Development of a Kinetic Model for Biotic Oxidation of Pyrite/Pyrrhotite on Rock Surfaces

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Abstract – A novel method was developed to predict the oxidation kinetics of sulfide bearing deposits. Waste rock samples were placed in a constant temperature column, inoculated with an *Acidithiobacillus ferrooxidans* suspension and sparged with humidified air. The humidified airflow was interrupted periodically by sealing the column and purged with a metered tracer gas to obtain oxygen concentration profiles. Integration and analysis of the concentration profiles yielded the oxygen consumption rate. The oxidation rate profile appeared to be fractional order with respect to the oxygen concentration. On the basis of the experimental results, a kinetic/mass transport model was proposed. The model assumed near steady state oxidation of pyrrhotite by either oxygen or ferric ion. Sulfide oxidation was assumed to be complete resulting in the production of ferric iron precipitate and sulfate. The reaction rate at the sulfide surface was made equal to the diffusive oxygen mass transfer through oxidized product (ferric hydroxide) layer to the surface. The two important parameters, the reaction rate constant and the apparent oxygen diffusion coefficient, were estimated using the Metropolis-Hastings algorithm. At 21% ambient oxygen concentration the maximum likelihood values of the initial oxygen flux, the oxygen diffusion coefficient through the oxidation product layer, and the surface reaction rate constant were 1.3×10^{-7} mol m^{-2} s^{-1}, 3.43×10^{-13} $m^2 s^{-1}$, and 2.89×10^{-7} $mol^{0.45} m^{-0.35} s^{-1}$, respectively.

Introduction

Sulfide containing waste rock oxidation is a serious environmental problem resulting from mining activities. Pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$) are the usually dominant iron sulfides and the most probable source of acidic drainage. It has been shown that the important parameters affecting pyrite oxidation are: pH, concentration of oxygen, presence of bacteria, concentration of ferric iron, temperature, and specific surface area of the mineral (Lowson, 1982; Nordstorm, 1982). Bacteria are effective catalysts of the oxidation. Based on studies by Paciorech *et al* (1981) and others, Halbert *et al* (1983) and Nicholson *et al* (1989) suggested that the rate of biotic oxidation might be orders of magnitude faster than abiotic oxidation.

The kinetics of pyrite oxidation has been the subject of several studies. Lowson (1982) suggested a molecular-transfer mechanism involving oxygen as being the rate-limiting step. This implies that the reaction rate with respect to oxygen concentration is first order. Similarly, Mathews and Robins (1974) and Nordstorm (1982) also proposed a first order oxygen dependence. If the rate limiting mechanism is an adsorption-desorption process, however, the reaction rate may be of partial order. This is because a partial order better approximates sorption mechanisms. Based on experimental work, Williamson and Rimstidt (1994) reported half order oxygen concentration dependence of pyrite oxidation rate. Using fine particles of pure pyrite in batch solutions, McKibben and Barnes (1986) also found that abiotic pyrite oxidation is half order with respect to oxygen. They postulated a stepwise mechanism involving i) adsorption of oxygen on the pyrite surface and concomitant reduction of oxygen to hydrogen peroxide (H_2O_2)

and ii) pyrite oxidation to oxyanions by hydrogen peroxide. Depending on the pH, different partially oxidized sulfur oxyanions may be present (Goldhaber, 1983). However, at low pH (pH 2-3), SO_4^{2-} is the dominant product and the formation of sulfate is stoichiometric.

Investigating pyrite oxidation at neutral pH, Nicholson (1988) proposed a mechanism involving the reversible adsorption of oxygen and the irreversible, rate limiting decomposition of intermediates (sulfoxy anions). The data fitted a Langmuir type adsorption model. A parameter

R_m was introduced representing the oxidation rate at oxygen saturation at the surface. Obviously, R_m was a function of available surface area and temperature. The oxidation product, ferric hydroxide, may precipitate at the surface (Jambor, 1994; Nicholson *et al*, 1989) and act as a barrier to oxygen transport. Several

researchers (Nicholson *et al,* 1989, Davis and Ritchie, 1986, and Jaynes *et al* 1984) had been employing the barrier concept together with a shrinking core model to simulate oxidation in tailings. The importance of a water layer to limit oxygen transport has been the subject of some debate. Nicholson (1989) estimated that the resistance to oxygen diffusion provided by the water layer is negligible, and only the oxidized layer provides a significant barrier to diffusive oxygen transport to the reactive surface.

While data for pyrite oxidation are generally available, pyrrhotite oxidation has not been studied extensively. This paper entails the development of a novel methodology for measuring the oxidation of pyrrhotite containing waste rock over extended time periods in a non-intrusive manner. The second part of the paper focuses on data analysis. In our view, previous attempts failed to evaluate unequivocally the reaction order or establish the relative significance of reactive and diffusive processes in oxidizing piles. We report the development of a method of data analysis that is most useful to resolve these issues.

Theoretical Development

Our preliminary results indicated that first order reaction kinetics is inappropriate to express the dependence of the reaction rate on oxygen. In our development of a model, we assume that sulfur oxidation occurs exclusively at the reactive iron sulfide surface. As sulfide is oxidized, the reactive sulfide surface recedes inward. The space previously occupied by sulfide becomes filled with oxidation products, thus forming a barrier to oxygen diffusion. Sulfide oxidation is assumed to be complete resulting in the production of ferric iron and sulfate. The stoichiometric coefficient for oxygen consumption is 2.25 moles O_2 per mole of FeS oxidized:

$$FeS + 2.25\ O_2 + 2.5\ H_2O \rightarrow SO_4^{2-} + Fe(OH)_3 + 2H^+ \qquad (1)$$

We further assume that the total reaction rate is directly proportional to sulfide surface area. This surface area remains constant during the oxidation. The resistance provided by water layer is neglected as being small in comparison to diffusivity through the oxidation layer (Nicholson *et al,* 1988). These assumptions are then used to develop the equations describing the process in terms of various parameters. The movement of the sulfide reactive front is given by:

$$\frac{dz}{dt} = \frac{r_{O_2}}{\rho\sigma} \qquad (2)$$

where :

z = distance to the reactive front from the ore surface (m)

t = time (s)

r = O_2 consumption rate (mol m^{-2} s^{-1})

ρ = molar density of FeS (mol m^{-3})

σ = stoichiometeric coefficient of oxygen consumption (mol O_2/mol FeS)

We assume a mixed diffusion/reaction control for the system. The model is illustrated in Figure 1, in which:

No_2 = The oxygen flux to the reactive zone (mol m^{-2} s^{-1})

D = effective diffusivity of O_2 through layer ($m^2 s^{-1}$)

z = axial depth (m)

z_o = initial thickness of the oxidation product (m)

z'_s = reactive front position (moving inward is the (m) positive z direction with time ($z_s = z_o + z'_s$))

It is assumed that neither diffusion nor reaction kinetics are dominant. The diffusion through the oxidation product zone is assumed to be at steady state and it may be represented by Fick's first law:

$$N_{o2} = \frac{D}{z_S}\left(C_o - C\right) \qquad (3)$$

C_0 = oxygen concentration in the pore space (mol m^{-3})

C = oxygen concentration at the sulfide mineral surface (mol m^{-3})

The surface reaction rate (in mol $m^{-2}s^{-1}$) with respect to oxygen is defined in terms of reaction order "α "as follows:

$$\frac{dC}{dt} = kC^{\alpha} \qquad (4)$$

k = surface rate constant ($mol^{1-\alpha}\ m^{3\alpha-2}\ s^{-1}$)

α = reaction order

The oxygen transport and the kinetic oxygen uptake (consumption) approach steady state. The specific surficial reaction rate becomes equal to the diffusive oxygen flux:

$$\frac{dC}{dt} = N_{O2} \qquad (5)$$

The oxygen consumption rate is defined in terms of "mole O_2 / m^2 FeS /s", consequently, the surface area is calculated by assuming that it is proportional to the mass percent of sulfide. The oxidation on the sulfide surface at near steady state resulted in a quadratic expression that, with some mathematical manipulation, was integrated with respect to time and product layer thickness. Using this procedure, one of the unknown variables, the thickness of the barrier layer, was eliminated resulting in the following equation:

$$\frac{C_0\alpha + C(1-\alpha)}{C^{2\alpha+1}}dC = -\frac{k^2}{\rho\sigma D}dt \qquad (6)$$

Equation (6) may be integrated and rearranged to yield:

$$\frac{C_0(2\alpha-1) + 2C(1-\alpha)}{C^{2\alpha}} = C_0^{1-2\alpha} + \frac{2(2\alpha-1)k^2 t}{\rho\sigma D} \qquad (7)$$

For a given k and D, the integral expression (Equation 7) was solved numerically using the Newton-Raphson method to estimate the oxygen concentration at the sulfide interface and consequently the oxygen consumption flux given by either Equation 3 or Equation 5 . The calculation procedure was repeated for discrete values of "α".

Experimental methods

Materials

Waste rock Waste rock obtained from the Whistle mine site in Sudbury, Ontario. The predominantly norite rock matrix contained pyrrhotite as the major sulfide with small amounts of pentlandite ($(Fe,Ni)_9S_8$) and chalcopyrite ($CuFeS_2$) (Anderson, 1997). The rock: was chisel crushed first, then jaw crushed, screened using standard sieves, washed several times in double de-ionised (DI) water until clear supernatant was attained, then soaked in 10% (v/v) HCl solution for 30 minutes, washed in DI water (4 rinses), soaked in 70% (v/v) ethanol for 2 hours, rinsed with DI water, air dried and re-sieved. Approximately 3.4 kg rock of 13-19 mm nominal size was packed into the each column. The rock charge contained 3.35% (by weight) S, 9.11% (by weight) Fe and 0.411% (by weight) carbonate.

Bacterial Inoculant An *Acidithiobacillus ferrooxidans* culture was isolated from acidic mine drainage at Elliot Lake, Ontario. The culture was adapted to the whistle mine waste rock by serial transfer in thiobacillus medium (Rojas *et al*,

1995) containing pulverized rock. After 4 serial transfers in a two-month period, the culture was harvested at the end of exponential phase of growth after the 4th transfer (Rojas *et al*, 1995) and counted using a Petroff-Hausser counting chamber. The bacterial population density was adjusted to 10^7cells/ml.

Humidified Reaction Columns (HRC) The 10 cm diameter PVC columns were equipped with inlet and outlet gas ports as well as a solution sample port for chemical analysis (see Figure 2). The columns were packed with rock, flooded with growth medium (Suzuki *et al*, 1990) for several hours, inoculated with the bacterial culture, and left undisturbed for 10 days to allow the micro-organisms to settle on the rock surface After 10

days the columns were drained and the columns were sparged with humidified air continuously

until the measurements of the oxidation rates commenced. The temperature in the columns was maintained at 25 ^{0}C. The humidified air saturated with water vapour was supplied at a

slightly higher temperature (30 ^{0}C) to keep the rock surfaces moist by the condensing vapour.

Oxidation rate measurement

For the measurement of the oxidation rate, the airflow was periodically interrupted and the columns were sealed for a defined length of time. After the interruption, a tracer gas (usually pure nitrogen) at a precisely metered flow rate was purged through the column and the oxygen concentration in the exiting gas was continuously monitored. The amount of oxygen in the column was determined by integrating the oxygen concentration profile during the trace gas purge:

$$n_{o2} = Q\int C_{o2}dt \qquad (8)$$

Where:

n = number of moles of O_2

Q = purge gas flow rate (mL/min)

C_{O2} = O_2 concentration in the HRC (mol/mL)

t = time (min)

Immediately after the experimental procedure described above the column was re-aerated, the aeration was stopped again, but the trace gas purge and the oxygen concentration monitoring commenced immediately. The oxygen consumption rate was determined from the O_2 deficit resulting from sealing the column.

Results and Discussion

Oxidation rate with respect to O_2 concentration

The dependence of the oxygen consumption rate on the oxygen concentration was investigated by aerating the columns with a nitrogen enriched gas mixture containing 0.025, 0.05, 0.10, 0.15 atm partial pressure of oxygen. The results are presented in Figure 3. It is evident from Figure 3 that the dependence of the oxidation rate on oxygen is not first order. Applying ordinary non-linear regression to the data and estimating the

coefficient of determination as the measure of the goodness of fit, a fractional reaction order of 0.513 provided a significantly better fit than assumed first order kinetics. The approximately half order kinetics is in good agreement with the results of Williamson and Rimstidt (1994) as well as McKibben and Barnes (1986) for pyrite oxidation under abiotic conditions.
It addition to the short-term kinetic data shown in Figure 3, it was necessary to prove that fractional reaction order remains the appropriate kinetic model in the long term as well. To prove this hypothesis, reaction rate data were collected over a period of 120 days and the data were used to establish the kinetic and transport parameters. Parameter estimation was an important aspect of the kinetic study. Conventional statistical methods, however, were inadequate to determine the parameter values. The two important parameters, the reaction rate constant and the apparent oxygen diffusion coefficient, were estimated using the Metropolis-Hastings algorithm as part of Markov Chain Monte Carlo (MCMC) method (Gilks, 1998). The MCMC method is based on parameter sampling and iteration to find the most probable value and posterior distribution of parameters. To initiate the sampling procedure, a triangular distribution was assumed for each parameter and the probability of

acceptance of a sampled value was estimated by evaluating the acceptance criterion, ξ(X,Y), as follows:

$$\xi(X,Y) = \min(1, \frac{\pi(Y)q(X|Y)}{\pi(X)q(Y|X)}) \qquad (9)$$

where

π = stationary distribution of parameter

q = proposal distribution of parameter

X = the current value of parameter

Y = the proposed value of parameter

A program for parameter sampling, solving Equation 7 numerically, and evaluating Equation 9 was written in MATLAB environment. The Metropolis-Hastings procedure was performed with discrete reaction order values ranging from α = 0.55(≈0.5), to α = 0.95(≈1)). The sum of least squares deviation between observed and predicted values was used as the criterion for accepting the best "α" value. After performing

over 100,000 iterations, the best "α" was found to be 0.55. This value was in excellent agreement with the short-term differential rate estimates shown in Figure 3. The posterior probability distributions of the diffusion coefficient, D, and reaction rate constant (@ α=0.55) are shown in Figure 4. The distribution profiles indicate that we were successful to resolve the parameter values by minimizing any correlation between the estimates. At 21% ambient oxygen concentration in the pore space, the maximum likelihood values (peak values of the posterior probability distributions) of the initial oxidation flux, the oxygen diffusion coefficient through the oxidation product layer, and the surface reaction rate constant were 1.3 $\times 10^{-7}$ mol m^{-2} s^{-1}, 3.4267 × 10^{-13} m^2 s^{-1}, 2.8878 × 10^{-7} $mol^{0.45}m^{-0.35}s^{-1}$, respectively. In Figure 5, the measured oxidation rates are compared with predicted rates. As it can be seen, the predicted values are in a very good agreement to the measured values. Thus, the proposed model based on partial reaction order and diffusive oxygen transport adequately predicts the oxidation behavior of waste rock. In the present application of the model, it was assumed that the pH was sufficiently high so that essentially all iron precipitates as $Fe(OH)_3$.The model, however, is easily adaptable to any situation by incorporating geochemical solubility/speciation equilibrium.

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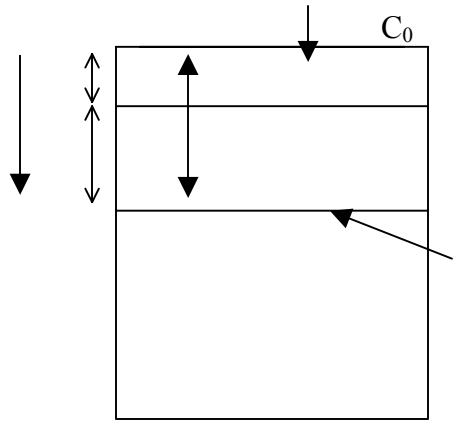

Figure 1. A Schematic Diagram of the Sulfide Oxidation Process

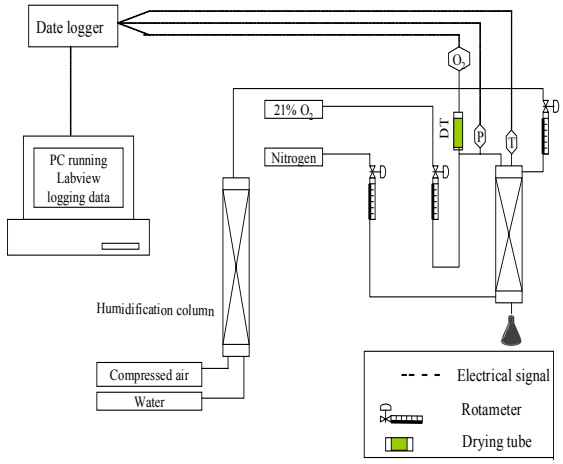

Figure 2. Reactor and Monitoring System Configuration

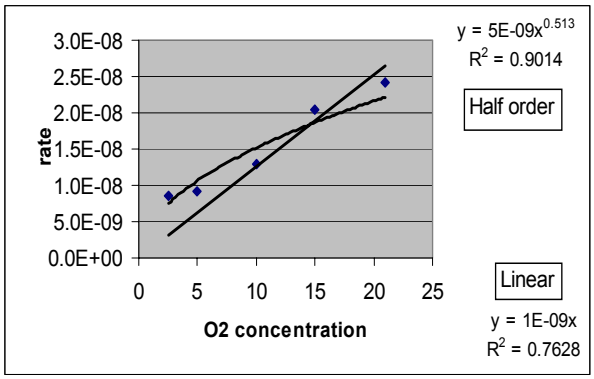

Figure 3. Dependence of Oxygen Consumption on Oxygen Concentration in Whistle Mine Waste Rock

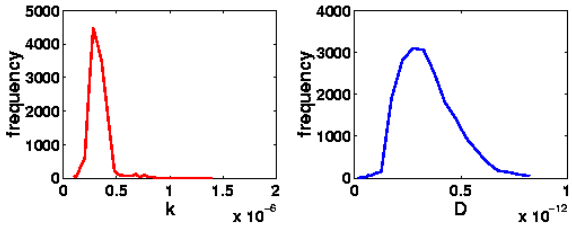

Figure 4. Posterior Probability Distribution of the Oxygen Diffusion Coefficient (D) and the Reaction Rate Constant (k)

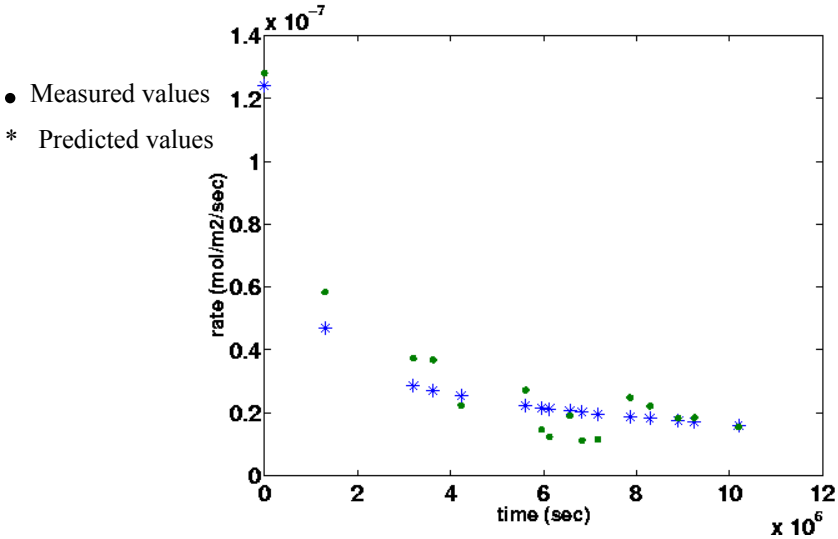

Figure 5. Comparison of Measured and Predicted Oxygen Consumption Rates in Waste Rock