



# An agglomerate scale model for the heap bioleaching of chalcocite

by N. Ogbonna\*, J. Petersen\*, and H. Lauriet†

## Synopsis

A mathematical model for bioleaching at the agglomerate scale is developed. The agglomerate is defined as a unit volume of a heap which contains a solid phase (a size distribution of ore particles), a liquid phase (stagnant and flowing leaching solution) and a gas phase (flowing air and air pockets). Leaching at the level of an ore particle is modelled using a diffusion-reaction equation, and oxidation by attached and detached microbes is treated separately. With the aid of the mathematical model, the effect of particle size distribution on the bioleaching of an ore containing a mixture of chalcocite and pyrite, and a culture of iron oxidizers, is investigated.

## Introduction

Bioleaching refers to the mobilization of metal ions from insoluble ores by biological oxidation and complexation (Rohwerder *et al.*, 2003). The application of bacterial leaching to metal recovery from mineral ores has progressed steadily in the last 20 years (Olson *et al.*, 2003). Heap bioleaching involves stacking the ore to form a heap, and applying acidified leaching solution to the top of the heap. This technique is used to treat mostly low grade ore, and copper is the primary targeted metal, although it is also considered for zinc, cobalt and nickel recovery. It is also used for the pretreatment of refractory gold ores. Despite the present widespread use of heap bioleaching in industry, the process is still plagued by low recoveries, long extraction times, and high operation costs. Hence there is a need to optimize heap operations.

Investigation of the interactions between the physical, chemical and biological processes that drive a heap provides knowledge that can be applied to optimize heaps. Such investigations can be carried out with the aid of mathematical models. A number of heap bioleaching models have been developed, some of which are reviewed by Dixon (2003). Most of the early heap bioleaching models dealt with leaching at the particle scale (Bartlett, 1992; Braun *et al.*, 1974; Davis *et al.*, 1986; Davis

and Ritchie, 1986, 1987; Roman and Olsen, 1974; Shafer *et al.*, 1979). On the other hand, more recent bioleaching models emphasize the effects of bulk scale phenomena, such as liquid flow, gas flow, and temperature distribution, on heap performance (Dixon, 2000; Dixon and Petersen, 2003; Leahy *et al.*, 2003, 2005a,b; Moreno *et al.*, 1999; Ogbonna *et al.*, 2005; Pantelis *et al.*, 2002; Petersen and Dixon, 1 2002; Sidborn *et al.*, 2003).

Although both particle scale and bulk scale effects are important in heap bioleaching, little has been done to systematically integrate particle scale models into bulk scale models. Most existing bulk scale models account for particle scale effects using simplified models such as the shrinking core model, applied to a single particle size. Implicit in this is an assumption regarding the relative significance of particle scale phenomena, and which process (diffusion or reaction kinetics) is limiting at the particle scale.

However, particle scale effects in heap bioleaching are influenced by several factors, including the particle size distribution, the mineralogy of the ore, and microbial interactions. In addition, particle scale phenomena can limit the rate of extraction under certain leach conditions, as highlighted in the study by Dixon and Petersen (2003). Therefore, it is difficult to decide *a priori* which process will be limiting.

This paper is concerned with the development of a mathematical model for heap bioleaching at an intermediate 'agglomerate' scale. The agglomerate model includes detailed particle scale processes, and can form the building blocks of (or be incorporated into an existing) bulk scale model. Hence, it provides a

\* Department of Chemical Engineering, University of Cape Town, South Africa.

† Department of Mathematics and Applied Mathematics, University of Cape Town, South Africa.

© The South African Institute of Mining and Metallurgy, 2006. SA ISSN 0038-223X/3.00 + 0.00. Paper received Feb. 2006; revised paper received Apr. 2006.

# An agglomerate scale model for the heap bioleaching of chalcocite

systematic link between particle and bulk scale heap bioleaching models. The agglomerate model can also be used to study bioleaching in short laboratory columns, which are more representative of an agglomerate scale than a full heap scale. The work in this paper derives from the heap scale model developed by Dixon and Petersen, a schematic representation of which is shown in Figure 1 (for a review, see (Ogbonna *et al.*, 2005)). This heap scale model adopts simplified particle scale interactions: at a computation node, a block of solid ore is assumed to be in contact with leaching solution. The proposed agglomerate model provides a more detailed description of the interactions at the level of a cluster of ore particles, and can be integrated into the heap scale model by assuming that the heap consists of agglomerate volumes, as shown in Figure 2. The agglomerate model will be applied to a case study of copper leaching from ore containing chalcocite and pyrite, in the presence of iron-oxidizing microbes.

## Theory

In this study, the agglomerate is defined as a unit volume of a heap that comprises a solid phase (a size distribution of ore particles), a liquid phase (stagnant and flowing leaching solution, which contains dissolved solutes, attached and planktonic microbes) and a gas phase (flowing air and air pockets). The unit volume approach to heap bioleaching was applied in an early model by Roman and Olsen (1974). However this application had limited sophistication, and the

concept is driven further here. A conceptual diagram of the agglomerate is shown in Figure 2. The agglomerate model can be extended to a heap scale model by stacking the unit volumes to form a unit heap column, and including in the model the interaction between neighboring unit volumes in the unit heap column, and bulk flow phenomena. Further development from this point will require a description of the interaction between adjacent heap columns. The focus of this study, however, is on the agglomerate model.

The significant processes that occur at the agglomerate level are:

- Mineral dissolution reactions
- Microbial processes (growth, oxidation and transport)
- Intra- and inter-particle diffusion of dissolved solutes
- Heat generation and diffusion
- Solution and gas flow through the agglomerate.

## Model assumptions

A number of simplifying assumptions are made, for the purpose of initial model development. The agglomerate model is developed under isothermal conditions. At the moment, the gas phase is not included explicitly; it is rather assumed that dissolved oxygen is present in the incoming flowing phase at a fixed concentration. The liquid phase in the agglomerate is separated into the stagnant (or bulk) and flowing phases, with exchange of chemical and microbial species occurring across these phases. This is done to capture the situation in heaps where solution distribution favours channelling between relatively large clusters of material, which are

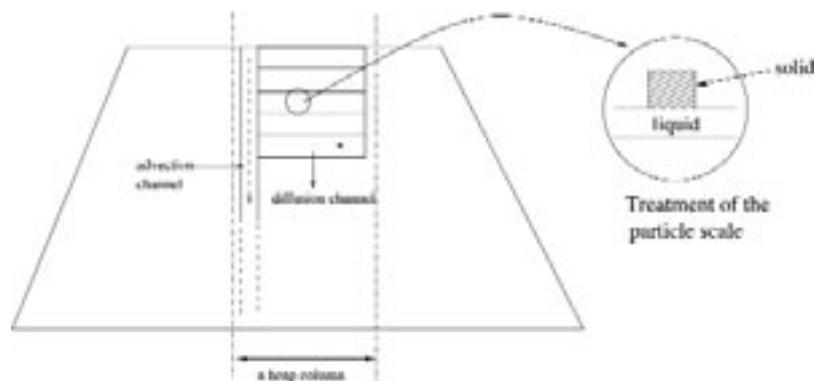


Figure 1—Schematic representation of heap scale model by Dixon and Petersen

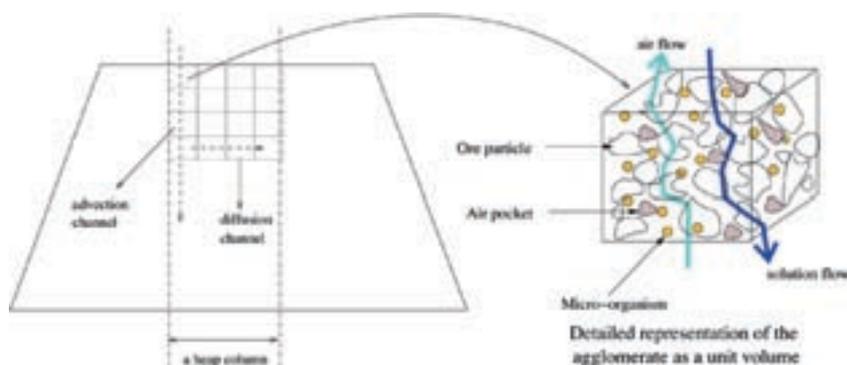


Figure 2—Modification of the model in Figure 1, treating the heap as a collection of agglomerate volumes

# An agglomerate scale model for the heap bioleaching of chalcocite

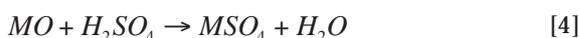
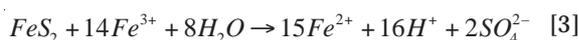
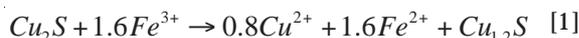
exposed only to stagnant solution (Dixon, 2003; Orr, 2002; Petersen and Dixon, 2003). It is assumed that the concentration gradient in the bulk phase in the agglomerate is small (relative to the scale of the heap), and so diffusion within the bulk solution will not be included in the model. Exchange across the agglomerate boundaries by diffusion is not considered. Chemical and microbial reactions in the flowing solution are not included in the model.

Although a size distribution of ore particles is investigated, it is assumed that the particles are uniformly distributed in the agglomerate. The ore particles are assumed to be spherical, and only radial diffusion of dissolved species in the ore particles is considered. The microbial species exist as adsorbed and planktonic microbes within the agglomerate. Adsorbed microbes form an exopolysaccharide (EPS) layer, which provides a reaction space within which the microbial oxidation reactions take place more rapidly (Rawlings, 1997, 2005; Rohwerder *et al.*, 2003). Microbial activity at the particle surface is accounted for by introducing a microbial source term at the particle surface. Hence, the growth rate of, and the oxidation by, adsorbed and planktonic microbial populations are treated differently. The partitioning of microbes into adsorbed and desorbed populations is implemented using the Langmuir isotherm.

## Model equations

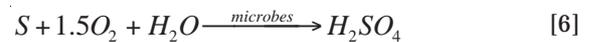
### Chemical reactions

Chalcocite leaches by a 2-stage mechanism: it reacts with ferric ions to release copper and a form covellite-like intermediate mineral (Equation [1]), which then reacts with ferric ions to release more copper and form elemental sulfur (Equation [2]). The kinetics of the two stages are different. The first stage (Equation [1]) proceeds quickly even at room temperature, releasing about 40% of the total copper, and has a relatively low activation energy (up to about 25 kJ/mol) (Petersen and Dixon, 2003). The second stage (Equation [2]) proceeds more slowly, and releases the remaining 60% of the total copper. The rate of the second stage increases significantly with temperature, with activation energy of the order of 100 kJ/mol (Petersen and Dixon, 2003). Pyrite is often found with chalcocite in practice, and so is included in the model. Pyrite leaches by reacting with ferric ions to release ferrous ions and acid (Equation [3]). The presence of gangue in the ore leads to acid consumption by gangue (Equation [4]).



Ferrous ions are oxidized to ferric ions (Equation [5]) in the presence of iron-oxidizing microbes such as *Leptospirillum ferriphilum* or *Acidithiobacillus ferrooxidans* (Rawlings, 2005). For many years, *At. ferrooxidans* was considered to be the most important micro-organism in commercial bioleaching and biooxidation plants that operate in the mesophilic temperature range. However, recent findings suggest that *Leptospirillum*-like bacteria may play a

more important role in commercial bioleaching/biooxidation processes (Rawlings, 2002). Elemental sulphur produced in Equation [2] may also be re-oxidized to sulphuric acid (Equation [6]) in the presence of sulphur-oxidizing microbes such as *Acidithiobacillus thiooxidans* and *Acidithiobacillus caldus* (Rawlings, 2005).



The rate of the sulfide mineral leaching reactions (Equation [1]–[3]) is a function of temperature, reactant concentration and the unreacted mineral fraction. It can be expressed in terms of the rate of change mineral conversion  $X$ :

$$S = \rho(1 - \epsilon) \frac{\partial g}{\partial t} = \rho(1 - \epsilon) g_0 \frac{\partial X}{\partial t}, \quad \text{where} \quad [7]$$

$$\frac{\partial X}{\partial t} = k(T) f(C) h(X) \quad [8]$$

(Dixon and Petersen, 2003). In Equation [7],  $\rho$  is the ore density,  $\epsilon$  is the particle porosity, and  $g_0$  is the initial mineral grade.  $k(T)$  in Equation [8] is the Arrhenius rate constant given by:

$$k(T) = k_{ref} \exp \left( -\frac{E}{R} \left[ \frac{1}{T} - \frac{1}{T_{ref}} \right] \right) \quad [9]$$

(Dixon and Petersen, 2003), where  $T_{ref}$  is the reference temperature (in Kelvin),  $k_{ref}$  is the Arrhenius constant at the reference temperature,  $E$  is the activation energy, and  $R = 8.314$  J/mol/K is the gas constant. The concentration function  $f(C)$  is obtained from the electrochemistry of the leaching process, and is expressed as:

$$f(C) = \frac{C_{Fe^{3+}}}{\left( k_A + C_{Fe^{3+}} \right)^{1-m} \left( k_B + C_{Fe^{2+}} \right)^m} \quad [10]$$

(Dixon and Petersen, 2003).  $h(X)$  is a topological term which accounts for the change in reacting surface. A power law, proposed by Dixon and Hendrix (1993), is implemented:

$$h(X) = (1 - X)^\phi \quad [11]$$

$\phi$  is an empirical parameter that usually falls between 0.5 and 2.0 (Petersen and Dixon, 2002).

The rate of microbial oxidation is related to the microbial growth rate  $\mu$  (through a stoichiometric factor, the yield coefficient  $Y$ ), and to the cell maintenance rate  $k_m$  (Dixon and Petersen, 2003; Ojumu *et al.*, 2005). The rate of microbial oxidation of a species  $i$  is expressed as:

$$\left( S = N_k \left[ \frac{\mu_k}{Y} + k_m f(T) \right] \right)_i \quad [12]$$

In Equation [12],  $N$  is the microbial population density, and the function  $f(T)$  describes the dependence of microbial activity on temperature. The subscript  $k$  identifies either the adsorbed or planktonic microbial population. The microbial growth rate  $\mu$  is given by the maximum growth rate of the microbes ( $\mu_{max}$ ) multiplied by limiting factors. For iron-oxidizing species, the limiting factors include acid, ferrous, and dissolved oxygen concentrations, temperature, and the microbial population (cell crowding factor):

# An agglomerate scale model for the heap bioleaching of chalcocite

$$\mu = \mu_{\max} f(T) \cdot \left( 1 - \exp \left[ - \frac{C_{acid}}{K_{acidlim}} \right] \right) \quad [13]$$

$$\left( \frac{C_{Fe^{2+}}}{K_{Fe^{2+}} + C_{Fe^{2+}}} \right) \cdot \left( \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \right) \cdot \left( \frac{K_I}{K_I + N} \right)$$

(Dixon and Petersen, 2003). The substrate concentrations in Equation [13] are either particle surface or bulk concentrations depending on whether adsorbed or desorbed microbial populations, respectively, are under consideration. The Ratkowsky equation (Franzmann *et al.*, 2005; Ratkowsky *et al.*, 1983) is employed to describe the dependence of microbial growth rate on temperature,  $f(T)$  (see Equation [12], Equation [13]). Describing  $f(T) = F(T)/F(T_{opt})$  as the normalized temperature function ( $T_{opt}$  is the temperature at which optimal microbial growth rate is achieved), the Ratkowsky function  $F(T)$  is given by:

$$F(T) = \sqrt{r} = b(T - T_{\min}) \quad [14]$$

$$\left( 1 - \exp(c(T - T_{\max})) \right),$$

where  $r$  is the growth rate constant,  $T$  is the temperature (in kelvin), and  $b$ ,  $c$  are fitting parameters.  $T_{\min}$ ,  $T_{\max}$  are the theoretical extrapolated minimum and maximum temperatures for microbial growth. Ratkowsky parameters for *Leptospirillum ferriphilum* (reported by Franzmann *et al.* (2005)) are used in this study.

## Mass balances

### Chemical species

Each particle size-class  $j$  is modelled by a representative (or mean) particle of radius  $R_j$ .

The mass balance equation in the ore particles for each dissolved chemical species  $i$ , in each size-class  $j$ , is given by the diffusion-reaction equation below:

$$\left[ \begin{aligned} \frac{\partial C_i}{\partial t} = D_i \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) + \sum_l v_{il} S_l + \delta(R-r) \sum_m v_{im} S_{surf,m} \end{aligned} \right]_j, \quad [15]$$

$$\left[ \frac{\text{mol}}{\text{cm}^3 \text{min}} \right]$$

where  $C_i$  is the species concentration,  $D_i$  is the species diffusion coefficient,  $v_{il}$  is the stoichiometry coefficient of a species  $i$  in chemical reaction  $l$  (see Equations [1]–[4]), and  $S_l$  is the rate term for mineral leaching reaction  $l$ , given in Equation [7]. At the surface of the particle, an extra source term is introduced to account for microbial oxidation, where  $v_{im}$  is the stoichiometry coefficient of a species  $i$  in reaction  $m$  (see Equations [5]–[6]), and  $S_{surf}$  is the microbial oxidation term at the particle surface, given in Equation [12]. The boundary conditions for Equation [15] are:

$$\frac{\partial C_i}{\partial r}(0, t) = 0, \quad [16]$$

$$-D_i \frac{\partial C_i}{\partial r} \Big|_{r=R} = -k_{bs} (C_{bi} - C_{Ri}), \quad [17]$$

where  $C_{bi}$  is the bulk concentration of the species, and  $k_{bs}$  is the mass transfer coefficient at the particle surface/bulk interface. At initial time, a constant concentration of species  $i$  in size-class  $j$  is assumed.

The rate of change of the concentration of a chemical species in the bulk solution is as a result of exchange at the particle surface/bulk interface, exchange at the bulk/flowing solution interface, and the rate of formation (or consumption) of the species within the bulk. This is represented by the mass balance equation below:

$$\varepsilon_b \frac{dC_{bi}}{dt} = -3\varepsilon_p \sum_j \frac{W_j}{R_j} k_{bs} (C_{bi} - C_{Rj}) + \quad [18]$$

$$k_{nbf} (C_{fi} - C_{bi}) + \varepsilon_b \sum_m v_{im} S_{bulk,m} \cdot \left[ \frac{\text{mol}}{\text{cm}^3 \text{min}} \right]$$

The symbols are defined in the nomenclature. The first term on the RHS in Equation [18] represents average exchange at the particle surface/bulk interface, where the subscript  $j$  stands for particle size-class. The second term represents exchange at the bulk/flowing interface.  $k_{nbf}$  is the mass transfer rate at this interface, given by

$$k_{nbf} = k_{bf} \cdot \frac{\text{exchange surface area}}{\text{agglomerate volume}},$$

where  $k_{bf}$  is the mass transfer coefficient at the bulk/flowing interface. The third term represents the generation or consumption of species in the bulk as a result of microbial oxidation reactions. In this study, only ferrous oxidation as represented in Equation [5] is considered.  $S_{bulk}$  is given in Equation [12].

The rate of change of the concentration of a chemical species in the flowing phase is due to advection, and the rate of exchange with the bulk solution. This is given by the equation below:

$$\varepsilon_f \frac{\partial C_{fi}}{\partial t} = -u \frac{\partial C_{fi}}{\partial z} - k_{nbf} (C_{fi} - C_{bi}), \quad \left[ \frac{\text{mol}}{\text{cm}^3 \text{min}} \right] \quad [19]$$

where  $u$  is the superficial velocity of the flowing solution.

### Microbial species

The rate of change of adsorbed microbes  $N_a$  is expressed as:

$$\left[ \frac{dN_a}{dt} = N_a (\mu_a - k_{death}) \right]_j, \quad \left[ \frac{\text{cells}}{g_{ore} \text{min}} \right] \quad [20]$$

for each size-class  $j$ , where  $\mu_a$  is the growth rate of the adsorbed microbes (see Equation [13]) and  $k_{death}$  is the microbial death rate. A constant  $k_{death}$  is assumed. Other models for the death rate are possible. For example, Dixon and Petersen (2003) implement a combination of an endogenous decay rate and a temperature dependent death rate.

The rate of change of desorbed microbes  $N_d$  is expressed as:

$$\varepsilon_b \frac{dN_d}{dt} = \varepsilon_b N_d (\mu_d - k_{death}) + \quad [21]$$

$$k_{nbf} (N_f - N_d), \quad \left[ \frac{\text{cells}}{\text{cm}^3 \text{min}} \right]$$

# An agglomerate scale model for the heap bioleaching of chalcocite

where  $\mu_d$  is the growth rate of the desorbed microbes, and  $N_f$  is the microbial population density in the flowing phase.

The adsorbed and desorbed microbial populations are assumed to be in equilibrium and related by the Langmuir isotherm:

$$\frac{N_a}{N_{amax}} = \frac{K_a N_d}{1 + K_a N_d} \quad [22]$$

The rate of change of the microbial population in the flowing solution is due to advection, and rate of exchange with the bulk solution. This is given by the equation below:

$$\epsilon_f \frac{\partial N_f}{\partial t} = -u \frac{\partial N_f}{\partial z} - k_{nbf} (N_f - N_d) \cdot \left[ \frac{\text{cells}}{\text{cm}^3 \text{ min}} \right] \quad [23]$$

## Numerical results and discussion

The mathematical model developed above was tested on a case study built by taking parameter values from literature. The equations were solved for the minerals (chalcocite, covellite, pyrite), the chemical species (copper, ferrous, ferric, acid, oxygen) and the iron-oxidizing microbial species. In programming the model equations, it was assumed that all the covellite available from chalcocite was present at initial time. This is a valid assumption as seen from the simulation results, which show that covellite in any region in the ore particle is not significantly leached till the chalcocite in that region has reacted completely. The partial differential equations were semi-discretized using method of lines, by applying second order finite difference discretization in space. The resulting system of ordinary differential equations was integrated using the `scipy.integrate.odeint` routine in Python. Mass balance tests were conducted at the end of each simulation, and a maximum relative error of 0.15% in the mass balance calculations was recorded. Simulations were run for three particle size-classes of radii 0.5 mm, 2.5 mm and 5 mm. The following initial conditions were used:

$$\begin{aligned} C_{b,Fe^{2+}}(0) &= 0.1 \text{ g/L}, \\ C_{b,Fe^{3+}}(0) &= 0.1 \text{ g/L}, \\ C_{b,O_2}(0) &= 0.008 \text{ g/L}, \\ C_{b,H_2SO_4}(0) &= 0.8 \text{ g/L}, \end{aligned} \quad [24]$$

$$\begin{aligned} N_d(0) &= 10^{10} \text{ cells/L} \\ N_a(0) &= 0 \text{ cells/g} \end{aligned} \quad [25]$$

$$\begin{aligned} C_{p,i}(r, 0) &= 0, \\ C_{f,i}(z, 0) &= C_{b,i}(0) \end{aligned} \quad [26]$$

$i$  in Equation [26] is one of the dissolved species [Cu, Fe<sup>3+</sup>, Fe<sup>2+</sup>, O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>].

A constant inlet concentration of species was assumed:

$$\begin{aligned} C_{f,Fe^{2+}}(0, t) &= 0.1 \text{ g/L}, \\ C_{f,Fe^{3+}}(0, t) &= 0.1 \text{ g/L}, \\ C_{f,O_2}(0, t) &= 0.008 \text{ g/L} \end{aligned} \quad [27]$$

$$C_{f,H_2SO_4}(0, t) = 0.8 \text{ g/L}, N_f(0, t) = 10^{10} \text{ cells/L} \quad [28]$$

Other parameter values are listed in Tables II-Table IV. The 'Unp.' references in these tables come from unpublished work by Dixon and Petersen.

## Abiotic leaching simulation

The bulk concentration of copper, and the average conversion of chalcocite, covellite and pyrite in each of the particle size-

Table I  
Microbial parameters

Param.	Unit	Value	Reference
$D$	m <sup>2</sup> /s	5 x 10 <sup>-9</sup>	-
$Y$	cells/mol substrate	2 x 10 <sup>13</sup>	(Bouffard and Dixon, 2003)
$\mu_{max}$	1/min	0.0017	(Dixon and Petersen, 2003)
$k_{death}$	1/min	0.00017	-
$k_m$	mol substrate/cell/min	0.0	-
$N_{amax}$	cell/g	1.5 x 10 <sup>9</sup>	(Bouffard and Dixon, 2003)
$K_a$	L/cell	67 x 10 <sup>-12</sup>	((Bouffard and Dixon)
$K_{Fe}$	mol/L	0.0001	(Bouffard and Dixon, 2003)
$K_{acid}$	mol/L	0.01	Unp.
$K_{O_2}$	mol/L	0.00005	(Bouffard and Dixon, 2003)
$K_i$	cells/L	10 <sup>12</sup>	Unp.
$T_{min}$	°C	10.7	(Franzmann <i>et al.</i> , 2005)
$T_{max}$	°C	48.5	(Franzmann <i>et al.</i> , 2005)
$T_{opt}$	°C	38.6	(Franzmann <i>et al.</i> , 2005)
$b$	(Ratkowsky fitting parameter)	0.01551	(Franzmann <i>et al.</i> , 2005)
$c$	(Ratkowsky fitting parameter)	0.22061	(Franzmann <i>et al.</i> , 2005)

Table II  
Mineral parameters

Parameter	Unit	Chalcocite	Covellite	Pyrite	Reference
$\phi$	-	1.3	0.6	2	Unp.
$m$	-	0.124	0.5	0.5	Unp.
$k_{ref}$	1/min	0.446	0.01	0.0005	Unp.
$T_{ref}$	°C	35	75	55	Unp.
$E$	kJ/mol	23.7	97.9	74.3	Unp.
$k_A$	mol/L	0.154	0.0147	0.00001	Unp.
$k_B$	mol/L	0.00001	0.00001	0.00001	Unp.
$g$	mol/kg	0.0566	0.0566	0.3	(Dixon and Petersen, 2003)

Table III  
Species parameters

Parameter	Unit	Copper	Ferric	Ferrous	Acid	Oxygen	Ref.
$D$	m <sup>2</sup> /s	10 <sup>-9</sup>	10 <sup>-9</sup>	10 <sup>-9</sup>	2 x 10 <sup>-9</sup>	10 <sup>-9</sup>	-
$k_{ref}$	1/min	-	-	31.17	3.3 x 10 <sup>-5</sup>	-	Unp.
$T_{ref}$	°C	-	-	100	20	-	Unp.
$E$	kJ/mol	-	-	68.6	20	-	Unp.

# An agglomerate scale model for the heap bioleaching of chalcocite

Table IV  
User-specified parameters

Parameter	Unit	Value
$\rho$	g/cm <sup>3</sup>	1.45
$\epsilon$	cm <sup>3</sup> /cm <sup>3</sup>	0.08
$\epsilon_b$	cm <sup>3</sup> /cm <sup>3</sup>	0.3
$\epsilon_f$	cm <sup>3</sup> /cm <sup>3</sup>	0.1
$T$	°C	38.6
$L$	cm	20
$u$	cm/min	0.05
$k_{bs}$	cm/min	0.1
$k_{nbf}$	1/min	0.1

$L$  in Table IV is the length of a side of the agglomerate volume

classes for the abiotic case are shown in Figure 3. Each size-class is equally weighted. The conversion graphs for each mineral were obtained by taking a volume average of the conversion in each particle size-class.

The bulk concentration of copper shows variations which are mostly influenced by mineral conversion in the 0.5 mm radius size-class. Figure 3(a) shows a sharp increase in the bulk concentration of copper in the first 5 days of leaching. This is because the rapid leaching of chalcocite in the 0.5 mm size-class in this time interval (conversion reaches about 10%) introduces copper into the system, and the resulting steep diffusion gradient causes the copper to diffuse at a fast rate into the bulk solution. Subsequent removal of copper by the flowing solution leads to a decrease in bulk copper

concentration, but in a less steep manner. Between days 50 and 150 of leaching, a fairly constant bulk concentration of copper is observed (see Figure 3(a)). This is due to an increased copper production rate in the 0.5 mm size-class, which in turn is a consequence of the increase in covellite conversion rate in this size-class. As chalcocite conversion releases 40% of the total copper while covellite conversion releases 60%, covellite leaching introduces a significant amount of copper into the system. Figure 3(b) and Figure 3(c), respectively, show that between days 50 and 150, the rate of chalcocite conversion in the 0.5 mm size-class is reduced, while the rate of covellite conversion in this sizeclass increases appreciably. This behaviour is linked to the relative intrinsic rates of chalcocite and covellite conversion.

As shown in Figure 4(a), chalcocite reacts more rapidly than covellite, and is primarily limited by diffusion of ferric ions into the particle. Initially, ferric ions diffusing into the particle come in contact (and react with) chalcocite. As chalcocite conversion progresses into the particle, ferric becomes available for covellite leaching in the outer regions, and consequently, less ferric reaches the inner regions of the particle to react with chalcocite. As a result, the average rate of chalcocite reaction in the particle decreases, while the average rate of covellite conversion in the particle increases appreciably.

From day 200, the bulk concentration of copper increases, reaching a peak at about 260 days. This rise in the bulk concentration of copper coincides with the completion of chalcocite conversion in the 0.5 mm size-class (see Figure 3(b)), which means that ferric becomes available for the leaching of covellite. Hence covellite conversion in the

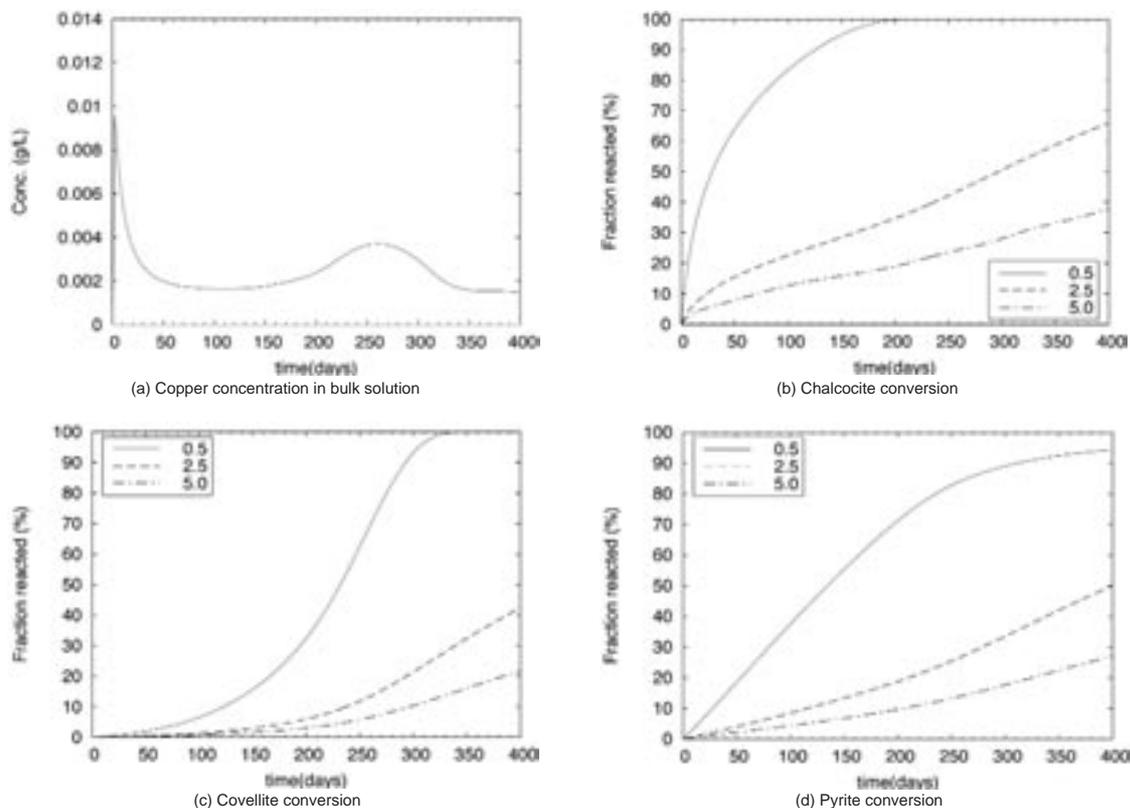


Figure 3—Abiotic simulation. (a) shows the bulk concentration of copper, (b)–(d) show the mineral conversion profiles in each of the size-classes

## An agglomerate scale model for the heap bioleaching of chalcocite

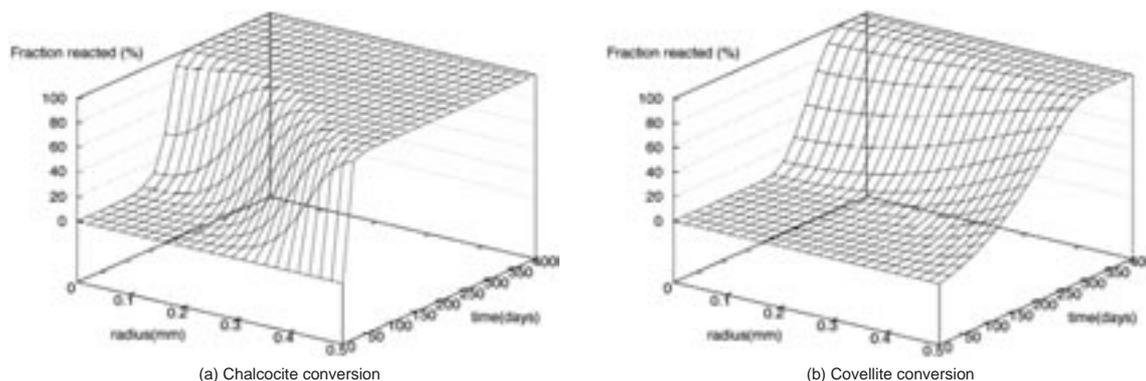


Figure 4—Chalcocite and covellite conversion profiles in the 0.5 mm radius size-class

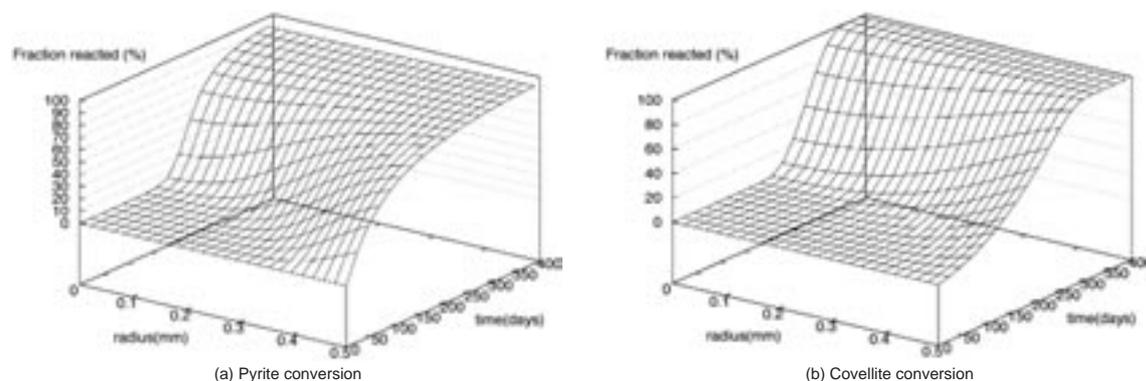


Figure 5—Pyrite and covellite conversion profiles in the 0.5 mm radius size-class

0.5 mm size-class is able to proceed rapidly, releasing a significant amount of copper into the system. The end of the 'bump' in bulk copper concentration coincides with the completion of covellite leaching in the 0.5 mm size-class, and the bulk concentration of copper following that is slowly varying, indicating the effect of diffusion limitation in the larger sized particles on copper extraction.

The average pyrite conversion increases somewhat linearly as long as chalcocite is present in the system (see Figure 3(d)). On completion of chalcocite leaching on day 200, pyrite conversion is at 70% while covellite conversion is at 32%. This high conversion of pyrite is due to the fact that there is about 5 times more pyrite than chalcocite in the system. Hence although the intrinsic rate of pyrite conversion is slower than that of covellite conversion, more pyrite than covellite is converted because of a higher pyrite concentration. However, the end of chalcocite conversion means more ferric is available in the 0.5 mm particles, and the faster covellite kinetics cause covellite to reach complete conversion before pyrite in this size-class.

### Biotic leaching simulation

The bulk concentration of copper, and the average conversion of chalcocite, covellite and pyrite in each of the particle size-classes for leaching in the presence of iron-oxidizing microbes are shown in Figure 6. All other conditions are kept the same as the abiotic leaching case. Comparing Figure 6 to Figure 3, it is seen that a faster rate of copper extraction is achieved in the presence of iron-oxidizing microbes. This is due to the microbial regeneration of ferrous, leading to a

higher ferric concentration in the system. The sharp increase in bulk copper concentration, (within the first 5 days of leaching), reaches a higher level of 0.014 g/L compared to 0.01 g/L in the abiotic case. In addition, the 'bump' in bulk copper concentration occurs about 100 days earlier in the biotic case than in the abiotic case.

The effect of iron-oxidizing microbes on the iron concentration in the system is clearly illustrated in Figure 7, which shows the ferric/ferrous ratio in the each particle size-class for abiotic and biotic cases. A higher ferric/ferrous ratio (in other words, a higher redox potential) is attained in the biotic case. Although this ratio is smaller than the values typically obtained in laboratory experiments ( $\geq 10$ ), it shows that the model predicts expected behaviour. It is anticipated that careful calibration of model parameters will yield results that are closer to observed values.

Figure 8 shows the average mineral conversion curves for the 0.5 mm size class after 400 days, and the 5 mm size class after 1000 days. The effect of diffusion distance on mineral leaching is illustrated by these graphs. Figure 8(a) shows that the minerals are leached at very different rates in the smaller sized particles. In the larger sized particles, on the other hand, not only are the minerals leached slower, but the rates of leaching are quite similar, especially for chalcocite and pyrite, even after 1 000 days (Figure 8(b)).

This behaviour is observed because as chalcocite leaching progresses into the particle, ferric ions diffusing into the particle come in contact (and react with) the unreacted covellite and pyrite before they can get to the chalcocite (Figure 9). Therefore, chalcocite cannot leach much faster

# An agglomerate scale model for the heap bioleaching of chalcocite

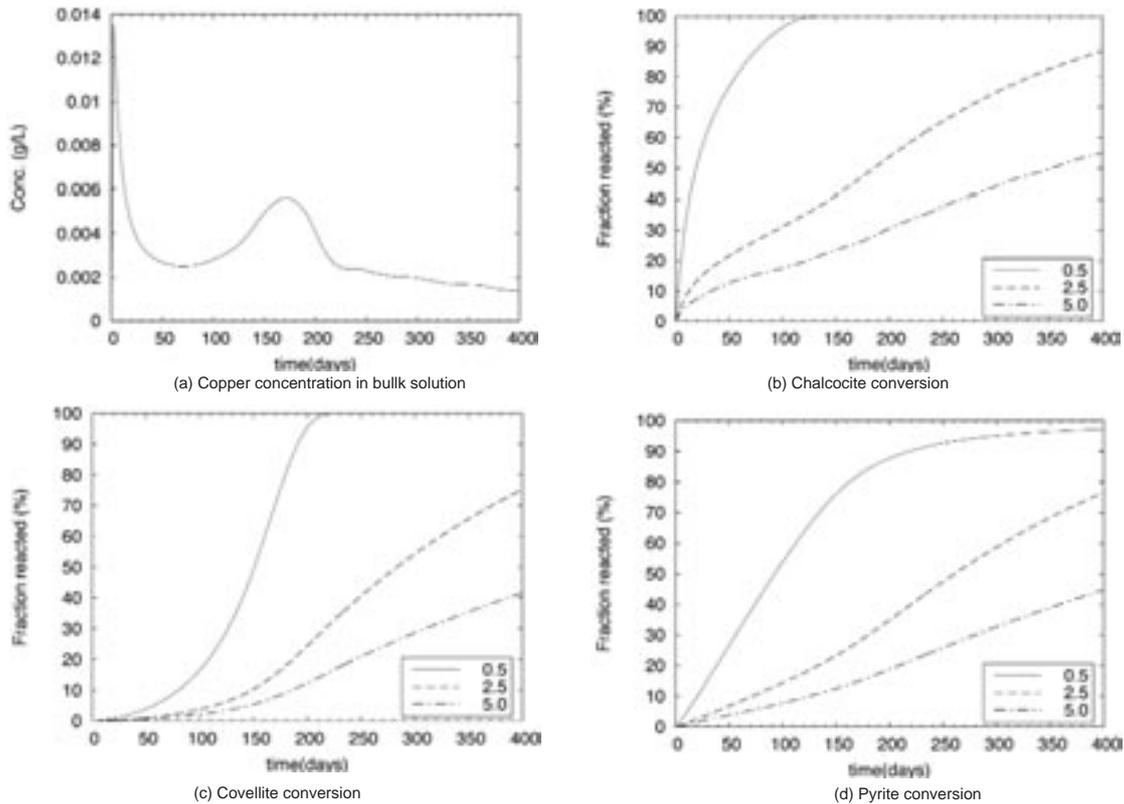


Figure 6—Biotic simulation. (a) shows the bulk concentration of copper, (b)–(d) show the mineral conversion profiles in each of the size-classes

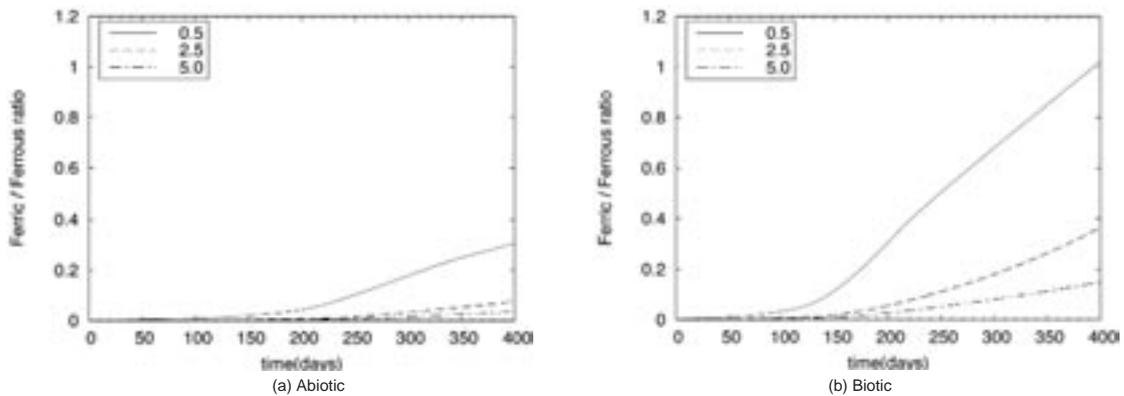


Figure 7—Ratio of ferric concentration to ferrous concentration for the abiotic and biotic case

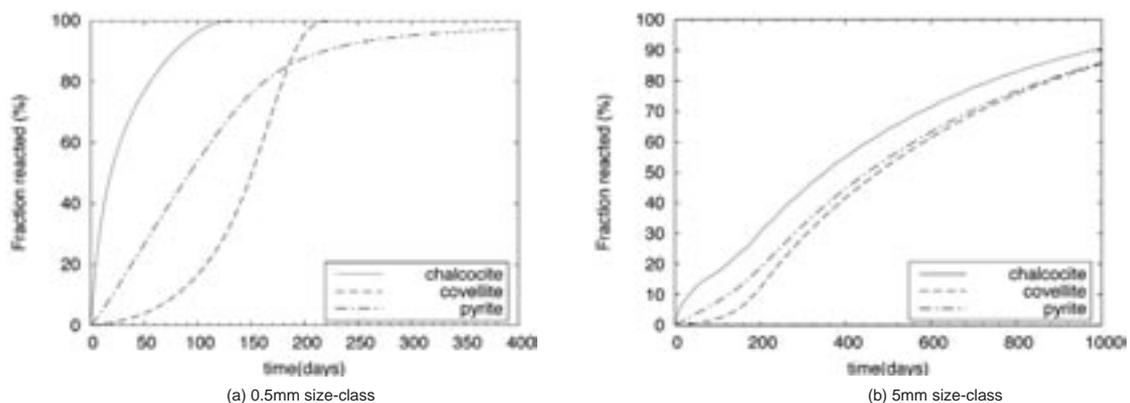


Figure 8—Comparison of average mineral leaching profiles in the 0.5 mm radius size-class after 400 days, and the 5 mm radius size-class after 1000 days

## An agglomerate scale model for the heap bioleaching of chalcocite

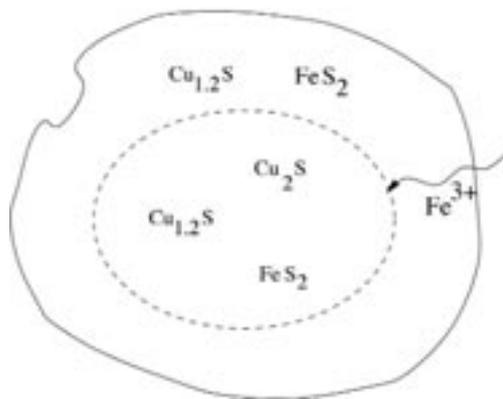


Figure 9—Mineral leaching in large particles

than pyrite or covellite. This behaviour is not observed in the smaller sized particles as ferric has only a short distance to travel. Pyrite in the unreacted region is consumed at a faster rate than covellite initially due to its predominance by mass. Hence, in larger sized particles, pyrite retards the rapid release of copper observed in the smaller particles.

### Effect of size class distribution

Figure 10 shows the cumulative copper recovery in the flowing solution, and the ferric/ferrous ratio in the bulk solution, for size the 0.5 mm, 2.5 mm and 5.0 mm class distributions, where the three size classes are equally weighted, distributed in a ratio of 0.2 : 0.2 : 0.6 and distributed in a ratio of 0.6 : 0.2 : 0.2. The model predicts that the most recovery is achieved when there is a higher proportion of 0.5 mm sized particles, as expected. The bulk ferric/ferrous ratio is at low levels for the duration of chalcocite leaching in the 0.5 mm particles. In the case where there is a higher proportion of fine particles, a significant increase in the ferric/ferrous ratio, accompanied by a rise in copper recovery, is attained on completion of chalcocite leaching in the 0.5 mm particles after about 150 days, as shown in Figure 10. This increase is less rapid as the mass fraction of fine particles is reduced.

### Conclusions and future work

This paper describes an agglomerate model for heap bioleaching, which is an intermediate model between particle

scale models and bulk scale models. By enabling the observation of particle scale leaching and the prediction of copper recovery, while allowing for the possibility of inclusion into a bulk scale model, the agglomerate model can serve as a link between particle scale and bulk scale modelling. With the aid of this model, abiotic and biotic leaching for an ore containing chalcocite and pyrite, in a system with a size distribution of particles was studied. It was observed that in larger sized particles, pyrite effectively retards the rapid release of copper observed in smaller size particles. It was also observed that with a higher proportion of fine particles, there is a marked increase in copper recovery at the onset of covellite leaching in the fine particles, which is in agreement with expected behaviour.

For the purpose of initial model development, oxygen gas-liquid transfer and temperature variation were not included. This assumption is limiting, as the mineral leaching reactions (especially covellite leaching), and the microbial growth rate, are temperature dependent. Also, the rate of gaseous oxygen uptake into solution, which is a temperature dependent mass transfer step, is an important parameter in heap modelling, since oxygen is a key reactant in the microbial oxidation reactions. Therefore, future work should include these processes. In addition, the integration of the agglomerate model into a bulk scale model should be addressed.

### Nomenclature

#### Greek Letters

$\epsilon$	Particle porosity	
$\mu$	Microbial growth rate	1/min
$\nu$	Stoichiometry coefficient	
$\rho$	Ore density	g/cm <sup>3</sup>
$\epsilon_b$	Stagnant liquid volume fraction	
$\epsilon_f$	Flowing liquid volume fraction	
$\epsilon_p$	Particle volume fraction	

#### Roman Letters

$C$	Concentration	mol/L
$D$	Diffusion coefficient	cm <sup>2</sup> /min
$E$	Activation energy	J/mol
$g$	Mineral grade	mol/g
$k_A$	Ferric mass transfer parameter	mol/L
$k_B$	Ferric reduction parameter	mol/L

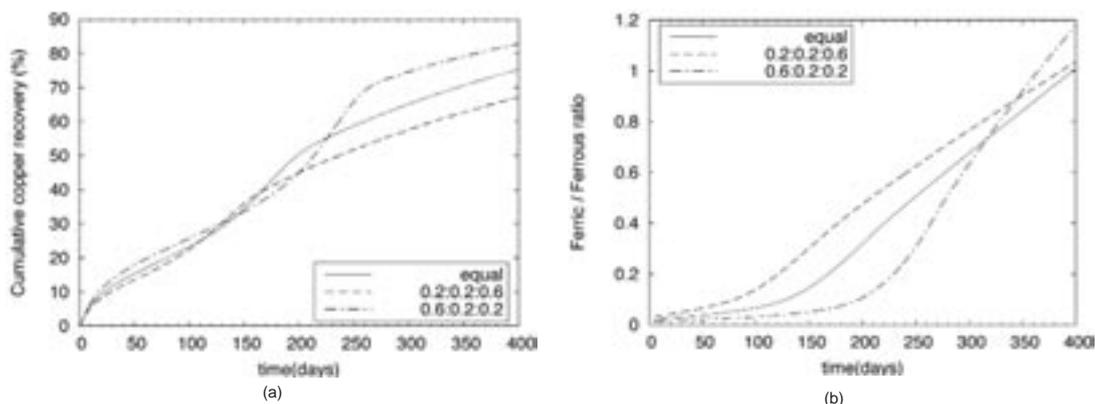


Figure 10—Effect of particle size class distribution on (a) cumulative copper recovery and (b) bulk ferric/ferrous ratio

# An agglomerate scale model for the heap bioleaching of chalcocite

$K_i$	Monod constant for substrate $i$	mol/L
$K_{acidlim}$	Acid limitation constant	mol/L
$K_a$	Adsorption equilibrium constant	L/cell
$k_{bs}$	Mass transfer coefficient (particle surface/bulk interface)	cm/min
$k_{death}$	Microbial specific death rate	1/min
$K_I$	Cell inhibition factor	cells/L
$k_m$	Microbial maintenance rate	mol Fe <sup>2+</sup> /cell/min
$k_{ref}$	Arrhenius constant	1/min
$k_{nbf}$	Mass transfer rate (bulk/flowing interface)	1/min
$N$	Microbial population density	cells/L or cells/g
$r$	Particle radius	mm
$S$	Source term	mol/cm <sup>3</sup> /min or mol/L/min
$T$	Temperature	K
$t$	Time	min
$u$	Superficial velocity	cm/min
$w$	Mass fraction	
$Y$	Microbial yield coefficient	cells/mol Fe <sup>2+</sup>

## Subscripts

b	Bulk
f	Flowing
p	Particle

## References

- BARTLETT, R.W. Simulation of ore heap leaching using deterministic models. *Hydrometallurgy*, vol. 29, 1992. pp.231–260.
- BOUFFARD, S.C. and DIXON, D.G. Mathematical modelling of pyritic refractory gold ore heap biooxidation: model development and isothermal column simulations. In C.A. Young, A.M. Alfantazi, C.G. Anderson, Dreisinger, D.B., Harris, B., and James, A. (eds.), *Hydrometallurgy 2003*, vol. 1, TMS, 2003. pp. 275–288.
- BRAUN, R.L., LEWIS, A.E., and WADSWORTH, M.E. In-place leaching of primary sulphide ores: Laboratory leaching data and kinetics model. *Solution Mining Symposium, AIME*, 1974. pp. 295–323.
- DAVIS, G.B., DOHERTY, G., and RITCHIE, A.I.M. A model of oxidation in pyritic mine Wastes: part 2 –Comparison of numerical and approximate solutions. *Applied Mathematical Modelling*, vol. 10, 1986. pp. 323–329.
- DAVIS, G.B. and RITCHIE, A.I.M. A model of oxidation in pyritic mine wastes: part 1 – Equations and approximate solution. *Applied Mathematical Modelling*, vol. 10, 1986. pp. 314–322.
- DAVIS, G.B. and RITCHIE, A.I.M. A model of oxidation in pyritic mine wastes: part 3 – Import of particle size distribution. *Applied Mathematical Modelling*, vol. 11, 1987. pp. 417–422.
- DIXON, D.G. Analysis of heat conservation during copper sulphide heap leaching. *Hydrometallurgy*, vol. 58, 2000. pp. 27–41.
- DIXON, D.G. Heap leach modelling—the current state of the art. In Young, C.A., Alfantazi, A.M., Anderson, C.G., Dreisinger, D.B., Harris, B., and James, A. (eds.), *Hydrometallurgy 2003*, vol. 1, TMS, 2003. pp. 289–314.
- DIXON, D.G. and HENDRIX, J.L. Theoretical basis for variable order assumption in the kinetics of leaching of discrete grains. *AIChE J*, vol. 39, 1993. pp. 904–907.
- DIXON, D.G. and PETERSEN, J. Comprehensive modelling study of chalcocite column and heap bioleaching. In P.A. Riveros, D. Dixon, D. Dreisinger, and J. Menacho, (eds.), *Copper 2003–Hydrometallurgy of Copper* (Book 2), vol. 6, CIM, 2003. pp. 493–516.
- FRANZMANN, P.D., HADDAD, C.M., HAWKES, R.B., ROBERTSON, W.J., and PLUMB, J.J. Effects of temperature on the rates of iron and sulfur oxidation by selected bioleaching Bacteria and Archaea: Application of the ratkowsky equation. *Minerals Engineering*, vol. 18, 2005. pp. 1304–1314.
- LEAHY, M.J., SCHWARZ, M.P., and DAVIDSON, M.R. An air sparging cfd model for heap bioleaching of copper sulphide. *Third International Conference on CFD in the Minerals and Process Industries*, Australia, 2003. CSIRO. pp. 581–586.
- LEAHY, M.J., DAVIDSON, M.R., and SCHWARZ, M.P. A model for heap bioleaching of chalcocite with heat balance: Bacterial temperature dependence. *Minerals Engineering*, vol. 18, 2005a. pp. 1239–1252.
- LEAHY, M.J., DAVIDSON, M.R., and SCHWARZ, M.P. A two-dimensional cfd model for heap bioleaching of chalcocite. *ANZIAM J*, vol. 46(E), 2005b. pp. C439–C457.
- MORENO, L., MARTINEZ, J., and CASAS, J. Modelling of bioleaching copper sulphide in heaps or dumps. R. Amils and A. Ballester, (eds.), *Biohydrometallurgy Symposium IBS 99*, 1999. pp. 443–451.
- OGBONNA, N., PETERSEN, J., and DIXON, D.G. Heapsim—unravelling the mathematics of heap bioleaching. Dixon, D.G. and Dry, M.J. (eds.), *International Symposium on Computational Analysis in Hydrometallurgy*, MetSoc, 2005. pp. 225–240.
- OJUMU, T.V., PETERSEN, J., SEARBY, G.E., and HANSFORD, G.S. A review of rate equations proposed for microbial ferrous-iron oxidation with a view to application to heap bioleaching. Harrison, S.T.L., Rawlings, D.E., and Petersen, J. (eds.), *16th International Biohydrometallurgy Symposium, IBS2005*, Cape Town, South Africa, 2005. pp. 85–93.
- OLSON, G.J., BRIERLEY, J.A., and BRIERLEY, C.L. Bioleaching review part B: Progress in bioleaching: applications of microbial processes by the minerals industries. *Applied Microbiology Biotechnology*, vol. 63, 2003. pp. 249–257.
- ORR, S. Enhanced heap leaching—part 1: Insights. *Mining Engineering*, 54, part, vol. 9, September 2002. pp. 49–56.
- PANTELS, G., RITCHIE, A.I.M., and STEPANYANTS, Y.A. A conceptual model for the description of oxidation and transport processes in sulphidic waste rock dumps. *Applied Mathematical Modelling*, vol. 26, 2002. pp. 751–770.
- PETERSEN, J. and DIXON, D.G. Systematic modelling of heap leach process for optimization and design. Patrick R., Taylor, D., Chandra, and Bautista, R.G. (es.), *EPD Congress 2002*, Pennsylvania, USA, 2002. TMS. pp. 757–771.
- PETERSEN, J. and DIXON, D.G. The dynamics of chalcocite heap bioleaching. Young, C.A., Alfantazi, A.M., Anderson, C.G., Dreisinger, D.B., Harris, B., and James, A. (eds.), *Hydrometallurgy 2003*, vol. 1, TMS, 2003. pp. 351–364.
- RATKOWSKY, D.A., LOWRY, R.K., McMEEKIN, T.A., STOKES, A.N., and CHANDLER, R.E. Model of bacterial culture growth rate throughout the entire biokinetic temperature range. *Journal of Bacteriology*, vol. 154, 1983. pp. 1222–1226.
- RAWLINGS, D.E. Mesophilic, autotrophic bioleaching bacteria: Description, physiology and role. chapter 11, Springer-Verlag, 1997. pp. 231–245.
- RAWLINGS, D.E. Heavy metal mining using microbes. *Annual Review of Microbiology*, vol. 56, 2002. pp. 65–91.
- RAWLINGS, D.E. Characteristics and adaptability of iron- and sulphur-oxidizing microorganisms used for the recovery of metals from minerals and their concentrates. *Microbial Cell Factories*, vol. 4, no. 13, 2005. [cited 7 October 2005]. Available from <http://www.microbialcellfactories.com/content/4/1/13>.
- ROHWERDER, T., GEHRKE, T., KINZLER, K., and SAND, W. Bioleaching review part A: Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulphide oxidation. *Applied Microbiology Biotechnology*, vol. 63, 2003. pp. 239–248.
- ROMAN, R.J. and OLSEN, C. Theoretical scale-up of heap leaching. Aplan, F.F., McKinney, W.A., and Pernichele, A.D. (eds.), *Solution Mining Symposium*, New York, 1974. AIME. pp. 211–229.
- SHAFFER, J.L., WHITE, M.L., and CAENEPEEL, C.L. Application of the shrinking core model for copper oxide leaching. *Mining Engineering*, vol. 31, 1979. pp. 165–171.
- SIDBORN, M., CASAS, J.M., MARTINEZ, J., and MORENO, L. Two dimensional dynamic model of a copper sulphide ore heap. *Hydrometallurgy*, vol. 71, 2003. pp. 67–74. ◆