Two-dimensional dynamic model of a copper sulphide ore bed

M. Sidborn[a], J. Casas[b], J. Martínez[a], L. Moreno[a],*

[a] Department of Chemical Engineering and Technology, Royal Institute of Technology, Kungl Tekniska Hogskolan, S-10044 Stockholm, Sweden
[b] Department of Chemical Engineering, University of Chile, Beauchef 861, PC-6511266, Santiago, Chile

Abstract

A two-dimensional dynamic model for bioleaching of secondary copper minerals from a pile has been developed. In the model, aeration of the pile is considered to be due to natural convection caused by the density gradient in the air within the bed. The rate of sulphide mineral dissolution is modelled according to the unreacted core model. The transport of ferric ions from the particle surface to the reaction zone is calculated considering film diffusion, diffusion within the particle and reaction kinetics. The rate of oxidation of the ferrous ion by bacteria attached to the ore surface is modelled using the Michaelis–Menten relationship. The influences of temperature, dissolved ferric iron and dissolved oxygen in the leaching solution are considered in the kinetic formulation. The set of partial differential equations is solved using the FEMLAB® software. The model was used to study the influence of process variables on copper recovery in the bed with time. This model is a useful tool to aid the design and optimisation of industrial operations.

1. Introduction

Leaching of copper from low-grade mineral and mine waste has become an important process in the mining industry. The large quantity of mining waste and the quantity of low-grade copper minerals generated make this a resource of great significance. The metal grades are often too low to support the high costs of ore grinding and agitation leaching. Copper minerals mainly include copper sulphides and oxides. The leaching agent used is sulphuric acid, which is continuously applied on top of the ore pile. Bioleaching processes are used for ores that contain the more stable sulphide minerals. The process is complex and involves a series of mechanisms including biotically mediated oxidation of ferrous ions producing ferric ions in the presence of oxygen. Ferrous minerals are present as a product of pyrite oxidation. The ferric ions, in turn, oxidise the copper sulphides. At present, copper leaching is also applied to high-grade copper ores due to its competitive cost.

The bioleaching rate is determined by the slowest of the following four steps: (1) the supply of oxygen to the bed, (2) bacterial oxidation of ferrous ions by the dissolved oxygen, (3) ferric ion diffusion through the ore particles and (4) the intrinsic rate of reaction of the sulphide minerals with the ferric ions. These steps may coexist in different zones in the ore bed (Ritchie, 1994; Casas et al., 1998).

Modelling of the leaching operation for sulphide ore beds has received considerable attention in the last 25 years (Ritchie, 1994; Casas et al., 1998; Neuburg et al.,

* Corresponding author. Tel.: +46-8-790-6412; fax: +46-8-105228.

E-mail address: lm@ket.kth.se (L. Moreno).

1991; Pantelis and Ritchie, 1992; Bartlett, 1997; Coderre and Dixon, 1999). The macroscopic models developed by Cathles (1994), Ritchie (1994) and Casas et al. (1998) showed that when the ore bed permeability is too low, the oxygen is supplied mainly through air diffusion inside the bed (Ritchie, 1994; Casas et al., 1998; Cathles, 1994). Under these circumstances, bacterial leaching of the sulphide minerals is too low since it is limited by the slow supply of oxygen. The improvement of the bed aeration by natural air convection requires an adequate level of bacterial population and an adequate bed permeability distribution. Today, the tendency is to use forced ventilation in order to improve the air supply and to obtain high bio-oxidation rates. This mode of operation involves higher capital and operating costs, but they are compensated for by the faster metal recovery (Bartlett, 1997).

This work is concerned with the modelling of a biochemical process using a modern simulation tool. The modelling of bacterial leaching when the aeration is caused by natural convection is addressed. The application to forced aeration is straightforward.

2. Theory

2.1. Leaching of copper ores

The copper-oxide mineral dissolution kinetics are rapid and oxide minerals are readily dissolved by sulphuric acid. On the other hand, copper sulphide minerals are much more stable and can only be dissolved under strong oxidising conditions. In copper leaching, the oxidising agent present is ferric ion, which diffuses through the pores of the ore particle and reacts with the metal sulphide (MS) according to:

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S \qquad (1)$$
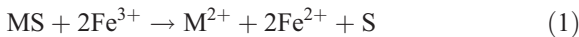
Microorganisms catalyse the reverse oxidation of ferrous ions to ferric ions. The most important bacteria for this purpose is *Acidithiobacillus ferrooxidans*. The bacterial oxidation takes place according to:

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{\text{bacteria}} 4Fe^{3+} + 2H_2O \qquad (2)$$
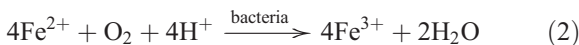
This reaction consumes oxygen that has to be transferred to the leaching solution from air in the ore pile. The rate of consumption of oxygen by

bacteria can be described in terms of the Michaelis–Menten equation:

$$R_{O_2} = XV_m \left(\frac{O_{2,L}}{K_m + O_{2,L}} \right) \qquad (3)$$

where R_{O_2} is the rate of consumption of oxygen by bacteria, X is the number of bacteria per volume of bed, V_m is the maximum specific respiration rate of bacteria, $O_{2,L}$ is the oxygen concentration in the liquid solution and K_m is the Michaelis constant for the system. In *A. ferrooxidans*, the maximum specific respiration rate V_m is dependent on the temperature according to (Casas et al., 1998)

$$V_m = \frac{6.8 \times 10^{-13} T e^{-\frac{7000}{T}}}{1 + e^{236 - \frac{74,000}{T}}} \qquad (4)$$

where T is the temperature in Kelvin. The rate-determining step in the bioleaching of small sulphide mineral particles is generally the slow intrinsic dissolution of sulphide mineral, provided that oxygen is available in the bed and that the pore diffusion does not limit the overall leaching rate. For larger ore particles, however, a mixed kinetics model has to be used to describe the leaching rate. Such a mixed kinetics model is the shrinking core model that includes resistances due to the intrinsic dissolution kinetics of the mineral, the diffusion resistance of ferric iron through an inert porous layer of reacted material and the diffusion of ferric iron through the liquid film on the ore particle surface. The rate of decrease of the unreacted core radius for a given mineral species can be written as:

$$\frac{-dr_C}{dt} = \frac{M_S}{\rho G \phi} \frac{[Fe^{3+}]}{\frac{1}{G\beta} + \left(\frac{\sigma}{D_{eff}}\right)\left(\frac{r_C}{R}\right)(R - r_C) + \left(\frac{1}{K_C}\right)\left(\frac{r_C}{R}\right)^2} \qquad (5)$$

where r_C is the rate of decrease of the unreacted core radius, M_S is the ore molecular weight, ρ is the mineral particle density, ϕ is the particle shape factor, G is the copper ore grade, β is the global specific kinetics factor, σ is the stoichiometric factor, D_{eff} is the effective diffusion coefficient, R is the mineral particle radius and K_C is the mass transfer coefficient in the liquid–solid film. $[Fe^{3+}]$ is the concentration of ferric ions in the leaching solution. The leaching rate of a given mineral species is related to the rate of

decrease of the unreacted core radius through the mass balance.

2.2. Liquid flow

During leaching, a solution of sulphuric acid is applied at the top of the bed. The liquid flow rate has to be adjusted so that a liquid film surrounds the particles and the particle pores are filled with solution without excluding the flow of air and oxygen required by the leaching reactions. Under steady state conditions, the liquid content in the ore bed is constant. The liquid flow is also constant and is given by the irrigation rate. The transport of solutes in the liquid phase is described by:

$$\varepsilon_L \frac{\partial C_i}{\partial t} = D_L \varepsilon_L \nabla^2 C_i - q_L \nabla C_i + R_i \tag{6}$$

where C_i is the concentration of species i, D_L is the dispersion, ε_L the volume fraction of liquid, q_L the liquid flow rate and R_i the reaction rate of species i. This equation may be applied to both ferric and copper ions.

2.3. Air transport through the bed

Air is transported through the ore bed by diffusion and by natural convection. Oxygen is consumed by the exothermic reactions that occur in the bed and as a result the temperature rises. Air is assumed to be saturated with respect to water vapour at the local temperature. For these reasons, the density of the gas varies through the ore bed with a resulting pressure gradient. The volume-flow of the gas also varies throughout the bed as a consequence of the oxygen depletion and the increasing temperature. The local velocity of air q_g can be expressed as:

$$q_g = -\frac{\rho_g k_{rg} k}{\mu} \nabla P \tag{7}$$

where k and k_{rg} are the intrinsic and relative gas permeabilities of the bed, ρ_g is the gas density, μ is the fluid viscosity and ∇P denotes the fluid pressure gradient. The transport of oxygen in the gaseous phase is described by the following equation:

$$\varepsilon_g \frac{\partial O_{2,g}}{\partial t} = \varepsilon_g D_g \nabla^2 O_{2,g} - q_g \nabla O_{2,g} - R_{O_2} \tag{8}$$

where $O_{2,g}$ is the concentration of oxygen, D_g is the dispersion in the gas phase and ε_g the volume fraction of air.

2.4. Energy balance

Energy is transported through the ore bed by conduction and convection. The energy transported by convection depends on both the liquid flow and the gas flow, which have opposite directions in the bed.

$$C_{p,B} \rho_B \frac{\partial T}{\partial t} = k_B \nabla^2 T - \rho_L q_L \nabla H_L - \rho_g q_g \nabla H_g$$
$$+ (-\Delta H_R - \Delta H_S) R_{ch} \tag{9}$$

where $C_{p,B}$ is the mean heat capacity of the ore bed, ρ_B is the bed density, k_B is the thermal conductivity of the ore bed, ρ_L is the liquid density, q_L and q_g denote the liquid and the gas flow, respectively, H_L and H_g denote the liquid and gas enthalpy, respectively. ΔH_R denotes the heat of reaction per mineral dissolved, and ΔH_S is the heat of solution of the products.

3. Cases modelled

A mineral consisting of chalcocite and pyrite was considered in these simulations. The pile was assumed to have a flat top and to slope downwards at the edges at an angle of $45°$. In the model, for the sake of simplicity, it is assumed that the ferrous ions are present in excess and that they are not a limiting factor for the oxidation reaction. Bacteria, the population of which is assumed to be constant, mediate the oxidation of ferrous ions. In an earlier paper (Moreno et al., 1999), the influence of temperature and oxygen concentration on the number of bacteria was studied. The ferric ions produced react with the copper mineral, and copper ions are leached to the solution. Steady-state as well as transient cases were modelled. In the transient model, the ferric ion diffusion resistance is taken into account, and a material balance for ferric ions is therefore needed. The air in the bed is assumed to be water-saturated and the mass flow of inert nitrogen is assumed to be constant. Here, we present the two-dimensional transient model in detail. Since the bed is symmetric, only half of the bed is modelled.

3.1. Two-dimensional transient model

In this transient model, which takes into account intra-particle diffusion resistance, five differential equations are solved in addition to the equation for the airflow. These equations consider the balances of ferric ions, copper ions, oxygen, and energy and the variation in the particle diameter as a result of the leaching process. The initial conditions for the model are ambient oxygen concentration and temperature, and zero concentration of ferric and copper ions. The unreacted core radius was set equal to the initial particle radius. The boundary conditions are described below.

3.1.1. Centre boundary

For reasons of symmetry, no liquid or gas flow occurs over this border. Moreover, neither mass diffusion nor heat conduction takes place.

$$\frac{\partial Fe^{3+}}{\partial x} = 0 \quad \frac{\partial Cu}{\partial x} = 0 \quad \frac{\partial T}{\partial x} = 0 \quad \frac{\partial O_{2,g}}{\partial x} = 0 \quad \frac{\partial r_C}{\partial x} = 0 \tag{10}$$

3.1.2. Bottom boundary

Energy and mass are transported out only by the liquid solution. Neither mass diffusion nor heat conduction takes place through the bottom boundary.

$$\frac{\partial Fe^{3+}}{\partial y} = 0 \quad \frac{\partial Cu}{\partial y} = 0 \quad \frac{\partial T}{\partial y} = 0 \quad \frac{\partial O_{2,g}}{\partial y} = 0 \quad \frac{\partial r_C}{\partial y} = 0 \tag{11}$$

3.1.3. Top boundary

Temperature and oxygen concentration are given at the top of the bed. No mass flow of ferric or copper ions takes place through the top boundary.

$$\frac{\partial Fe^{3+}}{\partial y} = 0 \quad \frac{\partial Cu}{\partial y} = 0 \quad T = T_0 \quad O_{2,g} = O_{2,g,0} \quad \frac{\partial r_C}{\partial y} = 0 \tag{12}$$

3.1.4. Slope boundary of the bed

Temperature and oxygen concentration are given along the slope of the bed. No mass flow of ferric or copper ions takes place through the slope boundary.

$$\frac{\partial Fe^{3+}}{\partial n} = 0 \quad \frac{\partial Cu}{\partial n} = 0 \quad T = T_0 \quad O_{2,g} = O_{2,g,0} \quad \frac{\partial r_C}{\partial n} = 0 \tag{13}$$

Table 1
Values of the parameters used in the simulations

Parameters	Unit	Value
Heap width	m	20
Heap height	m	10
Number of bacteria	bacteria/m^3 bed	$1.0 \cdot 10^{14}$
Michaelis constant	kg/m^3	0.001
Liquid flow	L/m^2 s	$2.8 \cdot 10^{-3}$
Gas permeability	m^2	$2.5 \cdot 10^{-9}$
Particle diffusion	m^2/s	$4.0 \cdot 10^{-10}$
Ambient temperature	°C	20
Particle radius	m	0.02
Ore copper concentration	%	0.63
FPY parameter	kg pyrite/kg Cu$_2$S	2.0

The parameters needed for these simulations are shown in Table 1. The system of differential equations was solved using the simulation tool FEMLAB®. When the governing equations and boundary conditions are properly defined, the implementation of the equation system into FEMLAB® is straightforward. FEMLAB® is available commercially (http://www.femlab.com/). References where the software FEMLAB® is used include, e.g., Wessen (2002) and Nilsson et al. (1999).

4. Result and discussion

4.1. Two-dimensional transient model

Although the two-dimensional transient model was simulated for a long leaching time, results are shown for only 6 months. Fig. 1 shows the gas flow profile through the bed after a leaching time of 6 months. The pressure gradients in the bed do not change much during the process, and as a consequence, the airflow profile does not change much with time. It is also observed that the airflow rate is relatively large along the slope and very small in the central part of the bed.

Fig. 2 shows the temperature profile in the ore bed after 6 months leaching time. For the conditions used in these simulations, the temperature increase is greater than 6 °C in a zone near the bottom and close to the slope at a time of 6 months. In the central part of the bed, the increase in temperature is small due to the low oxygen concentration, as shown in Fig. 3. For longer leaching times, copper and pyrite are almost depleted in some regions of the bed, and the heat
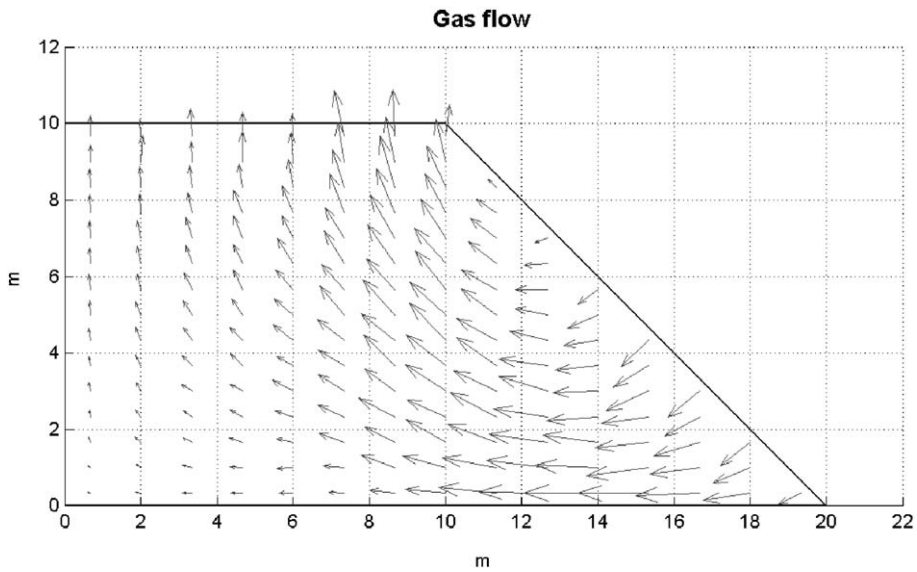
Gas flow

Fig. 1. Gas flow through the ore bed.

released by exothermic reactions is small. The infiltrating liquid then cools the bed with a decreasing bed temperature as a result.

Oxygen reacts with ferrous ions in a microbiologically mediated reaction to produce ferric ions. Since the model assumes that ferrous ions are present in excess during the whole process, the rate of this reaction is determined by the amount of oxygen available. The concentration of oxygen in the ore bed is shown in Fig. 3. This concentration is large along the slope boundary where oxygen is flowing into the bed due to natural convection. In the central
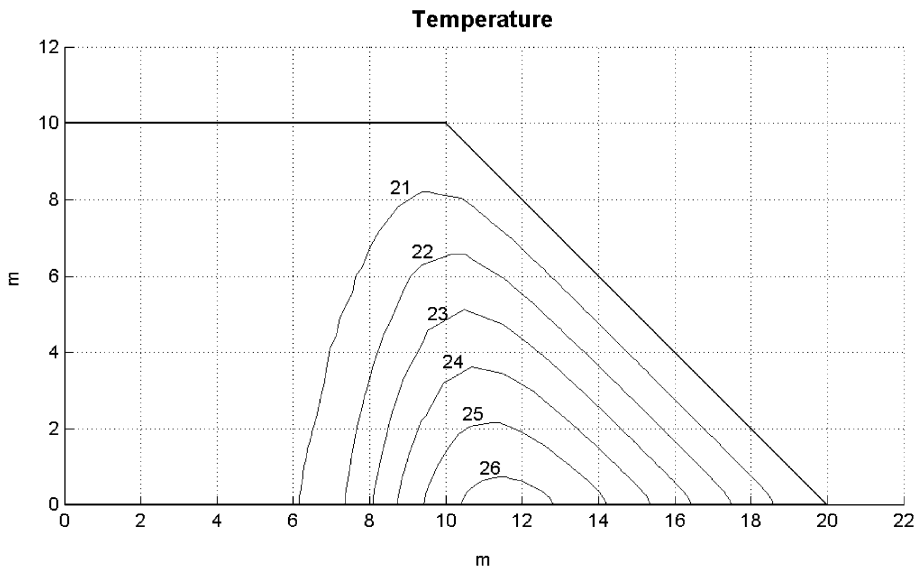
Temperature

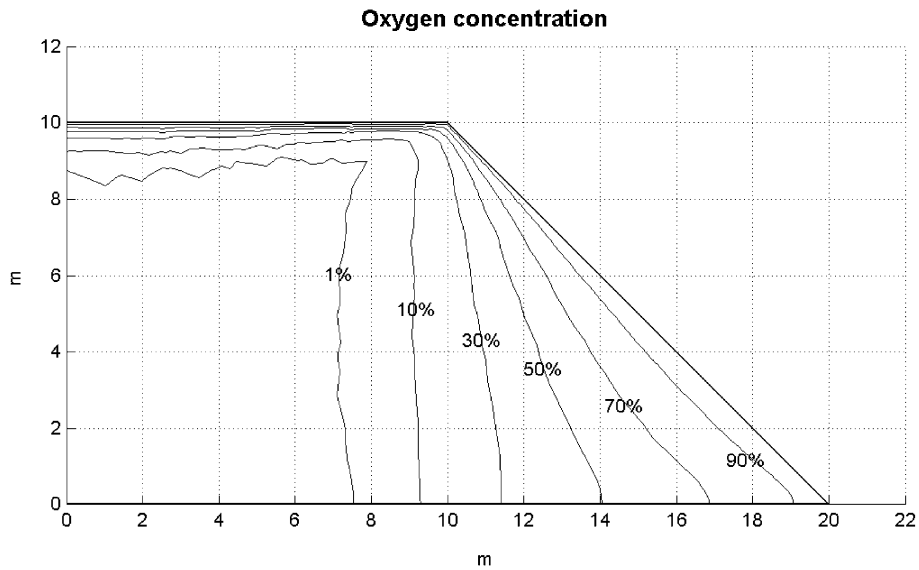Fig. 2. Temperature profile (°C) inside the ore bed.

Oxygen concentration

Fig. 3. Oxygen concentration profile ($O_{2,g}/O_{2,g}$ (initial)) inside the ore bed.

part of the bed, the oxygen is almost totally depleted. This means that the rate of the oxidation reaction is negligible in this region.

Fig. 4 shows the copper concentration in the leaching solution after 6 months. The flowing liquid transports copper, which hence accumulates at the bottom of the bed. The highest copper concentration is therefore found in the zone where the reaction takes place at the highest rate and the accumulation is greatest. With time, the copper is depleted under the slope of the bed and the concentration in the leaching solution is therefore low in this area. The leaching rate in the rest of the bed is low because of the low oxygen concentration.
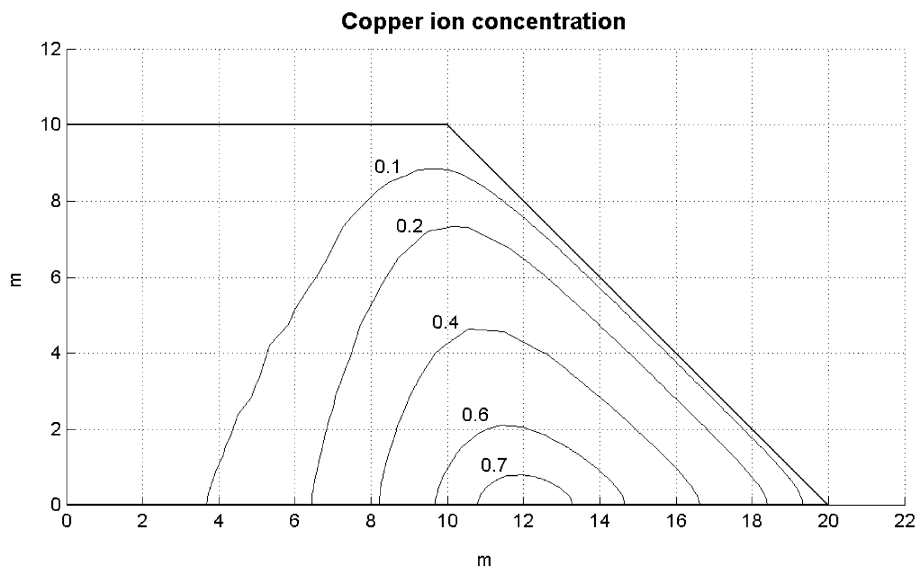
Copper ion concentration

Fig. 4. Copper concentration profile (kg copper/m³ liquid) inside the ore bed.
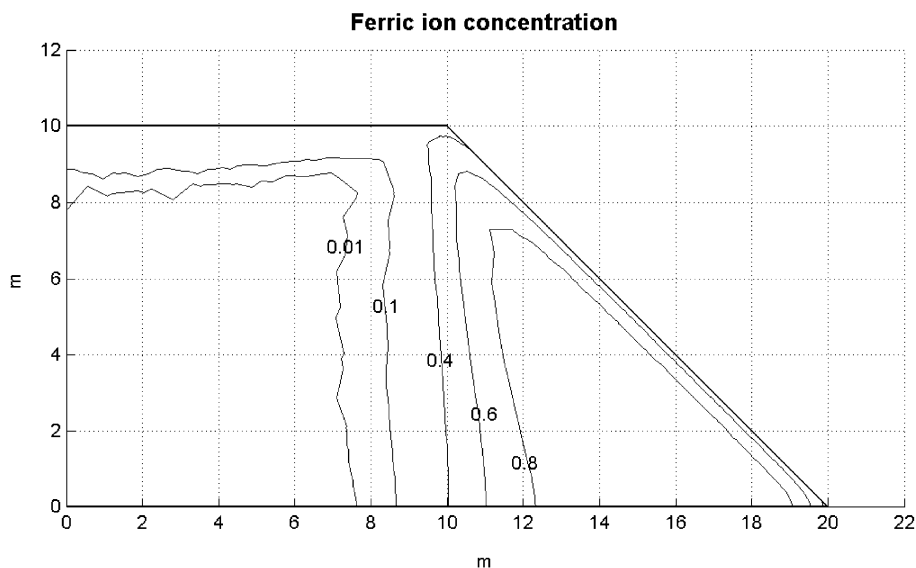
Ferric ion concentration

Fig. 5. Ferric ion concentration profile (kg ferric ions/m^3 liquid) inside the ore bed.

Initially, the ferric ion concentration in the ore bed is negligible. Ferrous ions are, however, present in excess. The microbially mediated oxidation of ferrous ions to ferric ions therefore occurs as long as oxygen is present in the bed. As oxygen is consumed, the ferric ion production decreases. Ferric ions diffuse into the ore particles and react with the copper mineral. In this reaction, ferric ions are reduced to ferrous ions. As the unreacted core shrinks, the diffusion resistance increases, and a larger fraction of the ferric ions are transported down by the liquid flow. Therefore, ferric ions are accumulated towards the bottom of the bed. The ferric ion concentration increases with time as the diffusion resistance in-
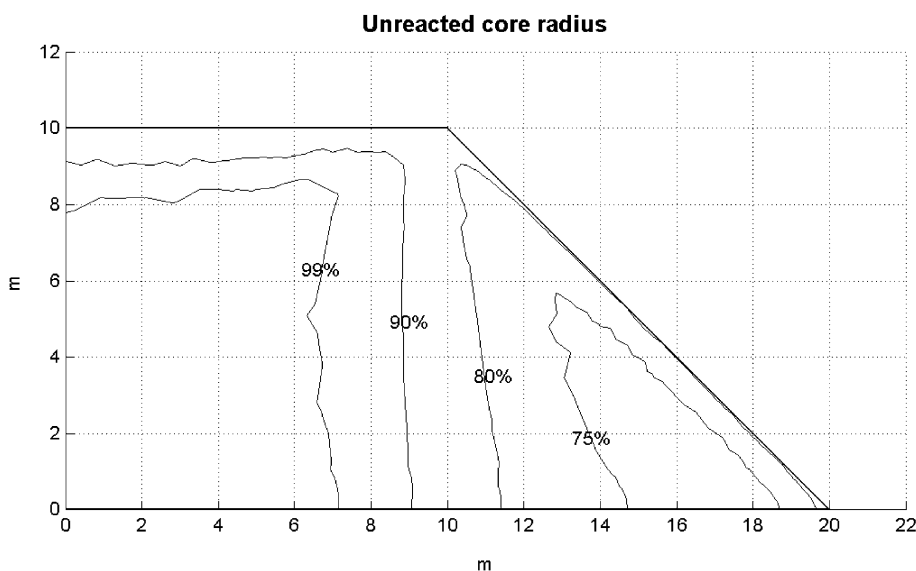
Unreacted core radius

Fig. 6. Unreacted core radius of particles (m/m (initial)) in the ore bed.

creases. The ferric ion concentration after 6 months is shown in Fig. 5.

Fig. 6 shows the unreacted core radius after 6 months. The smallest unreacted core is found close to the slope of the bed, where the concentration of oxygen is large and the temperature high, which cause a higher reaction rate. Because of the low oxygen concentration in the rest of the bed, the reaction rate is slow in these regions and thus only a small part of the particle is reacted.

5. Conclusions

A model for bioleaching of copper sulphide mineral was developed. Several cases with different degrees of complexity were simulated with the simulation tool FEMLAB®. The model parameters used in this paper were taken from the literature, and their applicability to this model has not been addressed in detail. For more confident results regarding the bioleaching of copper ores, the input parameters should be carefully evaluated and the model validated against field data.

Several assumptions were made in the conceptual model and some of them need to be further evaluated. The ferrous iron present in the bed was assumed to be present in excess. Consequently, the oxygen concentration profile in the bed reached an almost steadystate condition. In reality, ferrous iron is also depleted and hence oxygen can penetrate further into the ore bed. A material balance for ferrous ions should therefore be included in the model, and the Michaelis–Menten expression for oxygen depletion should be modified to include both oxygen and ferrous ion concentrations. The liquid leaching solution flow rate has a significant effect on the leaching performance and should therefore be evaluated more carefully. Additional simulations with a decrease in liquid flow rate have been performed, and these showed a great

impact on the parameters studied. The bacterial population was assumed to be constant throughout the process. A Monod-type expression for the bacterial population growth, with oxygen and ferrous ion concentrations as limiting substrates, could be included in the model (Moreno et al., 1999).

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