroactive elements in the ground water (Jackson and Patterson, 1982). In addition, Eh changes during restoration of an in-situ leach uranium R & D project have been related to iron equilibria and the decline in uranium, selenium, and vanadium (Johnson, in preparation).

These studies show that Eh measurements can be useful when used cautiously and considered, at best, semi-quantitative. Calculation of the saturation indexes of minerals containing electroactive elements with the measured Eh values determine the apparent disequilibrium of the system. As in the case of all equilibrium considerations, the differences between the measured Eh and the calculated-equilibrium Eh provides an indication of the conditions which the system is proceeding toward. Saturation indexes calculated for the same water composition at various Eh values provide a sensitivity analysis of Eh measurements.

MODEL OF MAJOR CHEMISTRY

The study of coal mine seepage provides a good example of a geochemical model of the major chemistry of water affected by seepage from overburden. The components of concern--TDS, iron, sulfate, and aluminum--demonstrate the use of data on the pH, Eh, and ionic elements. A fairly sound conceptual model, developed from previous studies, exists. This allows an illustration of how the quantitative model is developed from the conceptual basis. Also, the reaction rates of the minerals involved are known to be slow and, therefore, demonstrate the interpretation of thermodynamics in view of kinetics.

Conceptual Geochemical Reactions

Because of the depositional history of coal seams, the overburden associated with coal mining is generally fine-grained silicate rocks containing reduced organic material and sulfide minerals. Frequently, the fine fraction is characterized by abundant kaolinite. Calcite is oftentimes absent.

The oxidation of the reduced components when the mine spoils are exposed to the atmosphere is well recognized. As pyrite is oxidized, high concentrations of acidity, sulfate, and iron are produced (Equation 4). The acidic conditions create unstable conditions for the aluminosilicates, such as feldspars and clay minerals. Dissolution of the aluminosilicates release aluminum, silica, and interlayer cations and consume hydrogen ions (Equation 5). The solution becomes oversaturated with iron and aluminum basic sulfates, such as jarosite $(KFe_3(SO_4)_2(OH)_6)$ (Nordstrom et al., 1979) and jurbanite $(AlSO_4OH \cdot 5H_2O)$ (Nordstrom, 1982, and Van Breemen, 1973) (Equations 6 and 7). As the dissolution of the aluminosilicates reach equilibrium, the pH increases. Jarosite becomes unstable and iron hydroxide becomes supersaturated (Chapman et al., 1983) (Equation 8).

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{-2} + 16H^+ \quad (4)$$

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2SiO_2 + 2Al^{3+} + 5H_2O \quad (5)$$

$$K^+ + 3Fe^{3+} + 2SO_4^{-2} + 6H_2O = KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad (6)$$

$$Al^{3+} + SO_4^{-2} + 6H_2O = AlSO_4OH \cdot 5H_2O + H^+ \quad (7)$$

$$Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (8)$$
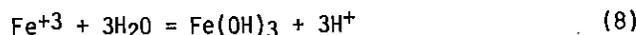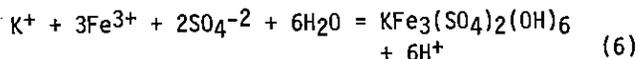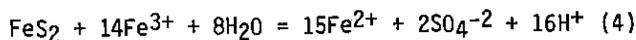
The rate-determining step of pyrite oxidation is thought to be oxidation of ferrous iron, which is slow under acidic pH conditions characteristic of acid-mine drainage (Jaynes et al., 1984). Therefore, pyrite equilibrium is not controlled by the partial pressure of oxygen. Under atmospheric conditions, the oxygen supply is in excess and thus, the redox potentials of acid-mine drainage are much higher than that required for equilibrium with pyrite. In acid-mine drainage, the steady-state iron concentrations are determined by the precipitation of jarosites and iron hydroxides. Nordstrom et al. (1979) conclude that the rate of jarosite formation is slow because of the calculated supersaturation of the water with respect to jarosite in the presence of jarosite in sediment of streams draining a source of acid-mine seepage. Chapman (1983), however, concludes that the rate of jarosite is relatively fast and accounts for the apparent supersaturation calculated by Nordstrom et al. (1979), by an error in the thermodynamic data used in the calculations.

Paces (1978) concluded that the concentrations of aluminum and silica in natural waters are often times controlled by the equilibrium of halloysite. Analysis of over 100 natural waters showed near equilibrium with respect to halloysite. Halloysite has the same composition as kaolinite with a slightly more stable crystal form. It is a product of alteration of primary aluminosilicates in near surface environments and

is commonly found in highly weathered shaly sediments. The rate of aluminosilicate dissolution is generally considered slow. Lerman et al. (1975) measured the silicate concentrations from the dissolution of aluminosilicates in seawater and found that silica steady state was reached between one and two hundred days. This suggests that equilibrium in ground water with respect to aluminosilicates is probably reached within a few years.

Geochemical Model of Soil Leachate and Ground Water Analysis

An example of column leach data from overburden on coal seams is given in table 1. The assigned pore volumes represent a near median of the pore volumes composited for the samples. Sulfate concentrations were adjusted to balance the cation and anion charges. Estimated Eh values are based upon Eh measurements of coalmine drainage by Nordstrom et al. (1979).

Table 1.--Chemical character of column effluent.

Pore volume	0.1	0.5	1	2	4
Element	Chemical characteristics				
pH	3.0	3.0	3.1	3.2	3.3
Eh, mV	700	700	650	625	600
Al, ppm	744	614	184	112	49
Ca, ppm	21	160	430	468	656
Cl, ppm	148	16	10	10	10
Fe, ppm	262	309	138	101	54
K, ppm	43	36	23	11	8.3
Mg, ppm	740	500	280	180	26
Mn, ppm	155	96	51	36	3.1
Na, ppm	840	550	160	24	4.8
SO_4, ppm	9,570	7,810	3,890	2,780	2,087
$Si(OH)_4$, ppm	200	200	200	150	150
TDS,ppm	12,700	10,300	5,370	3,880	3,050

Analysis of the equilibrium state of the column effluents (table 1) by PHREEQE showed a supersaturation with respect to the metal-basic sulfates, jarosite and jurbanite, and an undersaturation of the aluminosilicates (Appendix A). The calcium concentration increases with increasing pore volumes, which results in equilibrium with respect to gypsum.

The material used for the leaching contained about 22.7 g sulfur of which 9.1 g are sulfate, 5.2 g are pyritic sulfur, and 8.4 g are organic sulfur. Sulfate, being the most soluble sulfur form, would be expected to be leached from the column. The quantity of sulfur leached from the column after about 4.5 pore volumes was about 8.5 g, which is less than the total sulfate in the solid material. This indicates that some of the sulfate is in a rather insoluble form and that little or no pyrite was oxidized during the column leaching.

Calibration of the Model

The pre-mining, steady-state conditions between the minerals and chemical character of the ground water was determined by calculating the saturation indexes of background water. The pH of the ground waters sampled from the alluvium between the lignite seams range from 4.3 to 6.0. The ground water samples, as calculated by PHREEQE, are in near equilibrium with respect to silica, halloysite, jurbanite, and iron hydroxide, and undersaturated with respect to gypsum and jarosite.

Predictions of Ground Water Quality

The chemical character of post-mining ground water after reclamation was simulated by equilibrating the column effluents with halloysite, $SiO_2(am)$, $Fe(OH)_3$, and $AlSO_4OH \cdot 5H_2O$ as determined from the pre-mining ground waters (table 2). An example of the results from PHREEQE are in Appendix A. The predicted ground water compositions are well buffered at a pH near 5 by halloysite and at Eh of near 425 mV by iron hydroxide. If the Eh is lower in the ground water than that considered in the calculations, the equilibrium iron concentration is greater. For example, at an Eh of about 300 mV, 10 ppm iron would be in solution, in comparison to less than 1 ppm of iron at an Eh of 425 mV.

Table 2.--Chemical character of column effluents equilibrated with minerals to simulate ground water.

Pore volume	0.1	0.5	1	2	4
Element	Chemical characteristics				
pH	4.9	4.9	4.8	4.8	4.7
Eh, mV	420	421	426	429	432
Al, ppm	0.17	0.17	0.19	0.20	0.23
Ca, ppm	21	160	357	395	447
Fe, ppm	0.15	0.16	0.19	0.20	0.23
SO_4, ppm	4,882	3,720	2,406	1,726	1,190
$Si(OH)_4$, ppm	182	182	185	185	185
TDS, ppm	7,023	5,270	3,473	2,622	1,878

The chemical character of the predicted postmining ground water (table 2) compares well with the pre-mining ground water character except for higher sulfate concentrations in the post-mining ground water. The reason for this is that the pH and Eh conditions of the ground water after reclamation revert back to pre-mining conditions. Elements, such as iron and aluminum whose soluble concentrations are controlled by minerals dependent upon pH and Eh conditions, also revert back to pre-mining levels. Gypsum, however, was undersaturated in the pre-mining ground water. The addition of sulfate by the oxidation of pyrite increases the sulfate concentration to the maximum determined by gypsum and jurbanite equilibria.

The gypsum provides a constant source of sulfate to be slowly leached from the spoils. The data from the column experiments suggest that several pore volumes (several hundred years) are required to completely remove the sulfate from the system. The sulfate concentrations are the major contribution of the TDS, which decrease from 7000 ppm to less than 2000 ppm in 400 years.

Reactions not considered by the model are the adsorption of sulfate and the dissolution of calcite. Sulfate adsorption on the freshly precipitated iron hydroxides may provide additional reduction of sulfate concentrations in the ground water through time (Chang et al., 1963). The pH of the post-mining ground water may be higher than predicted if the neutralization of acid by calcite is considered. Although generally present in small quantities in the silicate units between coal seams, dissolution of calcite is a rapid reaction and would serve to neutralize the acid generated from the pyrite oxidation.

MODEL OF TRACE COMPONENTS

Models of trace components are of two types, depending upon the chemical characteristics of the trace element. Trace components, such as uranium, selenium, and molybdenum, often follow the controls of a steady state between the aqueous concentration and the mineral phases and can be modeled by thermodynamic calculations. Other trace elements, such as arsenic, chromium, cobalt, nickel, copper, zinc, cadmium, lead, and others, are generally involved in sorption processes. The sorption of these metals can be evaluated in view of the results of the thermodynamic model of the major chemistry.

Review of Sorption Processes

The most important sorption mechanisms are electrostatic and specific. Electrostatic adsorption results from coulombic forces of attraction between charged solute species and the adsorbing substrate and is referred to as ion-exchange. Uncomplexed cations are often adsorbed by this mechanism. Specific adsorption is the formation of chemical bonds between chemical groups exposed on the surface of the substrate and species in solution. An example of specific adsorption is the adsorption of anionic species by ferric and manganese oxides (Howard, 1971).

The mechanism of adsorption is dependent upon the aqueous species and the sorptive substrate. Clay minerals are considered good substrates because of their large, highly-charged surface areas. Clay minerals can sorb trace components by exchange with interlayer cations, electrostatic sorption of cations on the plane surfaces, and specific sorption of cations and anions on the edges as a function of pH. In addition to their sorption potential, Jenne (1977) proposed that another significant role of clay-sized minerals in trace element sorption is as a mechanical support for precipitation of secondary minerals. Abundant evidence is presented

relating the content of iron, manganese, and aluminum hydroxides to the proportion of clay-sized particles. The high sorptive capacities of the hydroxide minerals result from the amorphic nature of the fresh hydroxide precipitates. In cases where thermodynamic modeling predicts the precipitation of hydroxide minerals, they should be considered as effective substrates for sorption.

Example of Trace Metal Sorption

The retardation of trace metals from the seepage from uranium mill tailings provides a good example of the relationship between the precipitation of hydroxide minerals and the sorption of trace metals (Bush ne. Johnson, 1984). The seepage from the tailings is acidic with high concentrations of iron and aluminum. The soils below the tailings are rich in calcite, which provides a strong buffer to the pH of the ground water. As the acidic seepage mixes with the ground water, calcite dissolves to neutralize the acid from the tailings. The increase in pH causes the precipitation of large quantities of iron and aluminum hydroxides. The vertical distribution of trace components through the soil below the tailings shows that the metals are retarded within the zone of precipitation of the iron and aluminum.

Regression analysis of the concentrations of trace metals against the iron and aluminum concentrations in acid extracts of soil samples from two locations below the tailings relate the retardation of trace metals to the precipitation of iron and aluminum hydroxides. Average concentrations of acid-soluble iron and aluminum in background soils were deducted from the concentrations of iron and aluminum in the acid extracts of soils below the tailings. The data used in the analysis are from Markos and Bush ne. Johnson (1982). Regression analysis of the trace metals against both iron and aluminum were evaluated, and the regression with the greatest R^2 is shown in table 3. The effectiveness of retardation of the trace metals by the precipitation of iron and aluminum was evaluated by comparison of the slope of the regression equations with the ratio of the trace metal to iron or aluminum in the tailings solution (table 3).

Table 3.--Regression analysis between iron, aluminum, and trace metals in acid extracts of soil below Riverton tailings.

Regression equation	R^2	No. of samples	Ratio in tlgs solution
Cd=0.0002(Al)+0.01	0.84	6	Cd/Al=0.0002
Ni=0.007(Al)+0.40	0.77	6	Ni/Al=0.015
As=0.007(Fe)-0.41	0.81	8	As/Fe=0.006
U =0.018(Fe)+1.95	0.86	6	U/Fe=0.027

The slope of the regression equations compares well to the ratio in the tailings for the cadmium-aluminum and arsenic-iron couples. This suggests that the mechanisms operating between the precipitation of aluminum and iron hydroxides and the retardation of cadmium and arsenic remove essentially all of the trace metal from the tailings solution. In the case of nickel-aluminum and uranium-iron, the slopes of the regression lines are less than the ratios in the tailings solution. This implies that the capacity of the hydroxide precipitates becomes saturated with respect to retardation of nickel and uranium.

The retardation of uranium is more complicated than many of the trace metals. Uranium in the solid phase appears to be partitioned between hydroxide substrates and uranium hydroxides. The correlation between iron and uranium indicates the retardation by hydroxides. The large positive y-intercept in the uranium-iron regression equation may indicate the presence of a uranium precipitate, independent of sorption by iron hydroxide. The suggested presence of a uranium precipitate agrees with the results of the calculations by PHREEQE, which predict the precipitation of $UO_2(OH)_2$.

The mechanisms of retardation of the trace components by the iron and aluminum hydroxides have not been conclusively determined. However, the linear relationship between the quantity of major cations (Al^{+3} and Fe^{+3}) and the trace metals suggest a stoichiometric relationship. It is interesting to note that the cations (Cd^{+2} and Ni^{+2}) relate most closely to the quantity of aluminum hydroxide; whereas, the anionic species ($HAsO_4^{-2}$ and $UO_2(CO_3)_2^{-2}$) are most closely related to the quantity of iron hydroxide. Substitution of the aluminum ions by the trace metal cations in the crystal lattice may account for the retardation of cadmium and nickel. Specific adsorption between the anionic species and the ferric ions may be the mechanism of anion retardation. The interactions of anions with freshly precipitated hydrous iron oxides have been interpreted by Harrison and Berkheiser (1982) to be substitution by the anions for the hydroxyl groups within the ferric hydroxide lattice. This results in a rather irreversible incorporation of the anions by the mechanisms of specific adsorption.

CONCLUSIONS

Geochemical modeling is very useful for interpretation of the impacts on ground water from mining and reclamation activities. The application of geochemistry is based upon the facts that (1) there existed a steady state between the major chemistry of the pre-mining ground water and soil minerals, (2) the geohydrological system is in a predictable state of chemical disequilibrium caused by the mining activities, and (3) the behavior of trace components is determined by the major chemistry and mineralogy of the soil and rock. Thermodynamic

reactions of the major chemistry and the trace components which are controlled by precipitation/dissolution reactions. The bounding conditions of the thermodynamic model are the minerals buffering the ground-water system and their respective saturation indexes. The quality of the ground water under any set of geohydrological conditions can be calculated within the constraints of the minerals buffering the ground water. Thermodynamic calculations do not consider kinetics, and therefore, some time may be required before the ground-water quality predicted by thermodynamics is achieved. The behavior of trace components with concentrations controlled by sorption rather than precipitation/dissolution is a function of the aqueous species and the substrates available for sorption. Sorption can be evaluated by knowing the chemical character of the ground water and the precipitates likely to form in the reactions from chemical disequilibrium due to mining back to the steady-state conditions of the geohydrologic system.

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APPENDIX A

TOTAL CONCENTRATION OF AQUEOUS COMPONENTS **********

COMPONENTS	TOTAL MOLALITY	TOTAL LOG MOLALITY	TOTAL MG/KG
AL	2.7925E-02	-1.5540	7.4400E+02
HCO3	8.2986E-06	-5.0810	5.0000E-01
CA	5.3061E-04	-3.2752	2.1000E+01
CL	4.2276E-03	-2.3739	1.4800E+02
FE	4.7510E-03	-2.3232	2.6200E+02
K	1.1137E-03	-2.9532	4.3000E+01
MG	3.0825E-02	-1.5111	7.4000E+02
NA	3.7002E-02	-1.4318	8.4000E+02
SI	2.1073E-03	-2.6763	2.0000E+02
SO4	9.9098E-02	-1.0039	9.4000E+02

DESCRIPTION OF SOLUTION *****************************

pH	3.000
EH (mV)	699.910
IONIC STRENGTH (M)	.181
TDS (MG/KG)	1.272E+04

DISTRIBUTION OF AQUEOUS SPECIES ******************

SPECIES	MOLALITY	ACTIVITY	GAMMA
AL(SO4)2-	1.192E-02	8.767E-03	7.357E-01
AL+3	4.520E-03	6.160E-04	1.363E-01
ALOH+2	1.965E-05	6.287E-06	3.199E-01
ALSO4+	1.147E-02	8.438E-03	7.357E-01
CA+2	2.878E-04	9.498E-05	3.300E-01
CAHCO3+	5.741E-12	4.374E-12	7.619E-01
CASO4	2.428E-04	2.531E-04	1.042E+00
CL-	4.151E-03	2.986E-03	7.193E-01
CO2(AQ)	8.293E-06	8.645E-06	1.042E+00
CO3-2	5.452E-16	1.744E-16	3.199E-01
FE(OH)2+	3.343E-06	2.514E-06	7.521E-01
FE(OH)3	1.072E-05	1.117E-05	1.042E+00
FE(SO4)2-	8.877E-04	6.662E-04	7.505E-01
FE+2	6.914E-04	2.330E-04	3.370E-01
FE+3	1.081E-04	1.473E-05	1.363E-01
FE2(OH)2+4	2.415E-05	2.445E-07	1.013E-02
FE3(OH)4+5	2.055E-06	1.572E-09	7.647E-04
FECL+2	4.332E-06	1.335E-06	3.081E-01
FECL2+	2.390E-08	1.780E-08	7.451E-01
FEOH+	5.640E-08	4.202E-08	7.451E-01
FEOH+2	3.093E-04	9.532E-05	3.081E-01
FESO4	5.199E-04	5.420E-04	1.042E+00
FESO4+	2.162E-03	1.611E-03	7.451E-01
HCO3-	4.967E-09	3.736E-09	7.521E-01
SO4-	1.726E-03	1.270E-03	7.357E-01
+	1.021E-03	7.347E-04	7.193E-01
KCL	1.741E-06	1.815E-06	1.042E+00
KSO4-	9.047E-05	6.804E-05	7.521E-01
MG+2	1.729E-02	6.065E-03	3.508E-01
MGHCO3+	3.668E-10	2.662E-10	7.257E-01
MGSO4	1.353E-02	1.411E-02	1.042E+00
NA+	3.418E-02	2.559E-02	7.486E-01
NA2SO4	2.671E-04	2.784E-04	1.042E+00
NACL	6.138E-05	6.399E-05	1.042E+00
NAHCO3	5.168E-11	5.387E-11	1.042E+00
NASO4-	2.230E-03	1.677E-03	7.521E-01
SI(OH)4	2.107E-03	2.197E-03	1.042E+00
SO4-2	4.175E-02	1.308E-02	3.133E-01

STABILITY OF SOLID AND GAS PHASES *****************

PHASE		LOG IAP/KT
JAROSITE	KFe3(SO4)2(OH)6	5.828
JURBANITE	ALSO4OH*5H2O	1.701
FE(OH)3	crystalline	1.576
SIO2(AM)	amorphous	.054
GYPSUM	CaSO4*2H2O	-1.149
HALLOYSITE	AL2SI2O5(OH)4	-4.293
KAOLINITE	Al4Si4O10(OH)8	-9.481

EQUILIBRATING WITH SOLID AND GAS PHASES*****************

STEADY STATE WITH THE FOLLOWING SOLID AND GAS PHASES:
HALLOYSITE (SI = .0000)   FE(OH)3 (SI = .0000)
SIO2(AM) (SI = .0000)   JURBANITE (SI = .0000)

PHASE CHANGES ***************************************

PHASE	DELTA PHASE MOLES/KG	GRAMS/KG	CM**3/KG
HALLOYSITE	1.087E-02	2.806E+00	0.000E-01
FE(OH)3	-4.748E-03	-5.074E-01	-9.886E-02
SIO2(AM)	-2.196E-02	-1.319E+00	-4.982E-01
JURBANITE	-4.966E-02	-1.143E+01	0.000E-01

Negative DELTA PHASE indicates removal from solution.
Positive DELTA PHASE indicates addition to solution.

TOTAL CONCENTRATION OF AQUEOUS COMPONENTS ********

COMPONENTS	TOTAL MOLALITY	TOTAL LOG MOLALITY	TOTAL MG/KG
AL	6.4589E-06	-5.1898	1.7305E-01
HCO3	3.6094E-05	-4.4426	2.1869E+00
CA	5.3061E-04	-3.2752	2.1118E+01
CL	4.2276E-03	-2.3739	1.4883E+02
FE	2.8489E-06	-5.5453	1.5798E-01
K	1.1137E-03	-2.9532	4.3241E+01
MG	3.0825E-02	-1.5111	7.4414E+02
NA	3.7002E-02	-1.4318	8.4470E+02
SI	1.8866E-03	-2.7243	1.8006E+02
SO4	5.1184E-02	-1.2909	4.8823E+03

DESCRIPTION OF SOLUTION   ****************************

pH	4.930
EH (mV)	419.955
IONIC STRENGTH (M)	.127
TDS (MG/KG)	7.023E+03

DISTRIBUTION OF AQUEOUS SPECIES****************************

SPECIES	MOLALITY	ACTIVITY	GAMMA
AL(SO4)2-	2.432E-06	1.848E-06	7.601E-01
AL+3	9.893E-07	1.578E-07	1.595E-01
ALOH+2	3.833E-07	1.373E-07	3.583E-01
ALSO4+	2.580E-06	1.961E-06	7.601E-01
CA+2	2.858E-04	1.043E-04	3.648E-01
CAHCO3+	2.135E-09	1.670E-09	7.819E-01
CASO4	2.448E-04	2.520E-04	1.030E+00
CL-	4.149E-03	3.097E-03	7.463E-01
CO3-2	1.442E-11	5.168E-12	3.583E-01
FE(SO4)2-	3.056E-11	2.347E-11	7.679E-01
FE+2	1.443E-06	5.393E-07	3.738E-01
FE+3	3.953E-12	6.307E-13	1.595E-01
FECL+2	1.704E-13	5.925E-14	3.476E-01
FECL2+	1.067E-15	8.196E-16	7.679E-01
FEOH+	1.080E-08	8.294E-09	7.679E-01
FEOH+2	1.001E-09	3.479E-10	3.476E-01
FESO4	1.105E-06	1.138E-06	1.030E+00
FESO4+	8.144E-11	6.253E-11	7.679E-01
HCO3-	1.679E-06	1.299E-06	7.737E-01
HSO4-	1.778E-05	1.352E-05	7.601E-01
K+	1.028E-03	7.675E-04	7.463E-01
KCL	1.909E-06	1.966E-06	1.030E+00
KSO4-	8.333E-05	6.447E-05	7.737E-01
MG+2	1.728E-02	6.611E-03	3.826E-01
MGHCO3+	1.342E-07	1.009E-07	7.519E-01
MGSO4	1.355E-02	1.395E-02	1.030E+00
NA+	3.438E-02	2.642E-02	7.685E-01
NA2SO4	2.616E-04	2.693E-04	1.030E+00
NACL	6.656E-05	6.853E-05	1.030E+00
NASO4-	2.031E-03	1.571E-03	7.737E-01
SI(OH)4	1.887E-03	1.942E-03	1.030E+00
SO4-2	3.374E-02	1.187E-02	3.517E-01

STABILITY OF SOLID AND GAS PHASES   ******************

PHASE		LOG IAP/KT
SIO2(AM)	SiO2-amorphous	.000
FE(OH)3	Fe(OH)3-crystalline	.000
JURBANITE	ALSO4OH•5H2O	.000
HALLOYSITE	AL2SI2O5(OH)4	.000
KAOLINITE	Al4Si4O10(OH)8	-.895
GYPSUM	CaSO4•2H2O	-1.150
JAROSITE	KFe3(SO4)2(OH)6	-4.758

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