Diavik Waste Rock Project: Laboratory Studies

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Abstract

Humidity cell experiments are used to quantify the effect of mineral composition and mineral surface areaon observed pH and alkalinity measurements and iron, sulfate, and nickel loading ratesunder controlled conditions at the lab-scale.The reactive solute transport modeling package MIN3P is used to determine whether differences in measured loading rates of sulfate and nickel can be simulated using a global set of parameters that are only variable with respect to mineral amounts and surface area.Two sets of duplicatehumidity cell experiments were initiated in the laboratory using run-of-mine rock from the Diavik site. Sulfur content in these humidity cells initially ranged from 0.01wt % S to 0.26wt % S, primarily as pyrrhotite in the biotite schist of the country rock. Humidity cell experiments have been operational for over four years and continue to show evolution in geochemical parameters and metal-leaching rates. The humidity cells with >0.08 wt % S waste rock show the potential to generate acidic drainage whereas the humidity cells containing waste rock with <0.04 wt % S have not shown evidence of acid generation. MIN3P simulationsdemonstrate that observed loading rates of sulfate and nickel are approximated reasonably well using parameters that vary only with respect to mineral amounts and estimated mineral surface area, while remaining constant with respect to the physical flow system, reaction rate expressions, and included minerals

Key Words: reactivesolute transport, acid mine drainage, geochemical modeling, waste rock

Introduction

There is much interest in the reliability of humidity cell testing as a tool for acid mine drainage prediction (Sapsford et al., 2009). Humidity cell tests are relatively simple, standardized, and have the potential to provide valuable insight into the long-term fate and behavior of dissolved constituents in waste rock leachate. To date, several humidity cell experiments have been performed to investigate geochemical processes occurring in small volumes of waste rock (Murr et al., 1981; Stromberg &Banwart, 1999; Hollings et al., 2001). However, the use of humidity cells as tools for estimation of long-term behaviour of field-scale waste-rock piles is challenging because waste-rock piles are massive, irregularly shaped structures that are heterogeneous with respect to moisture content, grain size, and mineral composition (Smith, 2009) and subject to influence from environmental conditions that are difficult to measure and simulate (Amos et al., 2009; Chi 2011).

The Diavik Waste Rock Project was initiated to study the factors that control effluent water chemistry from waste rock material across multiple scales of observation. The project has included laboratory humidity cell experiments conducted on Diavik waste rock, and field scale experiments at the Diavik Diamond Mine in the Northwest Territories, Canada. Waste rock at the Diavik Diamond Mine is segregated based on sulfur content. Type I is comprised of mainly granitic rock, with target sulfur content of < 0.04 wt % S. Type II has a target sulfur contentof 0.04 – 0.08 wt % S, and Type III has the highest target sulfur content of > 0.08 wt % S and is comprised of granitic rock with some amount of biotite schist. The principal sulfur-bearing mineral is pyrrhotite, which is contained within the biotite schist portion of the country rock.

As a first step to addressing the question of how to use lab-scale measurements to estimate leachate properties at larger scales, the principal governing variables must be identified and quantified. This paper presentsresults from two sets of duplicate humidity cell experiments. One set of humidity cells initially contained an average of 0.02 % wt as sulfur (Type I) and the other set initially contained an average of 0.18 % wt as sulfur (Type III).The reactive transport model MIN3P was used to simulate each set of duplicate humidity cell experiments using a global set of flow parameters, reaction-rate expressions, and mineralogical constituents. Variable parameters were limited to measured mineral amountsand mineral surface areas estimated based on measured particle surface areas. The objectives of the reactive transport modeling study is to quantitatively determine if these variable parameters can

account for the observed differences in sulfur and metal release rates, and form the basis for more rigorous scale-up calculations.

Materials and Methods

Run of mine (ROM) samples of Type I and Type III rock types were collected in October 2004from the Diavik site. Sampleswere screened to a grain size of less than 2.54 cm (1 inch), and representative samples were prepared for analysis. All samples were collected from materials that had been dumped within two days of collection.

Four humidity cells were constructed (Moore et al., 2008) following the procedure in ASTM D 5744 Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell Designation D 5744 – 07 – designated leach method (ASTM, 2009). The cells had dimensions of 10.2 x 20.3 cm and 1 kg of sample was added to each cell. Material for each sample type was reduced to 2.54 cm (1 in.) following the standard reduction procedure outlined in ASTM C 702-98 Standard Practice for Reducing Samples of Aggregate to Testing Size, to help reduce the bias in sample selection (ASTM, 2009). Material less than 2.54 centimeters was split using a sample splitter. The four cells were stored at 22°C. Air of varying relative humidity (RH) was circulated through the humidity cells each week. The cycle consisted of a 3-day dry period (0% RH), a 3-day wet period (>95% RH) and a 1-day flood leach with 500 ml of distilled water (White and Lapakko, 2000). The four cellsconsist of twosets with duplicate rock material.

Each material type was subjected to a variety of characterization tests. Specific surface area was determined at the University of Waterloo using the BET Multipoint method. Three replicates were analyzed for each sample. Standard static tests were conducted, including Acid Base Accounting (ABA), Net Acid Generation (NAG) testing, and pH determination. In addition, samples were subjected to several geochemical analyses including total sulfur analysis, total sulfate content, total carbon content, total carbonate content, and whole rock analysis. Samples for whole rock analysis were sent to two commercial laboratories: SGS Lakefield, Ontario and Actlabs, Ancaster, Ontario. Blind replicates and sample splits were also submitted.

Leachate was collected for determination of pH, alkalinity, and electrical conductivity, and to provide samples for analysis of anions, and cations. Measurements for pH were obtained from unfiltered leachate, while filtered leachate was used for analysis of anions, cations, andalkalinity. Alkalinity was measured by titration with 0.1600N sulfuric acid using a HACH Digital Titratorand bromocresol greenmethyl red as the indicator. Samples were submitted to the University of Waterloo, Groundwater Geochemistry and Remediation Laboratory for cation and anion analysis, by Ion Chromatography (IC; Dionex DX-600) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)and Inductively Coupled Plasma Mass spectrometry (ICP-MS).

The mass load for each constituent in each cell for a given week was calculated according to equation (1)

$$L_n = \frac{C_n \times M_{e,n} \times M_m}{M_{Cell}} \quad (1)$$

where C_n is the concentration of a given constituent at week n, $M_{e,n}$ is the mass of humidity cell effluent at week n, M_m is molecular mass of the constituent and M_{Cell} is the mass of waste rock material in the humidity cell.

Experimental release rates were determined using the following equation:

$$R_n = \frac{\left(L_{n_2} - L_{n_1}\right)}{\left(n_2 - n_1\right)} \quad (2)$$

whereR_n is the release rate of the constituent between week n_1 and n_2.

Results and Discussion

Waste rock characterization

Mineralogical study of samples from the Diavik site indicates thatsulfur exists principally as sulfide in the form of pyrrhotite with an average composition of $(Fe_{0.852}Ni_{0.004}Co_{0.001})_{\Sigma 0.857}S$, contained in the biotite schist (Jambor, 1997). Lesser amounts of sulfur are contained in pyrite which is present in at very low concentrations in the granite portion of the country rock. The biotite schist occurs in the country rock as irregular xenoliths within the granite. Sub samples of ROM country rockcollected in October 2004 from the Diavik site were analyzed prior to humidity cell testing.Sulfur contents in the four humidity cells initially ranged from 0.01 to 0.26 % wtas sulfur (wt %S). The average sulfur contents of the Type I and Type III humidity cells was 0.02 % wt S and 0.18 % wt as sulfur respectively.The specific surface areas of the bulk material in Type I and Type III humidity cells were initially1.21 and 1.62 m^2g^{-1}respectively.The available surface area of specific minerals were estimated as the product of the bulk surface area and the mineral volume fraction

Humidity cell test results

Results from humidity cell experiments indicate that leachate pH of the Type I samples remained near neutral for the length of the experiments (Figure 1). In contrast, the leachate pH from the Type III samples remained near neutral for the first 14 weeks then declined and remained at pH values between 4 and 5 (Figure 1).These pH valuesare consistent with the results from ABA testing indicating that Type I material is non-acid generating but also suggest that the Type III material is potentially acid generating (Smith, 2009).

For net acid generation to occur the rate of acid production must be higher than that of acid neutralization. Calcite is present in samples in small amounts CaCO3 (Jambor, 1997). In addition, kinetically limited dissolution of aluminosilicate minerals, including biotite and anorthite may contribute to acid neutralization. Future modeling attempts will be used to help identify the acid neutralization processes. Type I material maintained a positive alkalinity throughout the entire 250 week test (Figure 2). In contrast, the alkalinity of the Type III material was consumed within the first 20 weeks of the test. This observation is consistent with the acid-base accounting results (Smith, 2009), which indicated where net acid generation potential for the Type III material.

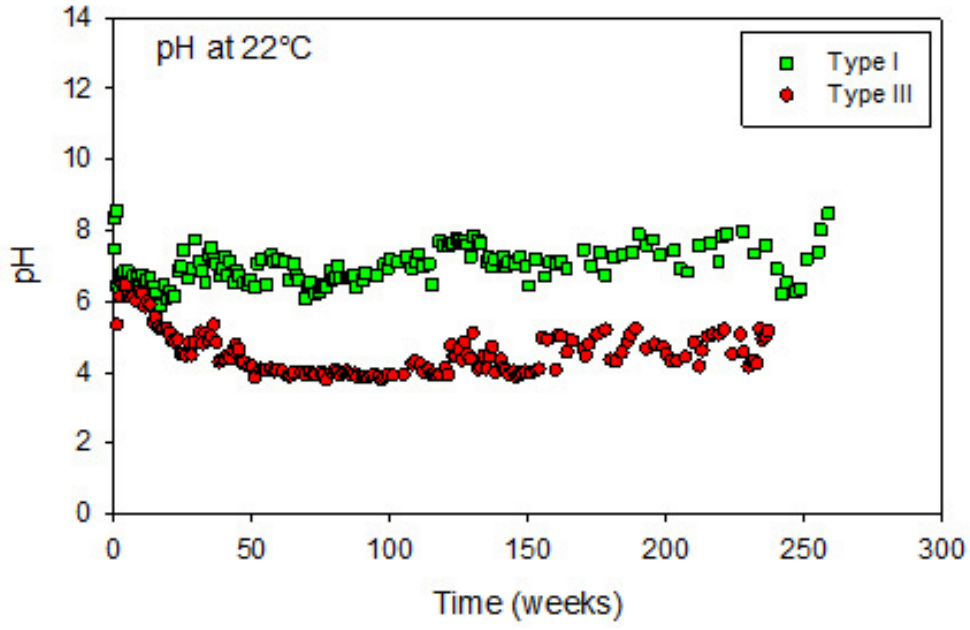

Figure 1.Values of pH for 2004 Type I and Type III waste rock at 22°C.

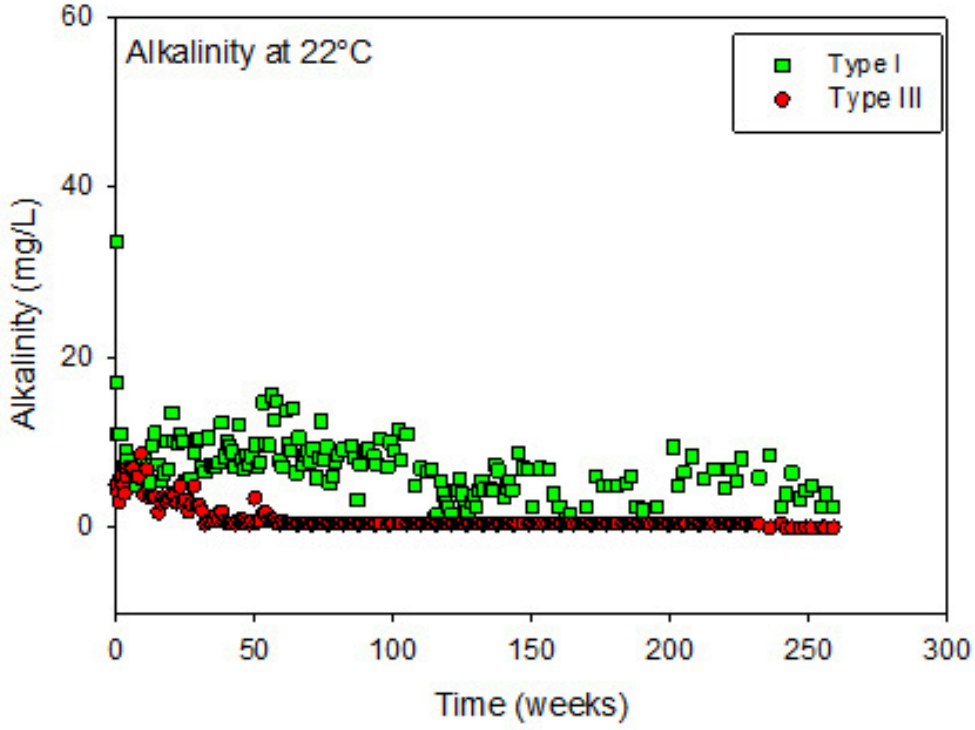

Figure 2. Alkalinity of 2004 Type I and Type III waste rock at 22°C.

In the Type III material, with greater sulfur content,resulted in higher sulfate concentrations in humidity cell leachate compared to the Type I material (Figure 3). At 22°Cthe rate of sulfate release decreasedrapidly for Type I and then remained constant at approximately 5 x 10^{-12}mol kg^{-1} s^{-1}over the entire experimental period. This early decline in sulfate release probably resulted from flushing of sulfide oxidation products that accumulated during blasting (Bailey et al., 2011) and following sample collection. The sulfate release rate of Type III rock showed a similar early decline, likely due to flushing of sulfate derived from blasting and from sulfate accumulated after sample collection, however, the rate stabilized at a higher value of approximately 7 x 10^{-11}mol kg^{-1} s^{-1}.

The rate of ironrelease increased in the Type III materials relative to the Type I material. Iron release rates for the Type III material are consistently below 3 x 10^{-11}mol kg^{-1} s^{-1}, well below the expected rate of 8 x 10^{-11}mol kg^{-1} s^{-1} given the stoichiometry of pyrrhotite in the Diavik waste rock, suggesting that there is a solubility control on dissolved iron.

Figure 5 shows nickel loading rates for Type I and Type III materials. The rate of nickel release follows a similar pattern as sulfate and iron with an initial drop and then rapid increase within the first 50 weeks followed by a gradual decline. Between weeks two and forty, nickel loading rates in the Type III material showed a marked increase from approximately 10^{-13} to $10^{-11} mol \cdot kg^{-1} \cdot s^{-1}$ respectively, followed by a gradual decline to approximately $3 \times 10^{-12} mol \cdot kg^{-1} \cdot s^{-1}$.

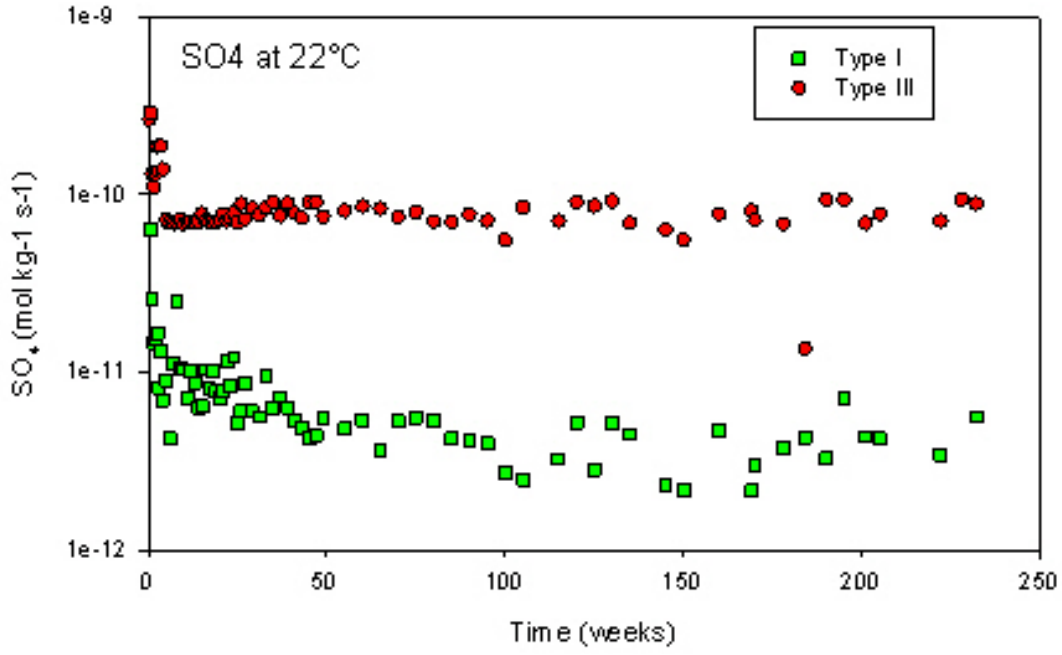

Figure 3. Sulfate release rates for 2004 Type I and Type III materials at 22°C

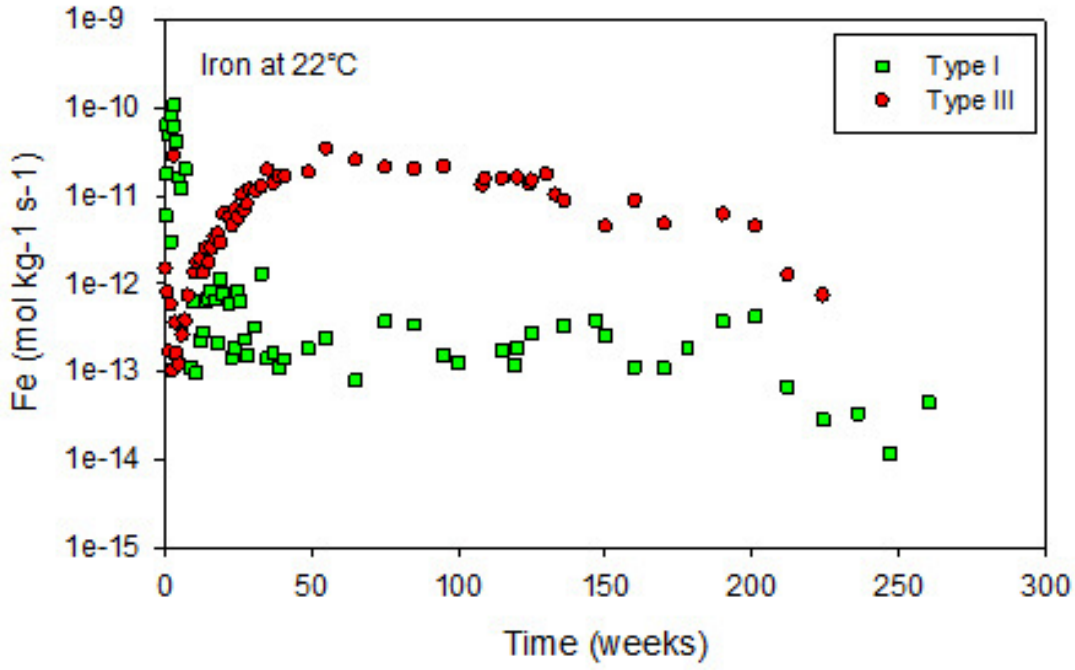

Figure 4. Iron release rates for 2004 Type I and Type III material at 22°C.

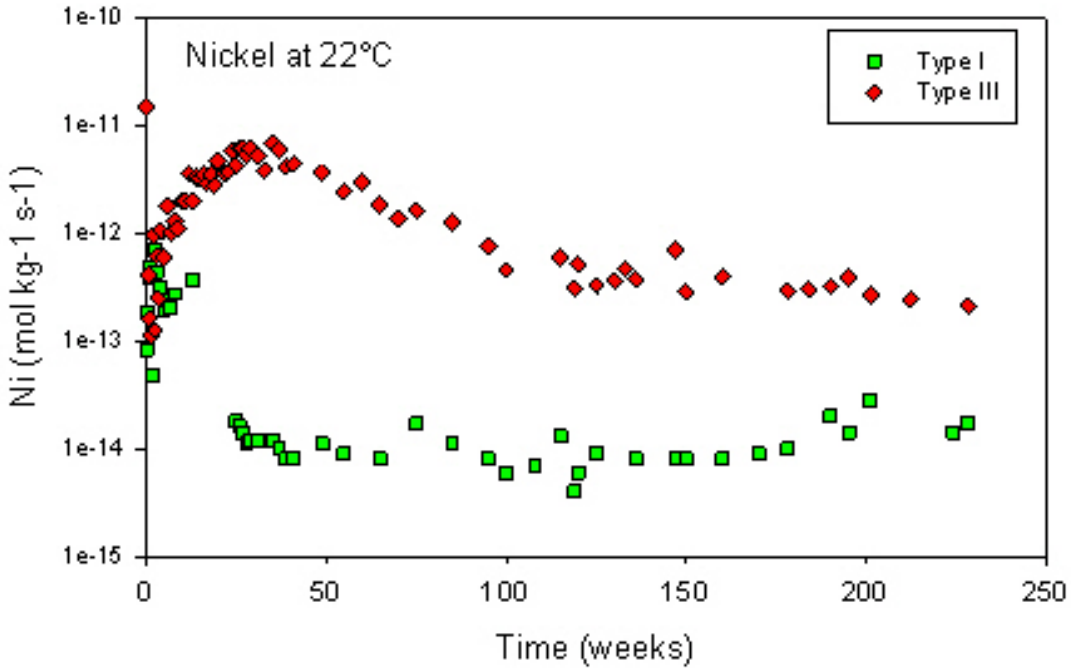

Figure 5. Nickel release rates for 2004 Type I and Type III materials at 22°C.

Modeling approach and preliminary results

Multicomponent reactive solute transport modeling can be used as a tool to isolate and understand the processes that control geochemical behavior across multiple scales provided that the conceptual model captures the important processes controlling geochemical behavior in a mechanistic manner. MIN3P is able to simulate solute transport in three-phase systems with homogenous processes including hydrolysis, complexation, and aqueous redox reactions, as well as heterogeneous processes including gas dissolution, mineral precipitation, and ion exchange reactions (Mayer et al., 2002).Of critical importance is that the model predictions are dependent only on measurable parameters and fitted parameters are eliminated or minimized.

Humidity cell testing involves the addition of 500 ml of water once per week to 1 kg of waste rock. This water addition typically takes 4-12 hours to flush through the cells. To simplify model simulations, the water flow is represented in MIN3P as a constant flux boundary on a one-dimensional simulated cell such that 500ml of waterflushes through 1 kg of waste rock in one week. The outflow boundary is set to a constant head of -0.3 mand represents a gravity drain such that moisture in the cell at steady state is sufficiently dry to allow an excess of oxygen without ever being completely dry to avoid water limitation. In the simulations presented, the steady state moisture content throughout the cell is between 0.3 and 0.4 (v_{water}/v_{pores}). The use of a constant flow system in the model is reasonable provided neither moisture content nor oxygen become limiting factors in either the physical or simulated scenario. Given the relatively low rate of sulfide oxidation, it is reasonable to assume that almost any non-zero moisture content will prevent water from limiting effective sulfide oxidation rates. The humidity cells had moist air flowing through them for half of the one week cycle, and were weighed as a means of tracking moisture content. The moist air and confinement in a cell was sufficient to ensure that waste rock in the cells did not dry completely between weekly water additions. Table 1 lists the physical flow parameters used in simulations. Given these assumptions, the simplified flow system provided simulation results that are comparable to measured results in terms of loading rates.

Table 1 Physical flow parameters used in simulations.

Parameter	Value	Units
Porosity	3.00E-01	-
Bulk Density	1.80E+00	g/cm
d_{10}	1.85E-04	m
Max Depth	1.00E-01	m
Kzz	1.00E-04	cm/s
Residual Saturation	2.50E-01	
Van Genuchten Alpha	1.50E+00	
Van Genuchten N	2.80E+00	
Specific Storage	1.00E-10	
Inflow Boundry (2nd)	1.48E-07	m/s
Outflow Boundary (1st)	0	m

In this scenario sulfide oxidation is based on the shrinking core model (Mayer, 2002).Conceptually, the shrinking core model represents dissolution reactions that are controlled by the diffusive mass flux of a single primary reactant through an alteration surface coating.Mathematically, reaction rates are calculated according to equation (2).

$$a_{kj}$$
(2)

whereR_k^{mt} is the reaction rate for the k_{th}surface-controlled dissolution-precipitation reaction for mineral *m* at timestep*t*. k_k^m is the rate constant for the mineral m in the k_{th} reaction.S_i is the reactive surface area of the material. The remaining terms are related to the reaction orders with respect to the total aqueous component concentrations and the activities of the dissolved species.Rate constants in the shrinking core model are expressed in terms of the physical parameters that control diffusion on the primary reactant.

$$k_k^m = 10^a D_k^m \left[\frac{r_i^p}{[(r]_i^p - r_i^r) r_i^r}\right] \quad (3)$$

r_i^p is the radius of an average particle and r_i^r is the radius of the unreacted portion of the mineral grain, which is updated with decreasing mineral content. D_k^m is the effective diffusion coefficient of the primary reactant through the protective surface layer (Mayer, 2002). The end result is that reaction rates decline over time, as the reaction proceeds and the altered mineral surface coating thickens.The decline in reaction rates is consistent with observations of Type III iron and nickel observations. Table 2 lists the shrinking core parameters used to simulate pyrrhotite dissolution.

Table 2. Shrinking core parameters used in simulations for pyrrhotite dissolution.

Scaling factor (including tortuosity of surface coating)	1.39E+02
Particle radius	1.85E-04
Radius of unreacted portion of particle	1.85E-04
Free phase diffusion coefficient of the primary reactant in water (in this case O2(aq)	2.41E-13
Stoichiometric coefficient of oxygen in the reaction equation	1.93E+00

Conversion factor	1.00E+03

The mass fractions of minerals used in MIN3P simulations were obtained from mineralogical analysis of each rock type (Jambor, 1997). Table 3 lists the mass fractions of each mineral component of the model. Surface areas for each mineral were estimated based on the fraction of a given mineral and the total surface area of the given rock type as determined using the BET multipoint method.

Table 3. Mineral mass fractions and surface areas used in MIN3P simulations.

Mineral Name	Composition	Mass Fraction		Surface Area	
		Type I	Type II	Type I	Type III
Silicon Oxide	$SiO2$	1.5E-01	6.7E-01	2.3E+02	1.4E+03
Potassium Feldspar	$KAl(H_4SiO_4)_3$	5.5E-01	5.0E-02	8.6E+02	1.0E+02
Albite	$NaAlH_4SiO_4$	2.0E-01	5.0E-02	3.1E+02	1.0E+02
Biotite	$(KMg_2Fe)Al(H_4SiO_4)_3$	4.0E-02	4.0E-02	5.5E+01	7.3E+01
Calcite	$CaCO3$	8.0E-04	8.0E-04	1.2E+00	1.6E+00
Anorthite	$CaAl_2H_4SiO_4$	1.0E-02	1.6E-01	1.5E+01	3.0E+02
Muscovite	$K(AlH_4SiO_4)_3$	4.0E-02	4.0E-02	5.7E+01	7.6E+01
Sphalerite	$ZnHS$	1.0E-03	1.0E-03	1.0E+00	1.3E+00
Pyrrhotite	$Fe_{0.852}Ni_{0.004}Co_{0.001}SO_4$	8.0E-04	1.6E-03	6.9E-01	1.9E+00

Figures 8 and 9 show measured and simulated results for sulfate and nickelrates for Type I and Type III waste rock. The model simulations for Type I and Type III waste rock used an identical set of parameters with the exception of mineral mass fractions and therefore surface areas, which are calculated from mass fractions. These results suggest that it is possible to represent the general trends observed for sulfate and nickel under controlled conditions by adjusting only the mineral composition.However, there is a significant discrepancy between the early-time concentrations and the simulation results. Further model calibration, and revision of the conceptual model, is required to better capture potential precipitation controls on iron, and reaction rates that better fit the early time data.

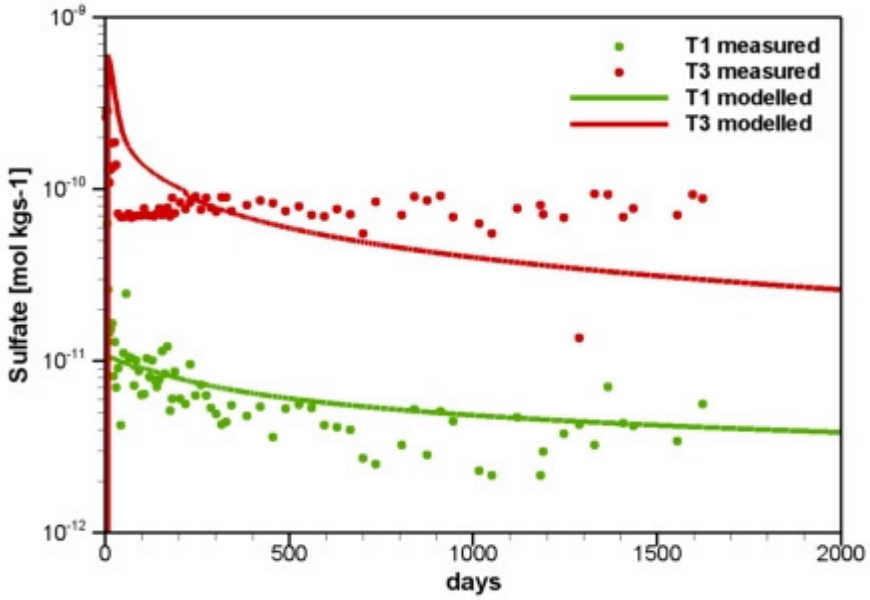

Figure 8. Sulfate loading rates for measured and modeled 2004 Type I and Type III materials.

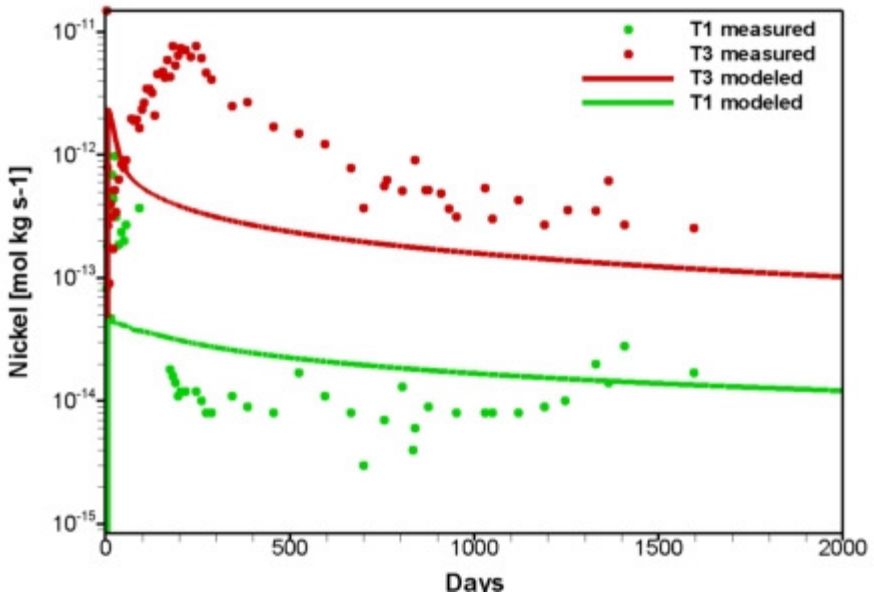

Figure 9.Nickel loading rates for measured and modeled 2004 Type I and Type III materials**.**

Conclusions

The preliminary results presented here suggest that mineral composition and reactive surface area govern the overall rate of sulfide oxidation and subsequent metal release in waste rock where water and oxygen are not limiting factors.This conceptual model is supported by simulations that show general agreement with measured results by changing only measured mineral amounts and surface areas. These results also demonstrate the use of multicomponent reactive solute transport modeling to test a hypothesis related to factors that are thought to govern the geochemical scenario at hand. Humidity cell results indicate that Type III waste rock containing 0.18 wt. %S has the potential to be acid generating, and Type I waste rock containing 0.02 wt. %S showed no evidence of acid generation after four years of humidity cell testing. The pH, and alkalinity, sulfate, iron, and nickel loading rates are consistent with the current conceptual model that oxidation of iron sulfide minerals results in acid production until alkalinity is consumed or become rate limited, at which time pH declines causing a subsequent increase in metal leaching. Further investigation is needed to determine possible precipitation controls on iron, the extent of acid neutralization by aluminosilicate mineral dissolution, and improvement of mineral dissolution rate estimates.

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