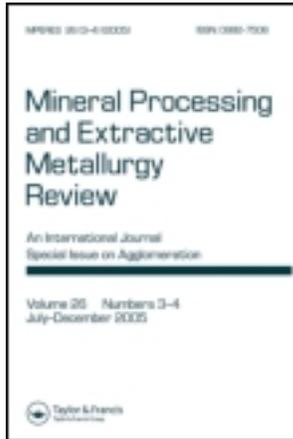


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The Indirect Mechanism of Bacterial Leaching

F. K. CRUNDWELL^a

^a School of Process and Materials Engineering, University of the Witwatersrand
Johannesburg, Private Bag 3, Wits, 2050, South Africa

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The Indirect Mechanism of Bacterial Leaching

F. K. CRUNDWELL

*School of Process and Materials Engineering, University of the Witwatersrand,
Johannesburg, Private Bag 3, Wits, 2050, South Africa*

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Mathematical models of the chemical leaching of a sulphide mineral and the bacterial oxidation of ferrous ions are combined in a mathematical model of bacterial leaching. It is shown that the models of the chemical leaching of sphalerite and the bacterial oxidation of ferrous ions are in excellent agreement with the experimental results. The indirect mechanism of bacterial leaching, which is a combination of these two sub-processes, is able to account for the shape of the reaction curve obtained from bacterial leaching experiments. It is also shown that even at very low concentrations of iron in solution the indirect mechanism may be the dominant pathway in bacterial leaching of sulphidic minerals.

Keywords: Bacterial leaching; mathematical models; chemical leaching

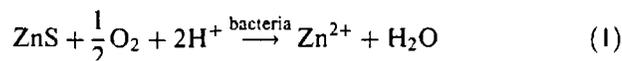
INTRODUCTION

The bacterial leaching of sulphide minerals is important in the formation of acid-mine drainage and in the extraction of metals from their ores. Since the discovery of *Thiobacillus ferrooxidans* in 1950 [1], there has been much research to utilise these bacteria in the extraction of metals [2, 3]. The most common operation that is dependent on bacterial leaching is the heap leaching of low-grade copper [2, 3]. Recently, a number of commercial leaching plants for the pretreatment of refractory gold ores have been commissioned [4]. The largest of these is the Sansu plant of the Ashanti Goldfields, Ltd, in Ghana [5], which treats over 1000 tons per day of sulphide. An understanding of

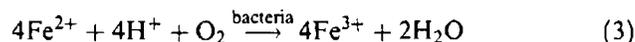
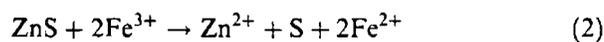
the mechanisms of bacterial leaching would assist the design and optimisation of bioremediation and process leaching plants.

Two broad mechanisms of bacterial leaching have been proposed (3): (i) the 'direct' mechanism, in which bacteria attach to the surface of the mineral, and biochemical activity enhances the rate of dissolution of the mineral at the point of attachment, and (ii) an 'indirect' mechanism, in which the bacteria oxidise ferrous ions in solution to ferric ions, and the ferric ions dissolve the sulphide mineral by chemical attack.

The direct mechanism of bacterial leaching of mineral sulphide such as zinc sulphide (sphalerite) may be represented by the reaction (3):



whereas the indirect mechanism requires the presence of iron in solution (3):



The bacterial leaching of many sulphide minerals has been studied extensively (2, 3). However, none of these studies have presented a thorough analysis of the chemical leaching of the mineral in addition to the study of the bacterial leaching of the same mineral sample. This makes it very difficult to determine the role that iron plays in the bacterial leaching experiment. In addition, all of the previous models of bacterial leaching include terms describing the direct mechanism, implying that the simplest hypothesis, that of the indirect mechanism, has not been thoroughly investigated [6].

In this paper we present a mathematical model of the indirect mechanism for the leaching of sulphidic minerals, which has the component models describing the chemical leaching of sphalerite and the bacterial oxidation of ferrous ions. The kinetic parameters for both of these individual processes are obtained by fitting the model to experimental data, and from these kinetic parameters, we are able to simulate the indirect mechanism of bacterial leaching. Throughout this paper we use the leaching of sphalerite (ZnS) as an example; however,

the models that we develop are general, and the results that we present are generally applicable to the leaching of other minerals.

MATHEMATICAL MODEL OF CHEMICAL LEACHING

The leaching of a mineral is described by the shrinking-particle model and by an electrochemical reaction at the surface [7–9]. The mass balance for the leaching of sphalerite in a batch reactor is given by [10]:

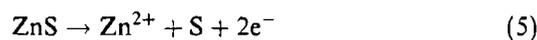
$$\frac{dN_{MS}}{dt} = -r_{MS}A \quad (4)$$

where N_{MS} represents the number of moles of mineral in the batch reactor, r_{MS} represents the rate of consumption of sphalerite by the leaching reaction (units of mol/m²s), and A represents the surface area (m²) of sphalerite that is available for reaction.

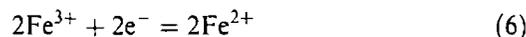
Expressions for the rate of reaction, r_{MS} , and for the available surface area, A , are obtained from the electrochemical mechanism of leaching and from the shrinking-particle model, respectively.

Electrochemical Model of Leaching

The dissolution of mineral sulphides is an electrochemical reaction and the rate of dissolution may be analysed in terms of the anodic and cathodic half-reactions. For example, the anodic half-reaction for the leaching of sphalerite is given by (7–9):



and the cathodic half-reaction is given by:



By combining the expression for the rate of the electrochemical reactions (5) and (6), we obtain an expression for the rate of dissolution of the mineral, r_{MS} (7):

$$r_{MS} = \frac{k}{2F} \left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)^\alpha \quad (7)$$

where F is the Faraday constant, and k is a rate constant. α is the order of reaction, and because it arises from the charge-transfer coefficient for the electron transfer at the mineral-solution interface, it is expected to have the value 0.5 ± 0.1 .

Shrinking-particle Model

The change in the number of moles of mineral is related to the change in size of the particle. For particles that are approximately spherical with radius l (or which maintain their geometric proportion during leaching), the following relationships are obtained:

$$dN_{MS} = 4\pi\ell^2 \rho_{MS} d\ell; \quad A = 4\pi\ell^2; \quad X = 1 - \left[\frac{\ell}{L} \right]^3 \quad (8)$$

where ρ_{MS} is the molar density of sphalerite, X is the reaction conversion, and L is the initial particle size.

Substituting equations (7) and (8) into the mass balance, equation (4), and after some rearrangement, the leaching of sphalerite in a batch reactor is described by:

$$\frac{dX}{dt} = \frac{3k^\infty}{2\rho_{MS}LF} (1-X)^{\frac{2}{3}} \left[\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right]^\alpha \exp \left[-\frac{E_a}{RT} \right] \quad (9)$$

where $k = k^\infty \exp(-\frac{E_a}{RT})$ and E_a is the activation energy. The initial condition is $X=0$ at $t=0$.

Equation (9) must be solved in combination with the solution mass balance, given by:

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_0 - bF_{MS} X \quad (10)$$

where b is the stoichiometric coefficient for the leaching reaction, and F_{MS} is the molar concentration of mineral added initially to the batch experiment.

Verbaan and Crundwell [7] presented results for the leaching of sphalerite. The sample of sphalerite that they studied assayed 50.9% zinc, and 9.1% iron, and the initial particle size was approximately 22 μm .

Figures 1 and 2 show equations (9) and (10) fitted to the leaching data presented by Verbaan and Crundwell [7]. The model is represented by the lines and the data by the points on these figures. The close correspondence between the model and the data suggests that the model is a good representation of the data.

All the lines in both Figures 1 and 2 have been obtained with the same set of parameters, that is, with $3k^\infty/2 \rho_{MS}LF = 1.88 \times 10^5 \text{ min}^{-1}$, $\alpha = 0.39$, and $E_a = 48 \text{ KJ/mol}$.

MATHEMATICAL MODEL OF BACTERIAL OXIDATION OF FERROUS ION

The rate of bacterial oxidation of ferrous ion is described by exponential growth kinetics combined with Monod-type kinetics. The rate of growth of the bacterial population size is given by:

$$\frac{1}{N} \frac{dN}{dt} = \mu \quad (11)$$

where N represents the size of the bacterial population.

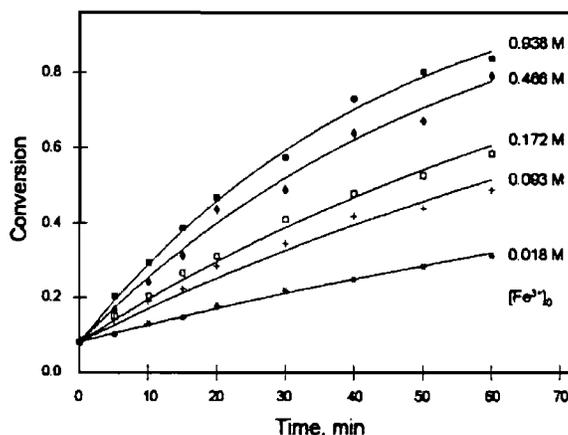


FIGURE 1 Leaching of sphalerite at 65°C, 0.038 M Fe^{2+} , 0.1 M H_2SO_4 , 1 g/L solids.

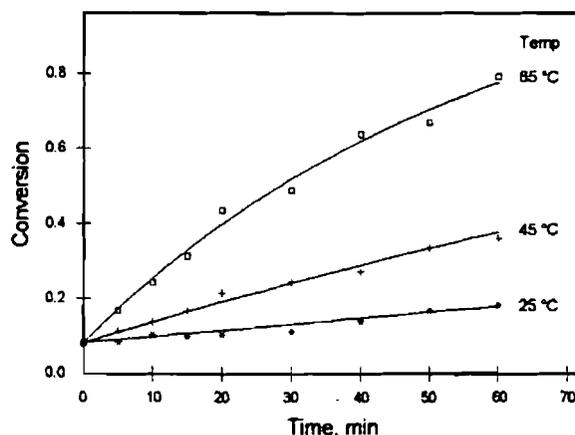


FIGURE 2 Leaching of sphalerite with 0.45 M Fe^{3+} , 0.04 M Fe^{2+} , 0.1 M H^2SO_4 , 1 g/L solids.

The energy derived from the consumption of substrate, Fe^{2+} , is utilised for both growth and maintenance activities, so that

$$\frac{d[\text{Fe}^{2+}]}{dt} = -\frac{1}{Y} \frac{dN}{dt} + m_s N \quad (12)$$

where Y is the bacterial yield coefficient, and m_s is the specific rate of substrate consumption due to cell maintenance. If it is assumed that m_s is small, then equation (12) may be integrated to give:

$$N = N_0 + Y([\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]) \quad (13)$$

where the subscript 0 indicates the initial value. Combining equations (11), (12) and (13), we get:

$$\frac{1}{\frac{N_0}{Y} + ([\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}])} \frac{d[\text{Fe}^{2+}]}{dt} = -\frac{\mu_{\max}}{[\text{Fe}^{2+}] + K_s(1 + K_i[\text{Fe}^{3+}])} \quad (14)$$

Figure 3 shows the fit of equation [14] to the batch oxidation data presented by Harvey and Crudwell [11]. Equation (14) is represented by the lines, and the data by the points. The close correspondence between the model and the data indicates that equation (14) describes the data.

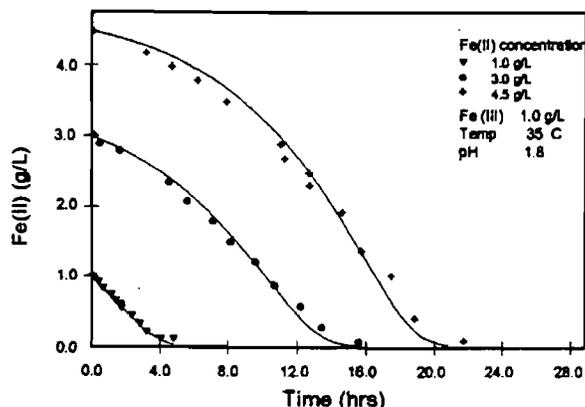


FIGURE 3 Oxidation of ferrous ion by *Thiobacillus ferrooxidans* in a stirred batch reactor.

The parameters for the model lines represented in Figure 3 are given in Table I, except for the values of N_0/Y , which has the values 1.68, 0.60, and 0.34 g/L for each of the curves with initial concentrations of 1.0, 3.0 and 4.5 g/L Fe^{2+} , respectively. This indicates that the size of the population that is adapted to higher concentrations of ferrous ion, given by N_0 , decreases as the concentration of ferrous ion increases [11].

SIMULATION OF THE INDIRECT MECHANISM OF BACTERIAL LEACHING

The indirect mechanism of bacterial leaching consists of following reactions: (i) growth of the size of bacterial population, (ii) bacterial oxidation of ferrous ions and (iii) chemical leaching of sphalerite,

TABLE I Kinetic parameters for the growth of *Thiobacillus ferrooxidans* in a batch reactor

μ_{max} (hr^{-1})	K_s (g/L)	K_o (L/g)
0.161	0.073	1.287

These three reactions are described by the three differential equations which represent the size of the bacterial population, the concentration of ferrous ions and the conversion of the mineral.

For the bacterial leaching of sphalerite these equations are:

$$\frac{dN^*}{dt} = \mu N^* \quad (15)$$

$$\frac{d[\text{Fe}^{2+}]}{dt} = -\frac{N_0}{Y} \mu N^* + 2F_{\text{ZnS}} \frac{dX}{dt} + 3F_{\text{FeS}} \frac{dX}{dt} \quad (16)$$

$$\frac{dX}{dt} = \frac{3k^\infty}{2\rho_{\text{ZnS}}RF} (1-X)^{\frac{1}{3}} \left[\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right]^\alpha \exp\left(-\frac{E_a}{RT}\right) \quad (17)$$

The concentration of ferric ions in the solution is described by:

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_0 + [\text{Fe}^{2+}]_0 + F_{\text{FeS}}X - [\text{Fe}^{2+}] \quad (18)$$

where F_{ZnS} and F_{FeS} are the initial molar concentrations of zinc and iron in the natural sphalerite added to the experiment. $N^* = N/N_0$, where N_0 is the initial number of active bacteria in the inoculum.

The initial conditions for these differential equations are $N^* = 1.0$, $[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_0$, $[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_0$ and $X = 0$ at time $t = 0$.

The conditions for the simulation study are given in Table II. These conditions are typical of bacterial leaching studies [12].

The results for the simulation of the bacterial leaching of the sphalerite using the fitted parameters for chemical leaching and for oxidation of ferrous ions by bacteria are shown in Figures 4 and 5.

These figures indicate that the indirect mechanism produces a reaction curve that is very similar to that reported in the bacterial leaching literature. The reaction time is generally much longer than chemical leaching with excess leaching agent (compare Fig. 2 with Fig. 4).

The reaction curve shown in Figure 4 passes through four separate rate-controlling regimes. At different stages of the reaction, each of the component reactions controls the rate of bacterial leaching. Experimental results similar in shape to the reaction curve shown in Figure 4 have been reported in the literature [12–14]. However, these results

TABLE II Simulation conditions and parameters

Variable	Value
Temperature	30°C
Initial mass sphalerite	10 g/L
% zinc in sphalerite	50.9
% iron in sphalerite	9.1
<i>Leaching parameters</i>	
$3k^\infty/2\rho_{ZnS}LF$	$1.88 \times 10^5 \text{ min}^{-1}$
α	0.39
E_a	48 kJ/mol
<i>Ferrous oxidation parameters</i>	
N_0/Y	0.34 g/L
μ_{max}, K_s, K_i	Table II

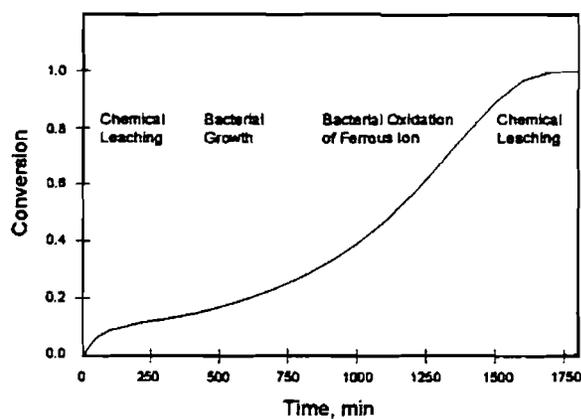


FIGURE 4 Simulation of bacterial leaching by the indirect mechanism, indicating the regions of the dominance of the three different processes of chemical leaching, bacterial growth, and bacterial oxidation of ferrous ions. Initial conditions: 1 g/L Fe^{3+} , 0 g/L Fe^{2+} , and other parameters given in Table II.

have not been interpreted in terms of the direct mechanism rather than the indirect mechanism of bacterial leaching. For example, Suzuki and Lizama [13] obtained a curve similar to that of Figure 4 for the extraction of zinc into solution, but argued that the process occurring during the initial period of slow leaching, represented by the first two regions in Figure 4, is an adaptation period required for the bacteria to

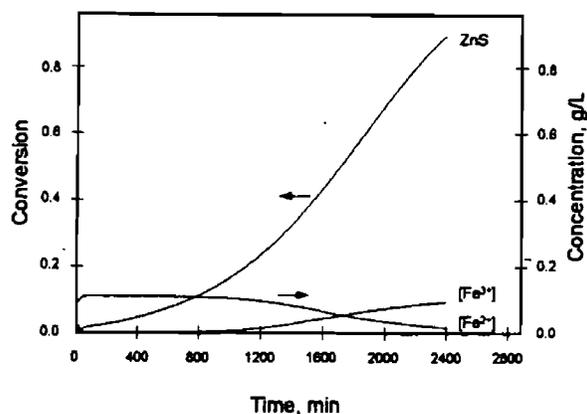


FIGURE 5 Simulation of bacterial leaching of sphalerite containing no iron with $F_{FeS} = 0.1$ g/L Fe^{3+} , 0.01 g/L Fe^{2+} . Other parameters given in Table II.

shift their metabolism from iron oxidation to sulphide oxidation. In agreement with the dominant paradigm in bacterial leaching, they consider that only the direct mechanism of leaching of a mineral sulphide is of any consequence.

The contribution of the indirect mechanism could possibly be eliminated by limiting the amount of iron that is present in the system. Typical bacterial leaching experiments in which this strategy is adopted still contain about 1 g/L total iron, mainly as a result of the iron that is present in the bacterial inoculum. Another source is the iron present in the mineral.

If the iron in solution is limited to a tenth of this concentration, that is, to 0.1 g/L total iron, and we assume that the mineral sample contains no iron, will the indirect mechanism still result in the leaching of sphalerite? The metal extraction curve for the simulation of these conditions is shown in Figure 5. These results indicate that the indirect leaching mechanism contributes significantly to the leaching of iron-free sphalerite and that leaching is complete in a shorter period than the reaction times given in the literature. In the simulation the reaction time was about 1.6 days, while the reaction time of at least 15 days was reported by Suzuki and Lizama [13]. The difference in reaction times is probably a result of differences in the reactivity and the initial particle sizes of the sphalerite samples. It is clear that even when the level of

iron are very low (0.1 g/L Fe) the indirect mechanism may still dominate the leaching process. Therefore, the removal of the iron to levels of about 1.0 g/L, as has been reported in the literature [12–14], cannot be used as evidence for the direct mechanism of bacterial leaching.

CONCLUSIONS

In this paper we have presented a mathematical model of the indirect mechanism of bacterial leaching of mineral sulphides. This model is the simplest possible reaction mechanism that may be envisaged, and does not require additional postulates about enzymatic reactions that have not yet been identified. The mechanism consists of the chemical leaching of the mineral, and the oxidation of ferrous ions by the bacteria. The parameters for the equations have been obtained from the independent experiments of chemical leaching and bacterial oxidation of ferrous ions. The reaction curves for the indirect mechanism have been simulated using these kinetic parameters. The simulation indicates that even if the concentration of iron in solution is limited to 0.1 g/L, the indirect mechanism may contribute significantly to the overall extraction of metal.

In the total absence of iron, another form of the indirect mechanism may occur. The mineral dissolves by acid attack, and the hydrogen sulphide that is produced in this reaction is consumed by the bacteria. The possibility of this alternative mechanism means that the total elimination of iron from the reaction system does not guarantee that there is a direct mechanism of bacterial leaching.

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