

# Modelling Humidity Cell Experimental Data by Making Use of the PHREEQC Code

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## ABSTRACT

Most of South Africa' energy is generated by coal fired power stations. South Africa has rich coal deposits concentrated in the north-east of the country and as the demands for electricity are growing so are the associated mining activities, a large number of which are shallow opencast mines. The mining method results in post-closure back filled pits and above ground disposal facilities. Leachate emanating from these disposal sites is saline and in most cases highly acidic. Currently the standard testing procedure to quantify expected leachate qualities include Acid Base Accounting (ABA) with static and kinetic leaching.

The aim of this study is to model standard humidity cell leach tests performed in these studies using the PHREEQC code. This model can then be scaled up to field conditions to model 1D reactive mass transport. It is commonly accepted that the rate of pyrite oxidation in backfilled pits and waste storage facilities is governed by the rate of oxygen ingress and that no pyrite oxidation takes place in the saturated zone. This is not the case for humidity cells, as sufficient oxygen is available for reaction. Pyrite reaction rates in humidity cells are expected to be governed by a combination of available reaction surface and ash layer resistance. This is modelled in PHREEQC (Parkhurst & Appelo, 1999) using the KINETIC block. Leachate composition is then modelled in the column, making use of the TRANSPORT block. The experimental data is fitted by means of the reactive surface and ash layer diffusion coefficient.

This model can then be used to estimate long term water qualities beyond the twenty week norm. The model can then be scaled up to field conditions by compensating for the oxygen ingress component.

**Keywords:** ABA, Humidity Cell, Leach Test, Shrinking Core Model, PHREEQC Modelling

## INTRODUCTION

Most of South Africa's energy is generated by coal fired power stations. South Africa has rich coal deposits concentrated in the north-east of the country and as the demands for electricity are growing so are the associated mining activities, a large number of which are shallow opencast mines. The mining method results in post-closure back filled pits and above ground disposal facilities comprising of mined out rock and discard from the beneficiation process respectively. Leachate emanating from these disposal sites may range from acidic to alkaline, with commonly observed elevated levels of sulfate, iron, manganese and aluminium (Usher et al., 2002). In order to implement a successful mitigation strategy, sources of pollution must be identified and there must be a good understanding of the related source term governing the pollution. According to Nordstrom (2000) several points must be considered when looking at geochemical modelling. Firstly when referring to a model, it is not necessarily implied that the model is a computer code or a mathematical approach. It can consist of a well constrained logical proposition with the goal to improve or refine a conceptual model of the problem. A geochemical model can provide invaluable insight in this regard and can assist in the interpretation of field data (Linklater et al., 2005). In order to develop such a model Usher et al. (2002) suggested the Acid-Base: Accounting, Technique and Evaluation (ABATE) strategy to develop a model of the geochemical problem at hand.

### Field data/Experimental data

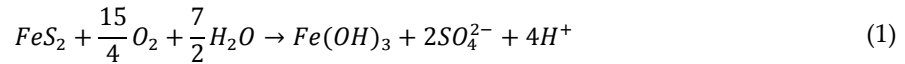
Acid Base Accounting (ABA) is generally used as a first order classification procedure in acid rock drainage (ARD) prediction methodologies (Usher et al., 2002) and results provide information about the potential of a sample to generate ARD (Price, 1997). Net Acid Generating (NAG) tests are also performed to aid in improving the interpretation of the ABA results (Miller et al., 1997). Usher et al., (2002) recommends a kinetic leach test methodology adapted from the D5744-96 Standard Test Method (ASTM, 2001). The minimum suggested duration of this leach test is twenty weeks and this is in some cases insufficient for sulphate production to stabilize. Static methods do not address the transient behaviour of ARD formation; humidity leach test supplements statics test in this regard and can assist in obtaining rates of reaction and a generalized indication of the potential mineral leaching behaviour of rock samples (Price, 1997). In the ABATE strategy mineralogy is required before the kinetic leach test is performed. In most cases mineralogy in the form of XRF is performed with the kinetic leach test.

### Numerical geochemical modelling

Numerical geochemical modelling is the last step in the ABATE strategy. The need for numerical modelling will depend on the objectives of the study. Kinetic modelling of a spoils heap becomes complex as the concentrations of chemical components in the effluent is a function of both space and time. In turn the concentrations depend on the sulfide mineral oxidation rate, water infiltration rate and chemical oxidation rates (Pantelis et al., 2001). Several mathematical models that describe the leaching process in spoils heaps, has been developed over the last couple of years (Davis & Ritchie, 1986; Molson et al., 2005; Linklater et al., 2005; Pantelis et al., 2001).

### Sulfide mineral oxidation

The dominant sulfide mineral in mine waste is pyrite (FeS<sub>2</sub>). The oxidation of pyrite is a multi-step complex reaction consisting of both the oxidation of disulphide (S<sub>2</sub><sup>2-</sup>) and of ferrous iron (Fe<sup>2+</sup>) (Appelo & Postma, 2005). The following balanced reaction is generally accepted to represent the overall oxidation of pyrite at atmospheric conditions (Appelo & Postma, 2005; Lefebvre et al., 2001):



Oxidation of pyrite by oxygen has been shown to be slow and does not account for the rapid decrease in pH commonly observed from field conditions. This may be explained by the influence of pyrite oxidation by ferric iron (Fe<sup>3+</sup>) (Lefebvre et al., 2001) and bacterial catalization of the reaction (Andre, 2009). Kinetics reported by Williams and Rimstidt, and also referenced by Appelo & Postma (2005) for the oxidation rate of pyrite by O<sub>2</sub> is as follows:

$$r = 10^{-8.19} m_{O_2}^{0.5} m_{H^+}^{-0.11} \quad (2)$$

where  $r$  is the rate with the units (mol/m<sup>2</sup>/s) and  $m_x$  denotes the molar concentration of  $x$ . It can be seen that the rate has a square root dependency on the concentration of O<sub>2</sub>. This results in a significant effect on the rate if the oxygen concentration is low and a small effect at high oxygen concentrations. This effect is explained by Appelo & Postma (2005) by referring to the work conducted by Nicolson et al., (1988) as the pyrite surface becomes saturated with oxygen. A general rate law describing the dissolution/precipitation of minerals can be written as follows (Appelo & Postma, 2005):

$$r = k \frac{A_0}{V} \left( \frac{m}{m_0} \right)^n g(C) \quad (3)$$

where  $r$  is the overall reaction rate with the units (mol/L/s) and  $k$  is the specific rate with the units (mol/m<sup>2</sup>/s). The initial area and solution volume is denoted by  $A_0$  and  $V$  respectively. The factor  $\left(\frac{m}{m_0}\right)^n$  accounts for the change in surface area where  $m_0$  is the initial moles of the solid and  $m$  is the moles at a given time. The function  $g(C)$  accounts for the effect of the solution composition on the rate e.g. the pH of the solution or the distance from equilibrium.

### Sulphate mineral oxidation in tailing facilities

In the well-known work of Davis & Ritchie (1986) and also later Molson et al. (2005) the shrinking core model is used to describe the reaction kinetics of pyrite oxidation in a waste dump. In this approach it is assumed that the rate of oxygen diffusion to the reaction area is the rate limiting step. This is also discussed as an important factor in the oxidation of pyrite soils (Appelo & Postma, 2005). It is noted that oxygen transport is only important in the unsaturated zone. In the saturated

zone the approximate amount of oxygen available for pyrite oxidation is 0.33 mM O<sub>2</sub>, suggesting that the unsaturated zone is the most reactive and the greatest source of sulfide oxidation.

Davis & Ritchie (1986) further assumes that the rate of unreacted core shrinkage is much slower than the oxygen diffusion rate within the particle (Levenspiel, 1962). It is assumed that the reaction at the surface of the particle is instantaneous and that ash layer diffusion is the rate determining step.

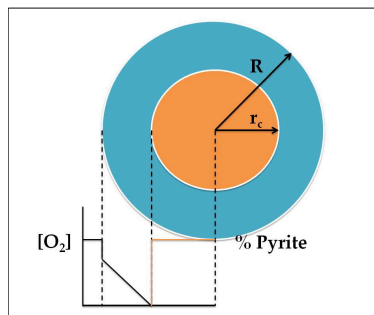
In the model developed by Davis & Ritchie (1986), it is assumed that diffusion is the only means of oxygen transport. Fick's second law with a consumption term is used to describe the diffusion process mathematically:

$$\frac{\partial U_A}{\partial t} = D_1 \frac{\partial^2 U_A}{\partial z^2} - q(z, t) \quad (4)$$

The model describes a two-stage diffusion process to the reaction sites. The first stage consists of oxygen diffusion through the air filled pores.  $D_1$  is the diffusion coefficient for this stage. The consumption term  $q(z, t)$  in Equation 4 represents the change in volume due to the oxidation of pyrite, and can be expressed as follows (Molson et al., 2005):

$$q(z, t) = D_2 \frac{3(1 - \theta)}{R^2} \left( \frac{r_c}{R - r_c} \right) \frac{[O_2]_a}{H} \quad (5)$$

where  $D_2$  is the diffusion coefficient,  $R$  is the particle radius,  $r_c$  is the unreacted core radius,  $\theta$  is the porosity,  $[O_2]_a$  the concentration of oxygen dissolving into the water film surrounding the particle and  $H$  is Henry's constant for a given temperature. The diffusion coefficient  $D_2$  represents the forming ash layer that is shielding the shrinking particle. The schematic representation of an oxidizing particle is shown in Figure 1.



**Figure 1** Schematic representation of an oxidizing particle (Davis, 1983)

From Equation 5 and Figure 1 it is clear that the change in oxygen due to pyrite oxidation can be related to the change in unreacted core radius ( $r_c$ ):

$$\frac{dr_c}{dt} = \frac{D_2(1-\theta)}{\epsilon\rho_s} \frac{R}{r_c(R-r_c)} \frac{[O_2]_a}{H} \quad (6)$$

where  $\epsilon$  represents the ratio of oxygen to sulphur consumed on the basis of reaction stoichiometry (Equation 1). The density  $\rho_s$  is calculated from the bulk density and the weight fraction of pyrite present.

### METHODOLOGY

Actual humidity cell leach test (HCT) data were modelled using the PHREEQC code. Only the main principles are discussed here. PHREEQC has the ability to model dynamic processes using such as reaction kinetics, 1D reactive transport using the RATES block and TRANSPORT block respectively.

#### HCT approximated as a continuous stirred tank reactor

The HCT is approximated as a continuous stirred tank reactor (CSTR) as shown in Figure 2. This may be an over simplification of the system as it do not account for preferential flow paths in the HCT. It is assumed that the leachate has come into contact with all the particles before exiting the cell or reactor.

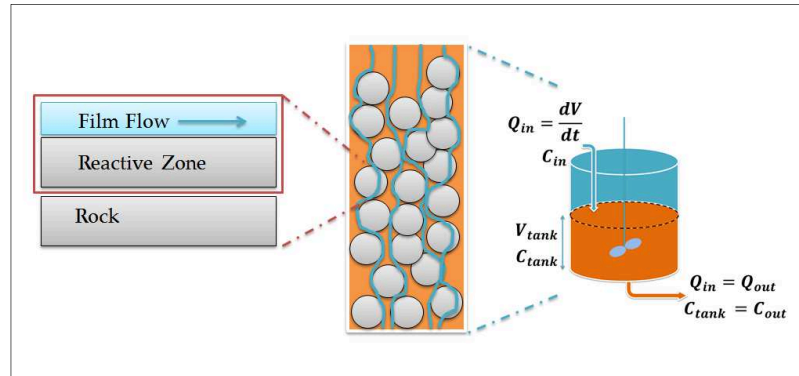


Figure 2 Schematic representation of the CSTR approximation (Andre, 2009)

The CSTR can be described by the following equation:

$$\tau = \frac{V_{tank}}{dV/dt} \quad (7)$$

where  $\tau$  is the residence time and  $V$  represents the volume of the tank. In work conducted by Tiruta-Barna (2008), a CSTR is modelled by solving the differential equation in the RATES block of PHREEQC. The reactor can also be modelled by making use of the TRANSPORT block in

PHREEQC. In the TRANSPORT block stagnant cells can be defined to interact with 'active' transport cells using the MIX block. Reaction kinetics and solution composition can then be defined for individual cells.

### Input parameters

The mineral composition of the sample was calculated from the XRD data of the sample (Table 1). The reaction kinetics of pyrite oxidation was defined substituting Equation 2 in Equation 3 and compensating for the influence of the saturation state, rendering the following rate expression:

$$r = \left(\frac{A_0}{V}\right) \left(\frac{m}{m_0}\right)^n (10^{-6.07} m_{O_2}^{0.5} m_{H^+}^{-0.11}) (1 - SR(Pyrite)) \quad (8)$$

The unit of the rate expression is (mol/L/s) and  $SR(Pyrite)$  represents the saturation state. The exponent  $n$  is a function of the particle geometry and for cubical dissolving particles a value of  $n = 2/3$  can be assumed (Appelo & Postma, 2005).

It was assumed that oxygen is present in excess. This was defined in the EQUILIBRIUM block of PHREEQC. The PHREEQC TRANSPORT block was used to describe the flow characteristics of the system approximated as a CSTR.

**Table 1** XRD data of sample used in the humidity cell leach test

Mineral	Weight %
Anatase	3.43
Dolomite	1.83
Kaolinite	51.69
Muscovite	5.45
Pyrite	6.98
Quartz	30.28
Siderite	0.33

### Shrinking core model

The shrinking core model can also be applied in PHREEQC by making use of the RATES block. The rate of pyrite oxidation (mole/litre bulk/s) is defined as follows (Mayer, 1999):

$$r = -10^3 S_i \frac{D_2}{3.5} \frac{R}{(R - r_c) r_c} [O_2]_a \quad (9)$$

where  $S_i$  is the reaction surface at time  $t_i$  and is defined as:

$$S_i = 10^{-3} \frac{3\varphi_i}{r_c} \quad (10)$$

where  $\varphi_i$  is the volume fraction of minerals defined in units ( $\text{m}^3$  mineral/ $\text{m}^3$  bulk). The concentration of oxygen dissolved in the liquid film can be calculated using Henry's law. Usually the Henry's law constants are reported at a reference temperature of 25°C and 1 atm. The following two equations can be used for temperature (Koretsky, 2003):

$$\left(\frac{\partial \ln H_i}{\partial P}\right) = \frac{H_i^\infty - h_i^v}{R} \quad (11)$$

where  $R$  is the gas constant,  $H_i^\infty$  is the partial molar enthalpy and  $h_i^v$  is the pure species enthalpy. A similar equation describes the correction for pressure, but it is beyond the scope of this study due to the fact that the pressure will always be at 1 atm. Assuming the mole fraction of oxygen in ambient conditions is  $y_{O_2} = 0.21$ , the partial pressure of  $O_2$  is then formulated as follows:

$$P_{O_2} = (0.21)P \quad (12)$$

where  $P$  is the atmospheric pressure. The concentration of oxygen in solution is then calculated using the Henry's coefficient for oxygen in water ( $H_{O_2} = 44252.9$  Bar @ 25°C and 1 atm):

$$x_{O_2} = \frac{y_{O_2}P}{H_{O_2}} = \frac{0.21(\text{bar})}{44253.9(\text{bar})} = 4.75 \times 10^{-6} \quad (13)$$

The concentration of oxygen,  $[O_2]$  in molality, is expressed as:

$$[O_2] = \frac{n_{O_2}}{V} \quad (14)$$

Where  $V$  is 1 litre of water and  $n_{O_2}$  is the molar amount of dissolved oxygen. The concentration of dissolved oxygen is then calculated as:

$$[O_2] = x_{O_2} \frac{n_{O_2}}{V} = 2.63 \times 10^{-4} M \quad (15)$$

By defining the partial pressure of oxygen as  $\log(P_{O_2}) = -0.67$  in the EQUILIBRIUM\_PHASES block and defining a set oxygen concentration in the liquid film surrounding the particles, the above described kinetics were used to model the oxidation of pyrite. The PHREEQC result together with the validation from the equivalent mathematical model in MATLAB is presented in Figure 3.

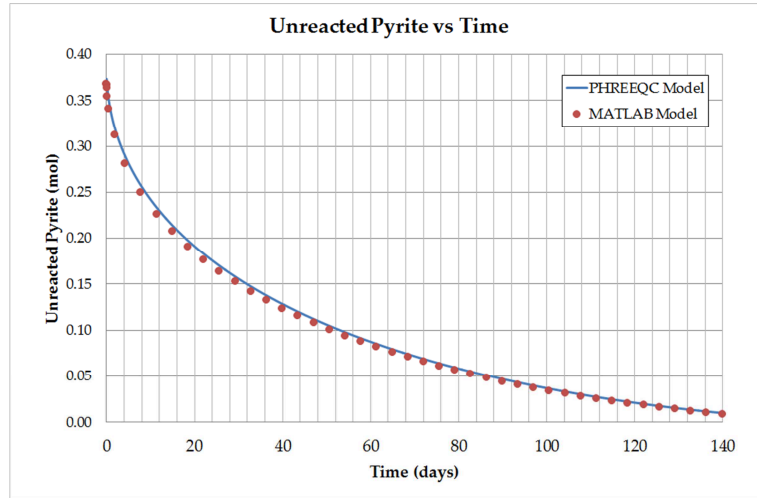


Figure 3 Model results of PHREEQC shrinking core model validated with MATLAB

PHREEQC does not have functionality for gas transport to describe the change in pore gas phase composition over time (Equation 4). This makes the use of this rate expression problematic as the gas phase composition will have to be changed for every time step outside the PHREEQC environment.

#### Analytical Approximate Solution

Due to the complexity of implementing Equation 4 in PHREEQC it is suggested to use the Analytical Approximate Solution (AAS) proposed by Davis & Ritchie (1986). By using this approach the rate of sulphate production already accounts for the rate limiting effect of oxygen diffusion.

In order to use the AAS model to describe a HTC, it must be assumed that oxygen is in fact rate limiting for sufficiently small particles (tailing samples) with a high moisture content. This assumption can be tested by making use of Fick's second law, and assuming an infinite homogeneous slab. The oxygen concentration profile can be described by the following equation:

$$U_a(x, t) = U_{a0} \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{D_1 t}} \right) \right] \quad (16)$$

where  $U_{a0}$  is the surface concentration of oxygen. The value of  $D_1$  can be calculated from the following equation:

$$D_1 = 3.98 \times 10^{-9} \left[ \frac{\theta_A - 0.05}{0.95} \right] T^{1.5} \quad (17)$$

where  $\theta_A$  is the effective porosity and  $T$  is the temperature (K). From Equation 16 and Equation 17 it is clear that the oxygen concentration decreases linearly for a standard leach cell and that the percentage of saturation will only influence the oxygen profile at high levels of water saturation.



## RESULTS AND DISCUSSION

The data obtained from an HCT was modelled using both the AAS model (Davis & Richie, 1986) and the Surface Kinetic (SK) model as shown in Figure 4. The SK model shows a better fit for the leach data. Although gypsum was not detected in the mineralogy, it is apparent from the leachate analysis that gypsum might be present as a minor component material and may not necessarily be picked up by the XRD analysis. In both models, gypsum was defined to dissolve kinetically to account for initial high sulfate leach values. The AAS method shows a moderately good fit to the data. It can clearly be seen that the shrinking core model does not describe the kinetic behavior of the oxidation of pyrite accurately under the conditions observed in the HCT. In the AAS model it is assumed that ash layer diffusion is the rate controlling step; this may be an over simplification of the system. The shrinking core model can be expressed to account for both ash layer controlled and chemical reaction controlled rates (Levenspiel, 1962). Although this approach may yield a better fit, it introduces more variables to the model and either the diffusion coefficient  $D_2$  or the rate constant of the chemical reaction rate must be determined experimentally to define the system in such a manner so that a reasonable model can be constructed.

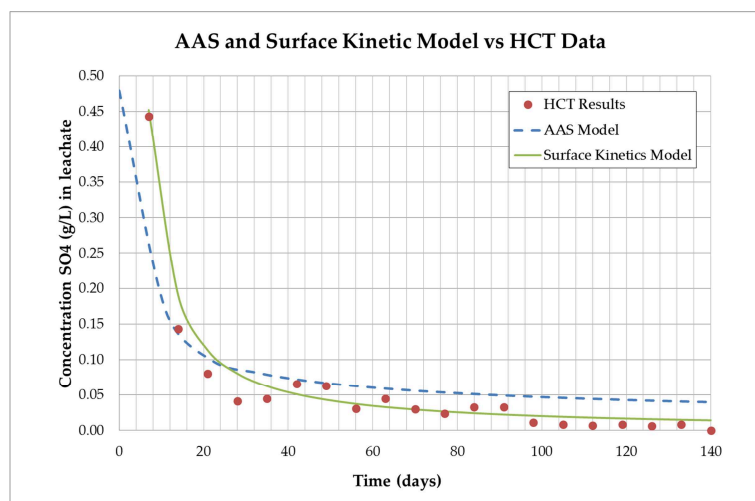


Figure 4 Comparison of AAS Model and SK Model fitted to HCT data

## CONCLUSION

Both the AAS model and the SK model showed a reasonable fit to the HCT data. The SK model does however describe the data better. It was found that assuming the ash layer diffusion as the only rate controlling factor is a gross over simplification of the system. This results in compensating for the influence of chemical reaction controls to obtain a more accurate model. The standard HCT setup will not provide this data and further experimental data will be required to obtain either the kinetic rate constant for the chemical reaction controlled step or the diffusion coefficient.

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