Carbonate Reactions that Dictate Drainage Chemistry and Carbonate Consumption Under Variable System Conditions

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Abstract

A material's potential to generate acidity is predicted based on the balance of acid-generating and acid-neutralizing minerals. The standard acid-base accounting and depletion calculations assume that pyrite and calcite are the primary reactive phases and that the relative rates of pyrite oxidation and calcite dissolution follow a specific reaction pathway associated with a defined pH and carbon dioxide partial pressure. This paper evaluates the effects of changes in system conditions on acid-base accounting using results from both laboratory-kinetic testing and reactive-transport modeling.

Keywords: Pyrite, calcite, oxidation, MIN3P

Introduction

In acid rock drainage (ARD) assessments, a principal objective is to determine whether the system of interest has sufficient neutralization potential (NP) to counteract the acidity generated by sulfide oxidation to maintain circumneutral pH. Assessments of ARD potential use available laboratory- and field-scale information, which are often supported by geochemical and hydrologic modeling (Pieretti *et al*. 2022). Inherent with these assessments is a tacit consideration regarding how variable boundary conditions may affect the hydrogeochemical behavior of the system.

Typically, kinetic testing is conducted to study the weathering of sulfidic mine materials in contact with oxygen and water. These tests provide an indication of a material's ability to effectively counteract the acidity generated by sulfide oxidation. Many minerals are capable of acid neutralization; however, mineral reaction mechanisms and rates vary widely (Jambor *et al*. 2006). Carbonate minerals (e.g., calcite and dolomite) provide effective NP (when present) due to their generally fast reaction kinetics and are often found at equilibrium in surface water and groundwater systems.

Standard kinetic testing methods use prescribed solid to water ratios that may not be representative of field conditions. Two widely adopted kinetic testing methods are the ASTM (2018) humidity cell test (HCT) and the AMIRA (2002) column test. Results from these tests are commonly used to confirm material classification with respect to ARD potential, estimate the lag time to the development of acidic conditions, if applicable, and to assess potential drainage chemistry during operations and post-closure.

Standard acid-base accounting (ABA) and depletion calculations are based on the reaction stoichiometry for pyrite (FeS_2) and calcite ($CaCO_3$) as shown in Equation 1.

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O + 2CaCO_3 = Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2H_2CO_3 \quad \text{(Equation 1)}$$

This reaction applies at pH values <6.3 when dissolved carbonate is present as carbonic acid (H_2CO_3). Standard ABA calculations assume that acidity (hydrogen ions) produced by pyrite oxidation are partially neutralized by calcite to a pH not greater than approximately 6 (i.e., two moles of calcite consumed per mole of pyrite oxidation, as shown in Equation 1). At pH values >6.3, dissolved carbonate is present as bicarbonate (HCO_3^-) wherein four moles of calcite are consumed to neutralize the acidity produced from the oxidation of one mole of pyrite.

Standard ABA calculations assume that calcite depletion is attributed to a single mechanism, specifically pyrite oxidation. This paper evaluates the potential for calcite depletion due to two mechanisms, referred to as "sulfide oxidation" (i.e., calcite dissolution to counteract the acidity generated by pyrite oxidation) and "carbonate flushing" (i.e., dissolution of calcite to maintain solution equilibrium conditions). For the conditions evaluated in this study, it is demonstrated how laboratory kinetic testing design can affect the contribution of carbonate flushing to total calcite depletion. Laboratory kinetic testing and reactive-transport modeling of a mine waste sample containing high concentrations of pyrite and calcite are presented.

Methods

The ASTM (2018) HCT methodology, which specifies a 2:1 or 1:1 solid to water ratio (1,000 g material flushed weekly with 500 mL or 1,000 mL of deionized water), is designed to thoroughly flush sulfide-oxidation products. The desired pore volume and generation of sufficient leachate for analytical purposes are among the factors for consideration in the selection of the weekly lixiviant volume. The AMIRA (2002) free-draining column method uses a monthly leach cycle and incorporates heat lamps to increase the system temperature. Laboratory testing for this study was based on the AMIRA column methodology (Fig. 1). Study conditions, as compared to ASTM (2018) and AMIRA (2002), are shown in Table 1. Lixiviant addition was increased during the latter weeks of laboratory column operation to evaluate the effects of a change in water to solids ratio on leachate composition.

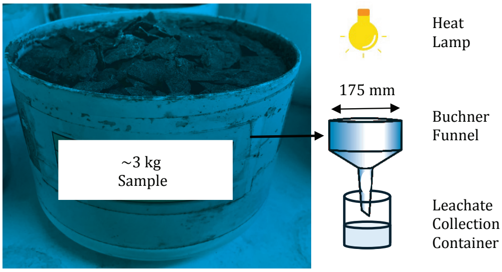

Figure 1 *Column testing photograph and schematic.*

For this study, the sample composition and laboratory-column procedure were designed to test extreme conditions and promote fast reaction kinetics (e.g., elevated sulfide concentration and higher temperature than field conditions). Column testing of a sample containing pyrite (~25%), calcite (~5%) and dolomite (~2%) was conducted over a period of nine years (118 leach cycles). Column leachates collected monthly were analyzed for a comprehensive suite of parameters including pH, major ions and metals. Geochemical modeling, using a reactive-transport code, was conducted to evaluate potential reactions occurring within the columns. The modeling, conducted when 7.7 years (100 leach cycles) of column-test data were available, focused on the investigation of the relative rates of sulfide- and carbonate-mineral depletion under variable system conditions. At the completion of the modeling study, the rate of lixiviant addition to the column was increased to evaluate changes in system behavior following a change in flow conditions and to examine the findings of the geochemical modeling. Week 4 lixiviant addition was increased from 800 mL to 1,600 mL for leach cycles 114 to 118.

MIN3P was used to evaluate the processes occurring in the laboratory column. MIN3P is a general-purpose reactive-transport model for simulating variably saturated water flow and transport, diffusive and advective gas flow, and thermodynamic and kinetic reactions between aqueous, mineral, and gas phases (Mayer *et al.* 2002). The MIN3P code also includes dissolution-precipitation, oxidation-reduction, and surface-complexation reactions. The ability of MIN3P to account for variably saturated flow conditions, gas transport, and the simultaneous simulation of flow, mineral weathering and transport reactions makes it a valuable tool (e.g., Steefel *et al.* 2015) to generate robust simulations of mine wastes and predict changes in mine water through time.

Table 1 *Study column test procedure design as compared to standard kinetic testing methods.*

Test Method (standard or study)	Solids Mass kg	Cycle Leach Water Volume L	Leach Cycle Time weeks	Temp. °C	Annual Water Volume L	Equivalent Annual Water Depth (d) mm
Humidity Cell – Option A (ASTM 2018)	1	0.5 – 1.0	1	25 (±2)	26 – 52	803 – 3,182; 1,607 – 6,364
Free Draining Column (AMIRA 2002)	2 (a)	1.4 (b)	4	30 – 35	18.2	757
Free Draining Column (current study)	3	1.4 – 2.2 (c)	4	~49	18.2 – 28.6	757 – 1,189

(a) 2 to 2.5 kg (typically)

(b) 0.7 L per kg of sample; for a 2-kg sample, 0.2 L in weeks 1 to 3 and 0.8 L in week 4

(c) 0.2 L in weeks 1 to 3 and 0.8 or 1.6 L in week 4

(d) Annual water volume converted to a depth in mm based on humidity cell (10.2 or 20.3 cm inner diameter for coarser [material screened or crushed to 100% passing 6.3 mm] and finer [<150 µm] materials, respectively) or column (17.5 cm inner diameter) surface area.

The model simulated a one-dimensional profile with a height equivalent to the height of the column (10 cm). Model parameterization of selected physical and chemical components of the system is shown in Table 2. Initial mineral concentrations were as follows: pyrite (24.6 wt.%), calcite (5.2 wt.%), and dolomite (2.2 wt.%). Gypsum and ferrihydrite (amorphous) were included in the model simulations with initial concentrations of 0 wt.%.

MIN3P simulates the weathering reactions of sulfide minerals using a shrinking core model (SCM) (Wunderly *et al.* 1996). As sulfide minerals react, a rind of secondary oxidation minerals forms on the exterior faces of the reacted sulfide-mineral grains. The oxidation rind forms a barrier that slows the transport of sulfide oxidation reactants (e.g., O_2, Fe^{+3}, H_2O) to the unreacted mineral surface as well as the transport of sulfide oxidation products (e.g., acidity, sulfate, and trace elements) away from the reacting mineral surface. The unreacted portion of the mineral grain shrinks as the sulfide mineral oxidizes and the oxidation rind thickens, consequentially decreasing the reaction rate through time.

MIN3P modeling included both calibration and predictive simulations. During model calibration (~8-year simulation period), input parameters were adjusted to achieve a match between simulated and measured leachate concentrations. Factors affecting the rate of pyrite oxidation (e.g., the effective diffusion coefficient that defines the rate of oxygen diffusion into the pyrite grain and pyrite grain size) and carbonate mineral reaction rates were adjusted until an acceptable match between simulated and measured leachate concentrations was achieved.

Table 2 *MIN3P model parameterization (selected parameters).*

Model Input	Value	Description
Dimensions – Height	10 cm	Column height
Boundary Conditions –		
Top – Infiltration Rate	3.1×10^{-9} m/s	Average column inflow
Bottom		Free draining column
Hydraulics –		
Porosity	0.46	Based on field-measured values
Hydraulic Conductivity	5.5×10^{-4} m/s	Richards' Equation parameterization
Lixiviant Composition	pH 5.6 PCO_2 (atm) $10^{-3.5}$ PO_2 (atm) 0.21	Deionized water at equilibrium with atmospheric carbon dioxide and oxygen

Selenium is present in column leachates, which is attributed to its occurrence as an impurity within the pyrite-crystal lattice. As a result, selenium was incorporated into pyrite as defined within the model. Selenium concentrations in column leachate, in addition to sulfate leachate concentrations, were matched during model calibration. Conservative transport of selenium was assumed. Following model calibration, the simulation period was extended from 10 years to 150 years (i.e., an extended period of time to allow for carbonate depletion). Sensitivity analyses were conducted to evaluate the effects of a change in flow rate through the columns.

Laboratory Testing Results

Column kinetic testing results (dissolved concentration and load for the full period of record) are shown in Fig. 2. Only a small fraction of the 1,800 mL of water added monthly (cycles 1 to 113) was recovered. Monthly water storage within the column was calculated to be small, thereby indicating a high amount of water loss due to evaporation. The increase in recovered leachate volume from cycle 114 onward corresponded to the period of higher lixiviant addition. An increase in constituent loading (results shown for sulfate, calcium and alkalinity) was observed in association with an increase in lixiviant volume.

Based on the column leachate results, speciation modeling of column leachates, and visual observations, the conceptual model for reactions occurring in the column is as follows:

- **Sulfide Oxidation** – Pyrite oxidation is occurring and releases sulfate, iron, and metals (e.g., Se). The gradual decrease in sulfate concentrations over time is attributed to oxidation rind development (e.g., shrinking core) and consequent decrease in the rate of pyrite oxidation.
- **Carbonate Dissolution** – Calcite and dolomite dissolution are occurring, resulting in the neutralization of acidity generated by sulfide oxidation. Circumneutral pH conditions are sustained within the column. Geochemical speciation modeling indicates that the leachates are often in equilibrium with calcite.
- **Secondary Mineral Reactions** – Some sulfide oxidation products are likely retained within the column. The low concentrations of iron in column leachates indicate iron attenuation within the col-

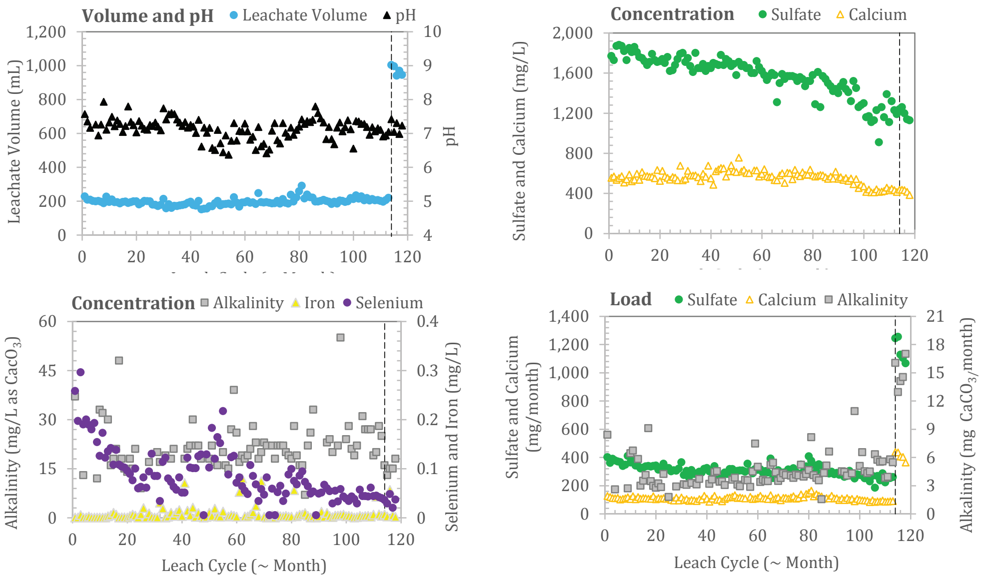

Figure 2 Column leachate chemistry. Dashed line at 114 months indicates when week 4 lixiviant addition increased from 800 to 1,600 mL.

umn, which is supported by geochemical modeling indicating the leachates are supersaturated with respect to ferrihydrite (amorphous). The early-time column leachates are in equilibrium with gypsum, suggesting gypsum precipitation. Mineralogical analysis of the sample did not identify the presence of gypsum; however, sulfate was detected as part of standard ABA sulfur speciation analysis. Early-time gypsum equilibrium may, therefore, be due to gypsum dissolution.

Reactive Transport Modeling Results

Calibrated model results compared to measured column leachate concentrations are shown in Fig. 3 (10-year simulation period). Because the model simulated a consistent flow rate through the column, the variability observed in column leachate concentrations due to changes in flow dynamics is not represented by the model. Mineral concentrations are shown in Fig. 4 (150-year simulation period). The model predicts pyrite oxidation through the full depth of the column at the same (or very similar) rate, indicating that oxygen diffusion into the column is not a limiting factor for sulfide oxidation. This is expected due to the very low modeled column saturation (i.e., average saturation of 6% does not limit oxygen ingress) and shallow column depth (10 cm). Calcite depletion also occurs through the full column depth, but calcite depletion is faster at the top of the column, attributed to equilibration of the lixiviant (deionized water) with calcite (i.e., flushing mechanism). Gypsum precipitation occurs within the first few years; however, as the rate of pyrite oxidation decreases over time, undersaturated conditions with respect to gypsum are predicted. Ferrihydrite precipitation is predicted over the ~8-year calibration period.

The effect of an increase in flow through the column was investigated through a series of sensitivity analyses. The infiltration rate into the column was increased by 2 times, 10 times, and 50 times compared to the base case simulation (Figs. 3 and 5) over a 150-year simulation.

An increase in flow increases the rate

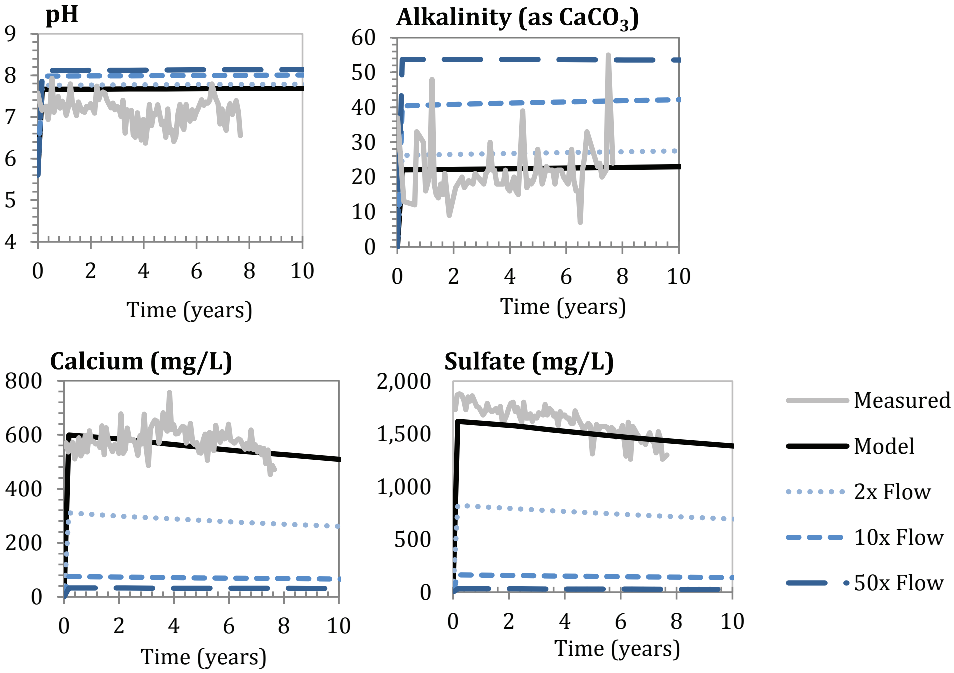

Figure 3 *Calibrated MIN3P model results (black line) compared to measured column leachate concentrations (grey line). Sensitivity model results for an increase in lixiviant volume (2x, 10x or 50x increase) represented by blue dashed lines.*

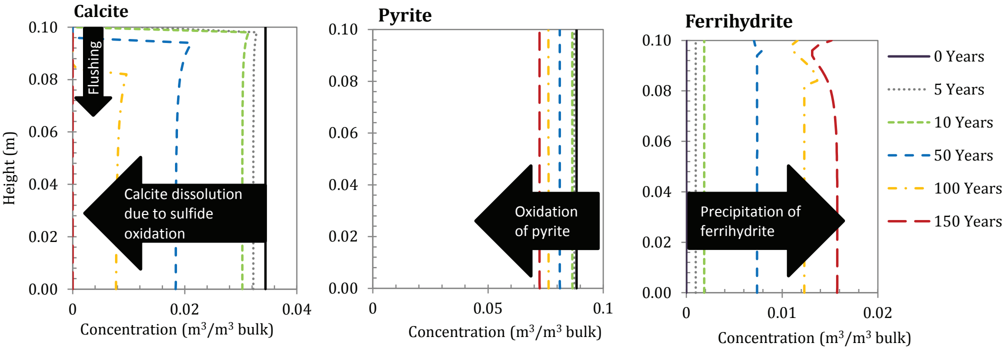

Figure 4 *Base case model mineral reactions (150-year simulation period).*

of calcite depletion and decreases the lag time to acidic conditions. However, based on the hydraulic properties of the material, the degree of saturation of the material is not affected by the higher flow rates and no significant change in the rate of pyrite oxidation is predicted. Fig. 5 shows the molar ratio of carbonate to pyrite depletion for each model simulation. At the lowest flow rate (base case model), the ratio of carbonate depletion to pyrite depletion initially is 2, consistent with Equation 1. As the rate of flow increases, equilibration of a higher volume of water with calcite increases the ratio of carbonate depletion to pyrite oxidation. The simulated flow volumes are representative of infiltration rates ranging from 0.2 (2x) to 4.9 m/a (50x). The simulated high range of flow (representative of a very wet climate) is within the standard HCT design (Table 1) but exceeds typical infiltration rates observed in most engineered mine waste facilities.

To test the behavior predicted by the model, the week 4 lixiviant volume was increased by a factor of two from cycle 114 onward. Results are available for five leach cycles (cycles 114 to 118). Similar to the MIN3P model results, an increase in alkalinity loading is observed with an increase in flow (Fig. 2). These empirical observations confirm that the rate of carbonate depletion is affected by the column test design.

Conclusions

Laboratory investigations and hydrogeochemical modeling of the weathering behavior of a mine waste sample containing pyrite and calcite have demonstrated that under the conditions evaluated, the rate of calcite depletion is sensitive to the water to rock ratio used in testing. Calcite depletion is interpreted to occur due to two mechanisms: (1) to counteract the acidity generated by pyrite oxidation and (2) dissolution to maintain calcite equilibration, termed flushing. Equilibration of calcite with larger flushing volumes of deionized water increases the rate of calcite depletion compared to that associated with neutralization of the acidity generated by pyrite oxidation alone. Consequently, the potential for calcite consumption due to flushing may warrant

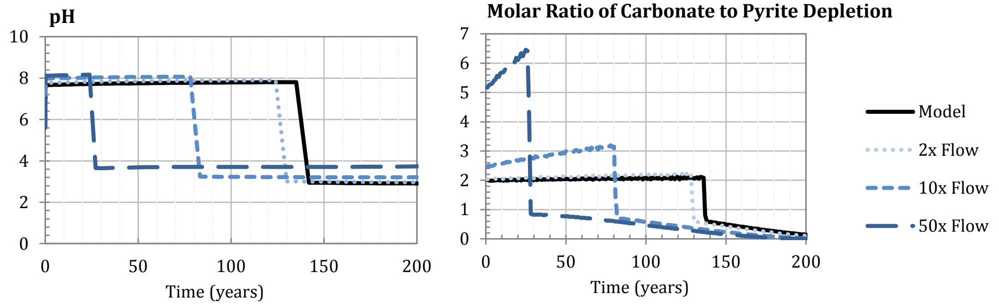

Figure 5 *Sensitivity model results following an increase in lixiviant volume (2x, 10x or 50x).*

consideration under some laboratory and field conditions. It is recommended that in addition to sulfide oxidation, consideration of the other factors that may affect NP consumption be incorporated into the interpretation of kinetic testing results and development of the conceptual model of system behavior.

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