Simulation of Column Leach Tests using Reactive Transport Modelling

Yuan Tian[1], Johan Fourie[2], Brent Usher[2]

[1]*Golder Associates Pty Ltd, Level 3, 1 Havelock Street, West Perth, WA 6005, Australia,*
ytian@golder.com.au, iamseanty@gmail.com

[2]*Klohn Crippen Berger Pty Ltd, Level 1, 154 Melbourne Street, South Brisbane QLD 4101, Australia*

Abstract

Reactive transport modelling, which accounts for geochemical reactions and transport of reaction products, has become an increasingly powerful tool to assist the mining industry for assessing the long-term geochemical behaviour of mine waste materials during operation and post-closure periods.

The reactive transport models were developed in this study to model the key geochemical processes that control sulfide oxidation and subsequent chemical reactions (e.g. dissolution/precipitation) for lab scale column leach tests. The models were refined to allow calibration of kinetic rates of several of the waste rock minerals based on leachate data. The reactive transport models form the basis of the predictive model of drainage water quality for full-scale mine waste facilities.

Keywords: reactive transport modelling, mine waste, column leach test, kinetic rates

Introduction

With the development of modelling codes in the past decades, reactive transport modelling has become increasingly powerful tool to assist the mining industry for assessing the long-term geochemical behaviour of mine waste materials over the course of LOM and mine closure.

By utilising a subset of the column leach tests currently underway to understand the geochemical evolution of the sulfidic waste rock at the mine, several reactive transport models were developed to represent the AMD and/or NMD processes for potentially acid generating and non-acid generating waste. With regular monitoring and chemical analysis of the leachate in column leach tests and field surface water and groundwater samples, these valuable datasets have provided a realistic 'selection-criteria' to assess the effectiveness and reliability of the reactive transport model by comparison to modelled results.

The reactive transport models were developed to model the key geochemical processes that control sulfide oxidation and subsequent chemical reactions (e.g. dissolution, precipitation and sorption) under the laboratory testing conditions. The reactive transport models form the basis of the predictive model of drainage water quality for larger scale field barrel and full-scale mine waste facilities.

Methods

The reactive transport model for lab-scale kinetic column test is schematically visualised in Figure 1 as a 1-D vertical drain system. The modelling domain had the same size as the actual sample material in the column, with its length calculated from sample weight, bulk density and the column internal diameter. The modelling domain was discretized to ten nodal blocks in the direction of drainage flow. The lixiviant (deionised water) recharge rate to the modelling domain was calculated from the average weekly leachate volume and was assumed to be constant in the model. Given the small scale of the column, both the lixiviant and the modelling domain were assumed to be in equilibrium with atmosphere, so temperature and the fugacity of CO_2 and O_2 were fixed throughout the simulation for all columns.

For the assigned column material, the mineralogical composition of column materials

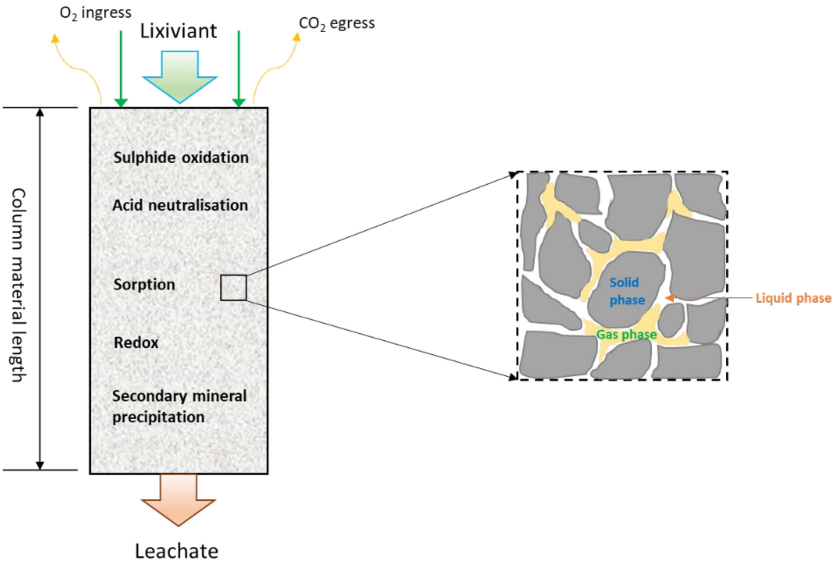

***Figure 1** Schematics of kinetic column leach test.*

was derived from quantitative XRD mineralogical tests. The physical properties of porous medium, including diffusion coefficient, bulk density, porosity, thermal conductivity, and heat capacity, were either derived from field measurements or the default setting of the GWB X2t program where data was unavailable. Due to the small scale of model, both longitudinal and transverse dispersivity were assumed to be zero. The permeability of the porous medium was calculated by GWB program from the porosity based on an empirical correlation (Bethke et al. 2019).

Two kinetic columns were selected for the reactive transport modelling as selected column samples were representative for all ABA and NAG parameters and classified as NAF (HC) and PAF (R), representing the most common types of waste materials.

The extended Lawrence Livermore National Laboratory database in GWB format was used for the reactive transport modelling. A two-layer model type sorption surface based on the dataset of Dzombak and Morel (1990) was used to account for sorption mechanism that is mainly induced by surface functional groups of iron-hydroxide, iron-oxide and iron-oxyhydroxide minerals to form a variety of surface complexes when in contact with aqueous species in water.

In the model, the dissolution rates of primary minerals were controlled by the kinetic rate law as defined by the following equation:

$$r = A_s * k * (1 - \frac{Q}{K})$$

Where r is the reaction rate in mol/s, A_S is the bulk reactive surface area in cm^2/mol; k is the rate constant in mol/cm^2/s, and Q and K are activity product and equilibrium constant for the dissolution reaction. The reduction of mineral reactive surface area was taken into account according to the shrinking core model when the chemical reaction is in progress. To account for the effect of temperature on kinetic rate, an activation energy and pre-exponential factor for the Arrhenius equation was implemented for the rate constant:

$$k = A * e^{-E_a/RT} * \prod_i {a_{(i)}}^{P(i)}$$

Where A is the pre-exponential factor, E_a is the activation energy in KJ/mol; R is gas constant; T is the absolute temperature in kelvin; $a(i)$ is the activity of promoting or prohibiting species i; $P(i)$ is the power of dependence respect to species i used in rate law. The parameters used in the kinetic rate law for various minerals are presented in Table 1.

Table 1 *Kinetic rate parameters for sulfides, sulfates and silicates in this study.*

Mineral	Formula	Pre-exp mol/cm²/sec	Ea KJ/mol	P(H⁺)	P(O₂)	P(Fe³⁺)	Reference
Pyrite	FeS_2	6.004E-03	56.9	-0.11	0.5		Williamson & Rimstidt, 1994
Arsenopyrite	FeAsS	6.777E-09	18.5	-0.12	0.76		Asta et al, 2010
Sphalerite	ZnS	1.467E-03	41.75	0.2659		0.154	Pan et al, 2013
Galena	PbS	3.162E-13	15	-0.78	0.3		Acero et al, 2007
Gypsum	$CaSO_4.2H_2O$	1.622E-07	0				Palandri & Kharaka, 2004
Kaolinite	$Al_2Si_2O_5(OH)_4$	5.120E-14	22.2				Same as above
K-feldspar	$KAlSi_3O_8$	1.767E-10	38				Same as above
Albite	$NaAlSi_3O_8$	4.661E-05	69.8				Same as above
Quartz	SiO_2	3.350E-02	90.9				Same as above
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	2.015E-14	22				Same as above
Chlorite	$Fe_2Al_2SiO_5(OH)_4$	7.887E-02	88				Same as above

* ***Parameters*** *for epsomite are estimated only as epsomite is readily soluble and there is no available data from literatures.*

Compared to the minerals listed in Table 2, the dissolution of dolomite and calcite is more complicated as their rate constants are subject to three promoting species: H^+, $H_2CO_{3(aq)}$ and H_2O with each species assigned with its own pre-exponential factor, activation energy and power of dependence. The rate constant k of calcite and dolomite is expressed as the equation below:

These three promoting species represent three pathways controlled by acidic, carbonate and neutral mechanisms, which was proposed and defined by Plummer (1978) for calcite dissolution and Busenberg and Plummer (1982) for dolomite dissolution. The kinetic parameters used in this study (Table 2) were fitted by Declercq and Oelkers (2014) based on a summary of several independent studies

$$k = A_{(H^+)} * e^{-\frac{E_{a(H^+)}}{RT}} * a_{(H^+)}{}^{P_{(H^+)}} + A_{(H_2CO_3)} * e^{-\frac{E_{a(H_2CO_3)}}{RT}} * a_{(H_2CO_3)}{}^{P_{(H_2CO_3)}} + A_{(H_2O)} * e^{-E_{a(H_2O)}/RT} * a_{(H_2O)}{}^{P_{(H_2O)}}$$

Table 2 *Kinetic rate parameters for calcite and dolomite.*

Parameter	Unit	Calcite	Dolomite
Pre-exp (H⁺)	mol/cm²/sec	2.13E-02	1.49E-02
Ea (H⁺)	KJ/mol	16	29
P (H⁺)	unitless	0.33	0.75
Pre-exp (H_2CO_3)	mol/cm²/sec	3.47E-03	1.00E-02
Ea (H_2CO_3)	KJ/mol	46	34.8
P (H_2CO_3)	unitless	0.33	0.75
Pre-exp (H_2O)	mol/cm²/sec	1.17E-02	2.20E-07
Ea (H_2O)	KJ/mol	46	52.2
P (H_2O)	unitless	0.33	0.75

related to calcite and dolomite dissolution under a range of pH, temperature, and chemical conditions.

Model Results

The modelled leachate water quality is compared with experimental results in the following figures. The experimental pH varied in the circum-neutral pH range, and modelled pH values were in broad agreement with experimental results in Figure 2, although some discrepancies can be observed in several leaching events. Figure 3 presents modelled and experimental sulfate concentrations for the NAF (HC) and PAF (R) column leachates. Concentrations of sulfate showed a rapid decline within the first 1-2 weeks, followed by a gradual decrease, and progressively stabilized from around the 100th day. The modelled sulfate concentrations typically captured the early peaks and demonstrated similar decreasing trendline and consistent concentrations that were stabilised in the recent 300 days.

Comparison of modelled and experimental data was made for calcium and magnesium in Figure 4 and Figure 5, respectively. Similar to sulfate, the trend and intensity of calcium and magnesium concentrations were largely reproduced by the model. The rapid decline of sulfate, calcium, and magnesium in the early leach events indicated the dissolution and depletion of secondary sulfate-rich minerals (e.g. gypsum and epsomite). These secondary minerals were present in the samples prior to the kinetic test and are generally readily soluble in response to flush or leach events.

To demonstrate the importance of sorption mechanism, the models simulated the leachate chemistry with and without the two-layer sorption surface. For example, modelled concentrations of arsenic and lead (Figure 6 and Figure 7) without the implementation of sorption surface were typically 2-3 orders of magnitude higher than those with the application sorption surface. And the latter overall showed good agreement with experimental results.

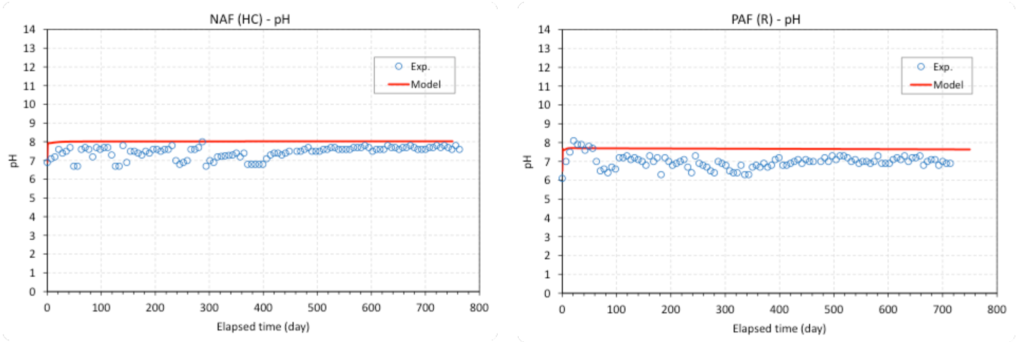

Figure 2 Modelled and experimental pH in column leachates.

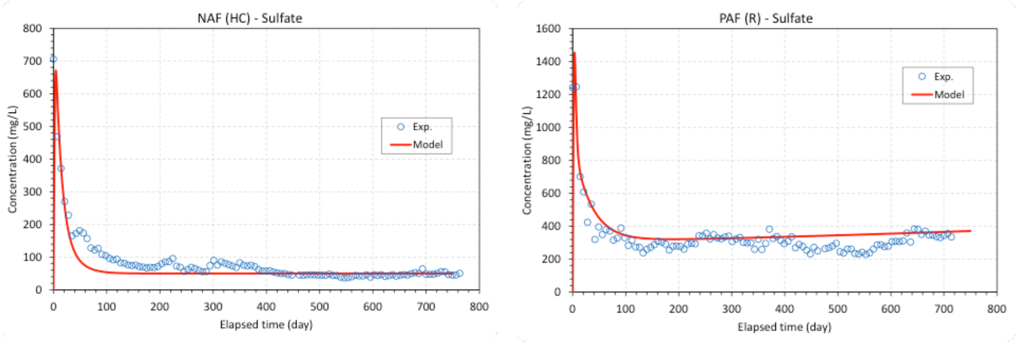

Figure 3 Modelled and experimental Sulfate concentrations in column leachates.

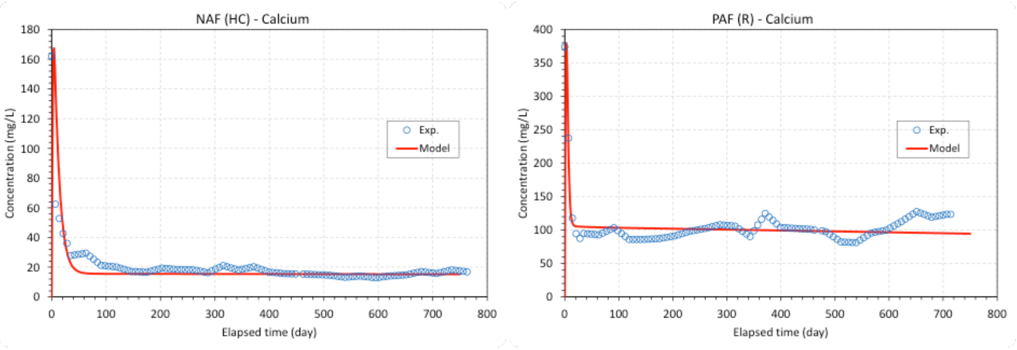

Figure 4 Modelled and experimental Calcium concentrations in column leachates.

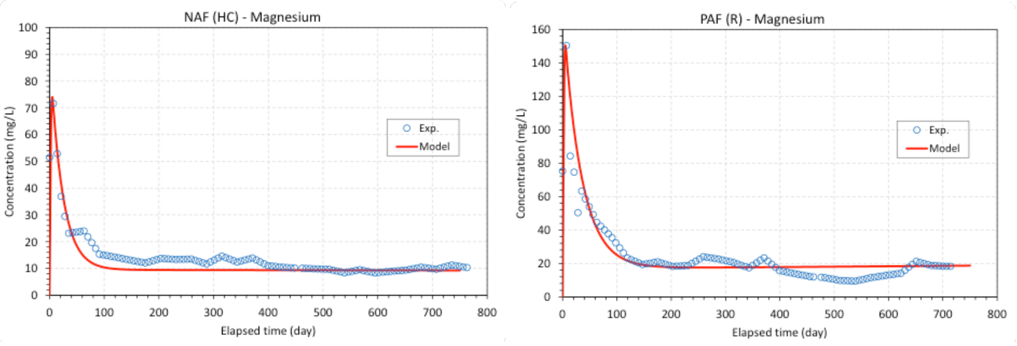

Figure 5 Modelled and experimental Magnesium concentrations in column leachates.

In contrast, the application of sorption mechanism makes negligible influence on the water quality of major cations/anions although related surface complexes were included in the sorption surface dataset of Dzombak and Morel (1990). This is a strong indication of the competition for surface complexation when metallic ions are being adsorbed to the ferrihydrite surfaces. It also demonstrates that sorption mechanism may play a critical role in the leachate water quality and the process may be 'element-selective', depending on the stability of surface complexes.

Conclusion

The reactive transport models developed in this study provided an example to predict drainage water quality for laboratory scale column leach tests. With the calibration to experimental data, the kinetic rates of the key mineral phases in the column samples were refined and the reactive transport model can be validated.

The reactive transport model can be up scaled by integrating site specific conditions (e.g. hydrogeological/meteorological condition) and the physical/chemical property of mine wastes. The model can be benefited from inputs derived from external simulation or measurements such as fluid flow, pore gas composition, mass and heat transport for a full-scale study.

Overall, reactive transport model has the potential to model the key geochemical processes that control sulfide oxidation and subsequent geochemical reactions to predict long-term evolution of mine waste materials and the seepage water quality from a variety of mine waste storage facilities under the mining influenced environment.

References

Acero, P., Cama, J., Ayora, C. (2007). Rate law for galena dissolution in acidic environment. Chemical Geology 245, 219–229

Asta, M.P., Cama, J., Ayora, C., Acero, P., De Giudici, G. (2010). Arsenopyrite dissolution

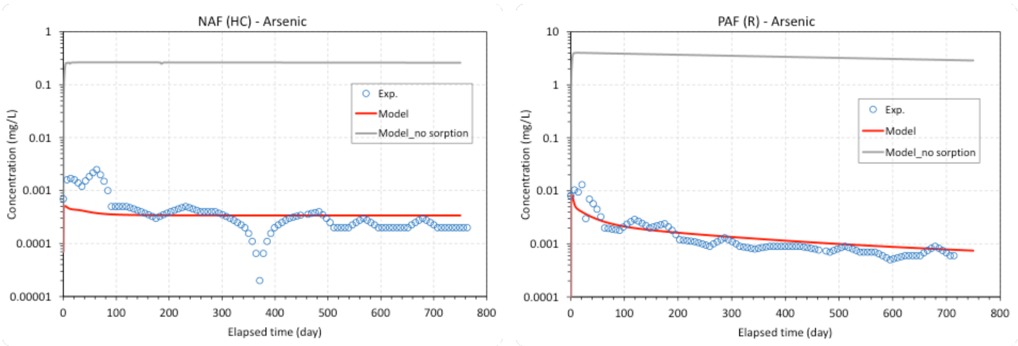

***Figure 6** Modelled and experimental Arsenic concentrations in column leachates.*

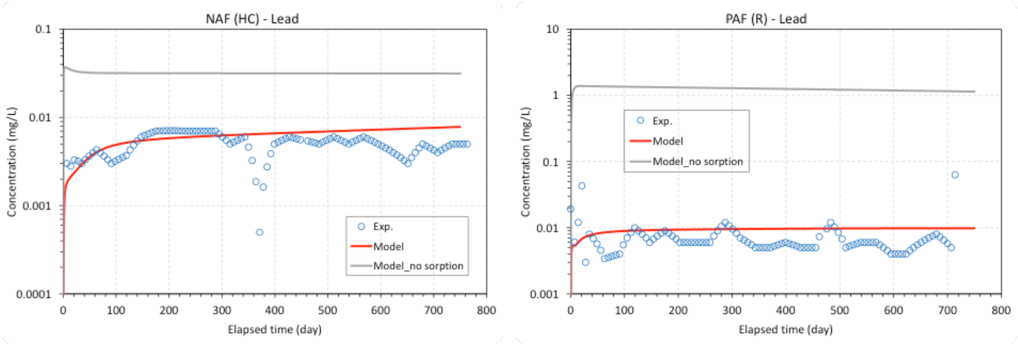

***Figure 7** Modelled and experimental Lead concentrations in column leachates.*

rates in O2-bearing solutions. Chemical Geology 273, 272–285.

Bethke, C.M., Farrell, B., Sharifi, M., and Yeakel. S. (2019). GWB Reactive Transport Modeling Guide, Release 12.

Busenberg, E., Plummer, L.N. (1982). The kinetics of dissolution of dolomite in CO2–H2O systems at 1.5 to 65 °C and 0 to 1 atm pCO2. Am. J. Sci. 282, 45–78.

Chirita, P. & Rimstidt, J.D. (2014). Pyrrhotite dissolution in acidic media. Appl. Geochem. 41, 1–10.

Declercq, J. & Oelkers, E.H. (2014). CarbFix Report 4 PHREEQC mineral dissolution kinetics database. CarbFix Project no. 281348. Geoscience Environement Toulouse, Belin, Toulouse. https://www.or.is/sites/or.is/files/kinetic_database.pdf

Dzombak, D. A. & Morel, F. M. M. (1990). Surface complexation modelling – Hydrous ferric oxide. New York:John Wiley. 393 p.

Palandri, J.L., & Kharaka, Y.K. (2004). A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling: USGS Open File Report 2004-1068, Menlo Park, California, National Energy Technology Laboratory – United States Department of Energy.

Pan Z.P. et al. (2012). A simulation experimental study on oxidative kinetics of sphalerite under hypergene condition. Chinese Journal of Geochemistry, 31(4), pp. 457-464.

Williamson, M. A. & Rimstidt, J. D. (1994). The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. Geochimica et Cosmochimica Acta 58, 5443–5454.

Abbreviation

AMD – Acid and Metalliferous Drainage
NMD – Neutral Mine Drainage
XRD – X-Ray Diffraction
GWB – Geochemist's workbench
ABA – Acid Base Accounting
NAG – Net Acid Generation
PAF (R) – Potentially Acid Forming (reactive)
NAF (HC) – Non-Acid Forming (high capacity)