Modeling, Simulation, and Optimization of Bacterial Leaching Reactors

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Abstract: Bacterial leaching represents an unusual problem in biochemical engineering, because the substrate for bacterial growth is not supplied directly, but is a product of another reaction, the leaching of mineral particles. In addition, leaching is a heterogeneous reaction dependent on the particle-size distribution in the feed and on the kinetics of particle shrinkage. In this study, these effects are incorporated in the material balance for each mineral by the number balance. Examination of the number balance gives rise to a novel analysis of the competing technologies for leaching. The model is completed by the addition of material balances for the ferrous and ferric ions, the dissolved oxygen, and for each bacterial species to the number balance for each mineral present in the feed. The model is compared with pilot plant data for three different ores. It is shown that the model is in excellent agreement with the data. The performance of a bacterial leaching reactor is explored using the model, and the washout and sensitivity criteria are determined. It is shown that there are three washout conditions, in which the leaching conversion drops to zero. The washout conditions are dependent on the growth rate of the bacteria, on the rate of dissolution of the mineral, and on the rate of mass transfer of oxygen to the reactor. The critical washout condition is that arising from the rate of mineral dissolution. The optimization of a plant in which continuous tank reactors are configured in series is addressed. This analysis shows that the primary reactor should be between 1.5 and 2 times the size of each of the secondary reactors in a series combination. © 2001 John Wiley & Sons, Inc. *Biotechnol Bioeng* 71: 255–265, 2000/2001.
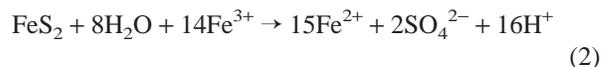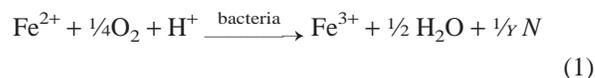
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INTRODUCTION

Bacterial leaching of sulfide minerals has found increasing application in the recovery of copper, gold, and cobalt. Commercial operations presently utilize bacterial species whose maximum temperature limit is between 45° and 55°C, such as *Thiobacillus ferrooxidans, Leptospirillum ferrooxidans,* and *Thiobacillus caldus.* Development of processes for the leaching of base metal sulfides for the recovery of copper and nickel has focused on the use of archae, such as *Sulfolobus* and *Metallosphaera* species, which have

a temperature limit in the range of 70° to 80°C (Dew et al., 1999). Oxidation of the sulfide minerals results in either the dissolution of the valuable metal, or the liberation of the valuable metal from a sulfide matrix. The valuable metal is recovered by further processing of the solution or the residue. For bacterial leaching to compete successfully with alternative processes, such as pressure leaching, the operation needs to be efficient. The design, operation, and optimization of the bacterial leaching process will benefit greatly from a detailed and thorough mathematical model.

The factors affecting the dissolution of sulfide minerals have been studied extensively (Fowler and Crundwell, 1998; Fowler et al., 1999; Holmes et al., 1999). Leaching arises from the bacterial oxidation of ferrous ions to ferric ions, which in turn oxidize the mineral. For the bacterial dissolution of pyrite, these reactions are:

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \xrightarrow{\text{bacteria}} Fe^{3+} + \tfrac{1}{2} H_2O + \tfrac{1}{Y} N \tag{1}$$

$$FeS_2 + 8H_2O + 14Fe^{3+} \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{2}$$

where Y represents a stoichiometric yield factor, and N represents a measure of the amount of bacteria. Reactions (1) and (2) represent a cyclic autocatalytic system. It is important to note that the substrate for the bacteria is produced by another reaction, because this has a significant bearing on the performance of the reactor.

Bacteria readily attach to the surfaces of particles, and their presence on the surface may affect the rate of dissolution, through a localized form of reactions (1) and (2) (Crundwell, 1994a, 1996; Fowler et al., 1999; Harvey and Crundwell 1997; Holmes et al., 1999). Fowler et al. showed that attached bacteria may increase the rate of dissolution above the chemical rate of dissolution at the same solution conditions in two cases: (i) if the rate of dissolution of the mineral is affected by the formation of a porous layer of sulfur by a phenomenon known as product layer diffusion, then the removal of the sulfur by the bacteria will result in an increase in the rate of leaching (Fowler and Crundwell 1998, 1999); and (ii) if the dissolution of the mineral is dependent on the pH at the mineral surface, then the attach-

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ment of bacteria to the surface may result in an increase in the pH at the surface, which increases the rate of reaction (Fowler et al., 1999; Holmes et al., 1999). In the second case, it was shown that, even though attached bacteria increased the rate of dissolution, the mechanism of leaching was the chemical dissolution by ferric ions, given by Reaction (2). It is significant that the leaching of the particles was described by the shrinking-particle model in both cases.

The mathematical description of continuous bacterial leaching is different from that of classical biochemical reactors. This is because the product of interest is the extent of conversion of the mineral, and not a biological product. In addition, the substrate for bacterial growth, ferrous ions, is produced in the reactor by the cyclic reactions represented by Reactions (1) and (2). In addition, the process is different from that in leaching reactors, because of the presence of bacteria and the possibility of bacterial washout. (In general, washout occurs when the reactor fails to operate; that is, the outlet conditions are equal to the inlet conditions. Bacterial washout is the particular condition that occurs when the bacteria fail to multiple sufficiently quickly so that washout takes place.)

Several models of the bacterial leaching process have been published. These were discussed by Crundwell (1994a) and in more detail by Haddadin et al. (1995). Many of the previous models focused on the description of bacterial growth, and often ignored the phenomena surrounding the leaching reaction. In addition, these models are often limited to particular rate expressions, or to the description of only the first reactor in the series of reactors. The model proposed recently by Breed and Hansford (1999) suffers from both of these problems. Their model is incorrect because they ignored the material balances of ferric and ferrous ions. In addition, their model did not account for the effect of particle size on the rate of leaching, even though Hansford and Miller (1993), among others, showed that the rate of bacterial leaching is strongly affected by particle size. Other conceptual concerns about Breed and Hansford's description of bacterial leaching have been discussed by Crundwell (1999).

Nagpal et al. (1994) accounted for the change in particle surface area on reaction. However, because they did not use either of the two models of particulate reactors—that is, the segregated-flow model (Dixon, 1996) or the population balance model (Crundwell and Bryson, 1992)—their description of the change in particle-size distribution on reaction is incorrect. In addition, their kinetic expression for the rate of leaching depends on potential rather than the concentrations in solution.

In this study, a general model of the bacterial leaching process is formulated. This model accounts for the kinetics of growth of both attached and planktonic cells, for the effect of the distribution of particle sizes on the performance of the reactor, and for the leaching kinetics. Of particular concern herein is the use of the model to determine the sensitivity of a bacterial leaching reactor to the kinetic and operating parameters, and for the optimization of bacterial leaching plants. For example, the sensitivity analysis can determine the bacterial washout conditions, and conditions similar to bacterial washout in which the reactor fails to operate. Establishing these criteria is important for the design and operation of the reactors. None of the previously published models examined these questions. The implications of the results of the model on the interpretation of bacterial leaching kinetics and on the operation and control of a bacterial leaching facility are discussed. We begin with a mathematical description of a continuous particulate (leaching) reactor, followed by a description of the bacterial oxidation processes.

THE MAIN ISSUE IN LEACHING: ACCOUNTING FOR PARTICLE SIZE IN THE MATERIAL BALANCES

Leaching is a particulate reaction dependent on the distribution of sizes of the particles in the feed to the reactor. This sets bacterial leaching apart from other biochemical reactors, because few other bacterial processes include the reaction of particulate material. Mathematical models of leaching of particulate material in continuous stirred-tank reactors have received much attention (Crundwell, 1994a, 1994b; Crundwell and Bryson, 1992; Dixon, 1996; Sepulveda and Herbst, 1979). The particle size distribution is influenced by both reaction and flow into and out of the continuous reactor, and because the rate of dissolution is dependent on the particle size, these phenomena must be explicitly described. There are two methods of describing particulate processes, either by the number balance or by the segregated-flow model. Crundwell (1994b) examined the relationship between these two models in detail. In this work, the number balance is used because the assumptions concerning micromixing are the same as those for the conventional mass balance for a continuous stirred-tank reactor (CSTR) (Crundwell, 1994b; Crundwell 1995).

Consider a feed stream to a tank reactor containing a slurry of sulfide minerals. The particles in the slurry have a distribution of size, $n(\ell)$, where $n(\ell)d\ell$ is the number of particles per unit volume of slurry in the size range ℓ to $\ell + d\ell$. If this is the only distributed property of the particles that is necessary for a complete description of the particle kinetics, then the change in the distribution with reaction and flow in a tank reactor at steady state is given by:

$$Qn_0(\ell) = Qn(\ell) + V\frac{dRn(\ell)}{d\ell} \qquad (3)$$

where R is the linear rate of particle shrinkage, V is the tank volume, and Q is the slurry feed rate to the tank. The $n_0(\ell)$ and $n(\ell)$ terms represent the inlet and outlet size probability density functions on a number basis, respectively. R may be dependent on the particle size and the concentrations of species in solution. Equation (3) is analogous to the more familiar CSTR material balance (Crundwell, 1994b). The left-hand side represents the probability density of the particle size coming into the reactor, the first term on the right-hand side represents the probability density of the particle

size leaving the reactor, and the second term on the right-hand side represents the change in probability density of the particle size as a result of reaction. The boundary condition is chosen at large sizes, because the particles in this system shrink. Therefore, the boundary condition is $Rn(\ell) \to 0$ as $\ell \to \infty$.

In many cases, the rate of dissolution of sulfide minerals is controlled by the intrinsic reaction at the surface, so that the rate of shrinkage of the particles is given by:

$$R = -k_s f(\tilde{C}) \qquad (4)$$

where k_s is the rate constant for the intrinsic leaching reaction, and $f(\tilde{C})$ is a function of the vector of concentrations in the reactor, $\tilde{C}$. Eq. (4) represents the shrinking particle model, because integration of $R = d\ell/dt = -k_s f(\tilde{C})$ for the batch reactor with a constant concentration of reagents in solution yields the well-known equation $1 - (1 - X)^{1/3} = k_s f(\tilde{C})t/\ell_0$, where ℓ_0 the initial particle size.

Substitution of Eq. (4) into Eq. (3) and rearrangement of terms into a dimensionless form yields the following equation (Crundwell, 1994b):

$$n_0(\ell^*) = n(\ell^*) - \frac{\bar{t}k_s f(\tilde{C})}{\bar{\ell}} \frac{dn(\ell^*)}{d\ell^*} \qquad (5)$$

where $\bar{t}$ is the mean residence time given by V/Q, $\bar{\ell}$ is the mean particle size in the feed, and ℓ^* is $\ell/\bar{\ell}$. The size distribution (on a mass basis) of the feed particles was described by a Rosin–Rammler distribution from which $n_0(\ell^*)$ was calculated.

To obtain the amount of material leached in the reactor, Eq. (5) must be integrated subject to the boundary condition and the inlet distribution to obtain the size distribution of particles leaving the reactor. The inlet and outlet size distributions are related to the conversion of mineral, X, by

$$1 - X = \frac{\int_0^\infty \ell^{*3} n(\ell^*) \, d\ell^*}{\int_0^\infty \ell^{*3} n_0(\ell^*) \, d\ell^*} \qquad (6)$$

The conversion is the fraction of feed of that mineral that is dissolved. For example, for each mineral, we obtain:

$$F_0 = F(1 - X) \qquad (7)$$

where F_0 is the molar flow rate of the mineral in the feed, and F is the molar flow rate of the mineral from the reactor. Thus, the sequential solution of Eqs. (5)–(7) defines the exit molar flow rate and size distribution leaving the reactor. A set of Eqs. (5)–(7) is written for each mineral in the system,

thus making the addition of more minerals to the model straightforward. Because these equations represent a single tank reactor, any configuration of tank reactors may be described.

The effect of the concentration of the reactants in the solution on the rate of leaching is accounted for in the factor $f(\tilde{C})$ in Eq. (5). Leaching reactions are often described by the electrochemical leaching model (Nicol et al., 1975), in which case:

$$f(\tilde{C}) = \left(\frac{[\text{Fe}^{3+}]}{1 + k[\text{Fe}^{2+}]} \right)^\alpha \qquad (8)$$

The value of α is close to 0.5. The rate of dissolution may be dependent on the pH of the solution. Holmes and Crundwell (2000) and Holmes et al. (1999) reported that the kinetics of the dissolution of pyrite increase with increasing values of pH.

Eq. (5) has an immediate explanatory value possessed by none of the previous models of bacterial leaching. The dimensionless leaching number, N_c, is the expression preceding the differential term in Eq. (5), given by:

$$N_C = \frac{\bar{t}k_s f(\tilde{C})}{\bar{\ell}} \qquad (9)$$

This expression indicates that, to increase the amount of material dissolved, the leaching number must increase. This means that either the residence time, $\bar{t}$, or the leaching rate, $k_s f(\tilde{C})$, must increase, or the mean particle size in the feed, $\bar{\ell}$, must decrease.

Two other leaching technologies that compete with bacterial leaching for the processing of sulfide minerals in the technology marketplace are pressure oxidation, and leaching after fine milling. The set of reactions in each of these technologies is similar to or even the same as that in bacterial leaching. Each of these leaching technologies balances the leaching number, N_C, at roughly the same value as that obtained in bacterial leaching by changing the values of the parameters of N_C. These operating regimes are summarized in Table I. Thus, the fine grinding and leaching process decreases $\bar{t}$ and $\bar{\ell}$, and increases temperature (which increases k_s through the activation energy) compared with bacterial leaching. Pressure leaching increases temperature and decreases $\bar{t}$ compared with bacterial leaching. (In addition, some processes have attempted to increase the intrinsic leaching rate by the addition of agents known to increase the rate of dissolution reactions, such as halide ions.) The leaching number establishes the theoretical relationship between the technologies. Some base metal sulfides, such as chal-

Table I. Operating regimes based on the dimensionless leaching number, N_C.

Technology	Temperature	Residence time	Particle size	N_C
Bacterial leaching	Low	High	Moderate	Moderate
Pressure leaching	High	Low	Moderate	Moderate
Fine grinding and leaching	Moderate	Moderate	Low	Moderate

copyrite, dissolve very slowly. The move to employ thermophilic organisms in the bioprocessing of these minerals is due to the need to increase the leaching rate, and hence the leaching number, by operating at higher temperatures.

Therefore, not only does the number balance account for the effect of particle size on the performance of the reactor, but it also yields valuable new insight into the relationship between various competing leaching technologies.

MATERIAL BALANCE MODELS FOR THE SOLUTION COMPONENTS AND THE BACTERIA

In addition to the leaching reaction, the process consists of the bacterial oxidation of ferrous ions, given by Reaction (1), and the mass transfer of oxygen from the gas phase to the liquid phase.

These reactions affect the concentrations of ferrous and ferric ions, and oxygen in solution. The material balance for ferrous and ferric ions is given by:

$$Q[Fe^{2+}]_0 = Q[Fe^{2+}] + \left(r_{Fe^{2+}} - \frac{r_{FeS_2}}{15} \right) V \qquad (10)$$

$$Q[Fe^{3+}]_0 = Q[Fe^{3+}] + \left(\frac{r_{FeS_2}}{14} - r_{Fe^{2+}} \right) V \qquad (11)$$

where r_{Fe}^{2+} is the rate of bacterial oxidation of ferrous ions, and r_{FeS_2} is the overall rate of mineral dissolution, in this case, pyrite. Q is the volumetric flow rate of solution into the reactor, and V is the volume of solution in the reactor. The overall rate of mineral dissolution is given by $r_{FeS_2} = F_{FeS_2} X_{FeS_2}/V$, where F_{FeS_2} is the molar feed rate of pyrite to the reactor, and X_{FeS_2} is the conversion of pyrite obtained from the solution of Eqs. (5), (6), and (7). Thus, r_{FeS_2} is easily obtained from the solution of Eqs. (5)–(7).

This formulation is general, so the addition of more leaching reactions or other processes affecting the concentration of ferrous and ferric ions in solution, such as the chemical oxidation of ferrous ions or the precipitation of basic ferric sulfates, is straightforward. This overcomes a limitation of many of the previous models.

The material balance for the bacteria is given by:

$$Q[N]_0 = Q[N] + \mu[N]V \qquad (12)$$

where $[N]$ represents a measure of the concentration of bacteria and μ is the bacterial growth rate.

The rate equation for the bacterial growth is a Monod-type expression, although any functional form may be used. This is given by:

$$\mu = \frac{\mu_{max} [Fe^{2+}]}{K_s + [Fe^{2+}] + K_{Fe} [Fe^{3+}] + \sum_i K_i C_i} \frac{[O_2]}{K_{O_2} + [O_2]}$$

$$(13)$$

where μ_{max} is the maximum growth rate achieved, and the other parameters are constants. The rate of bacterial oxida-

tion of ferrous ions, r_{Fe}^{2+}, which is required in Eqs. (10) and (11) is related to μ by $r_{Fe}^{2+} = \mu[N]/Y$.

It should be noted that Crundwell (1997) derived a theoretical expression for the growth of bacteria on ferrous ion based on the electrochemical kinetics of the electron transport chain. This expression is similar to Monod Eq. (13), except that the right-hand side of Eq. (13) is raised to the power of one-half. The application of either expression yields similar results in this work.

Different bacterial species may compete for the same substrate in the reactor. However, only the species with the highest growth rate will dominate due to the washout of the slower growing organisms. There may be a number of species growing on either sulfur or on intermediate sulfur oxyanions, depending on the stoichiometry of the leaching reaction. Thus, in most cases there will only be two dominant species in the reactor: one growing on ferrous ions and one growing on a sulfur product. The material balance for the growth on either elemental sulfur or on a partially oxidized sulfur oxyanion is the in same as in Eq. (13), except that the expression for the growth rate, μ, is dependent on the amount of sulfur present.

The material balance for the transfer of oxygen in the disperse phase is given by:

$$Q[O_2]_0 = Q[O_2] - k_L a([O_2]_{sat} - [O_2])V + \frac{r_{Fe}^{2+}}{4} V$$

$$(14)$$

while the gas phase balance is given by:

$$G_{O_2,0} = G_{O_2} + k_L a([O_2]_{sat} - [O_2])V \qquad (15)$$

where $k_L a$ is the mass transfer coefficient, and G is the molar flow rate in the gas phase. The saturated concentration of oxygen in solution may be calculated by the method given by Tromans (1998). Both the depletion of oxygen in the gas bubbles due to consumption of oxygen by reaction and the evaporation of water in the gas bubbles are taken into account in the calculation of $[O_2]_{sat}$. This is particularly important in describing reactors operating with thermophilic microorganisms, where the partial pressure of water vapor is high if the temperature is above about 70°C, and where the oxygen utilization is high if oxygen-enriched gas is used.

Thus, the model of the reactor consists of the simultaneous solution of leaching equations [Eqs. (5), (6), and (7)], the material balances for ferrous and ferric ions [Eqs. (10) and (11)], the material balance for the growth of bacteria [Eq. (12)], and the material balances for the mass transfer of oxygen [Eqs. (14) and (15)]. The solution of these equations, together with the kinetic expressions given by Eqs. (8) and (13), gives the exit concentrations of the solid, solution, and gaseous components from the tank reactor. Numerical solution of this set of differential and nonlinear algebraic equations is performed first by recasting the equations in terms of the extent of reaction (see Crundwell and Bryson, 1992), expressing the solution to the differential equation in integral form, and using multidimensional Newton–

Raphson to solve the set of simultaneous nonlinear equations.

It should be noted that this model has the two correct limiting cases: (i) when no bacteria are present, the model describes chemical leaching; and (ii) when no minerals are present, the model describes the bacterial generation of ferric ions from ferrous ions. None of the previously published models have the two correct limiting cases.

## COMPARISON OF THE MODEL WITH DATA FROM PILOT PLANTS

Nicholson et al. (1994) described the design of the bacterial leaching plant at the Sansu plant, which is owned by Ashanti Goldfields Corp. (Ghana), Limited. They provided sufficient data on the pilot plant operation to enable a comparison of model predictions with the results from the pilot plant. Miller (1990), Hansford and Miller (1993), and Dew (1995) described the operation of a pilot plant for the bacterial leaching of the concentrate from Fairview (South Africa), and Pinches et al. (1988) described the operation of a continuous pilot plant at Mintek (South Africa). The input data and the model parameters are given in Table II for each of these operations.

Each of these pilot plants consisted of a series of CSTRs. The data in Figure 1 represents the cumulative conversion against the cumulative residence time at each point along the train of reactors.

The model predictions and the pilot plant results are shown in Figure 1, which indicates that the model provides

Table II. Parameters used in the modeling of the pilot plant data from Ashanti (Nicholson et al., 1994), Fairview (Dew, 1995; Miller, 1990), and Mintek (Pinches et al., 1988).

	Ashanti	Fairview	Mintek
Source	Nicholson	Miller	Pinches
Volume tank 1 (L)	58.8	10000	45
Volume tank 2 (L)	22.8	5000	45
Volume tank 3 (L)	22.8	5000	45
Volume tank 4 (L)	22.8	5000	—
Solid feed rate (kg/h)	0.309	11.347	0.143
% Solids	20	20	15
% FeS$_2$	7.0	37.2	54.5
% FeS	14.0	0.0	0.0
% FeAsS	18.0	15.5	0.0
% Gangue	61.0	47.3	45.5
Mean particle size (μm)	15	25	25
Leaching kinetics			
k_{s,FeS_2} (m/min)	3.90×10^{-9}	4.88×10^{-9}	3.90×10^{-9}
$k_{s,FeS}$ (m/min)	8.29×10^{-9}		
$k_{s,FeAsS}$ (m/min)	8.29×10^{-9}	7.81×10^{-9}	
k (L/mol)	0	0	0
Bacterial growth kinetics			
μ_{max} (1/min)	0.001	0.001	0.001
K_s (g/L)	0.073	0.073	0.073
K_{Fe}	0.094	0.094	0.094
K_{O_2} (mg/L)	0.64	0.64	0.64
k_La (1/min)	2.5	2.5	2.5
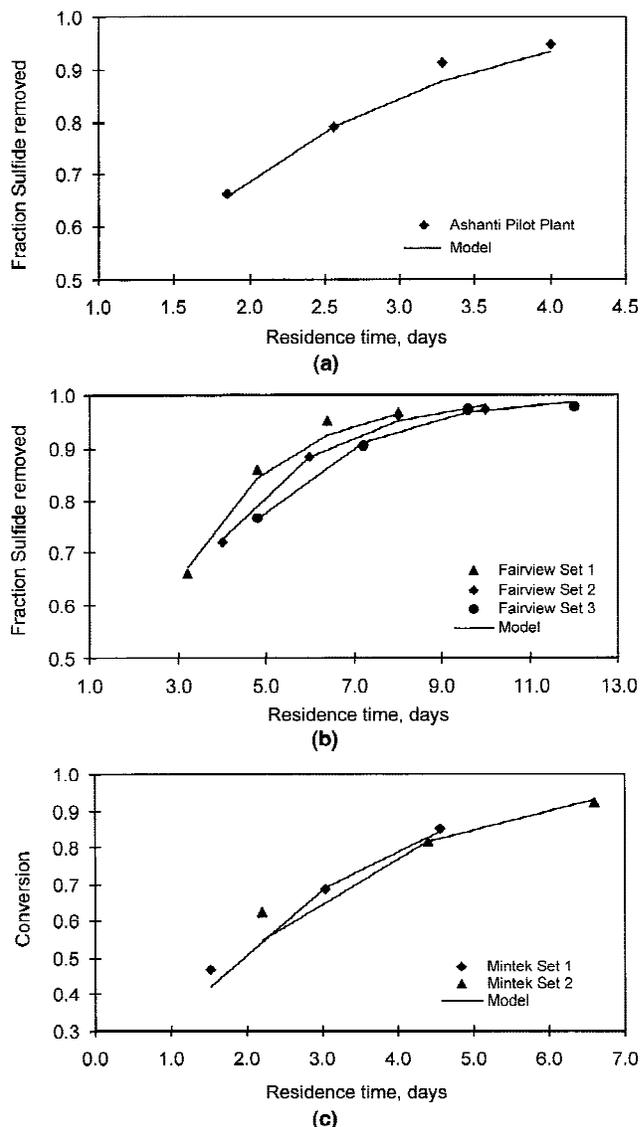
Figure 1. Correspondence of the model and the pilot plant data for three different operations. (a) Ashanti pilot plant data (Nicholson et al., 1994); (b) Fairview pilot plant data (Dew, 1995; Miller, 1990); and (c) Mintek pilot plant data (Pinches et al., 1988). The model parameters for each of the simulations are given in Table II.

a very good description of all three sets of pilot plant data. It is remarkable to note the good correspondence between the leaching parameters for the different minerals from widely different sources. In addition, the same bacterial growth parameters were used for all of the simulations of the pilot plant data.

SIMULATION OF THE PERFORMANCE OF A BACTERIAL LEACHING REACTOR

An important objective in the modeling of bacterial leaching is to develop a thorough design procedure through a detailed understanding of the process occurring in the reactor, and from this to obtain a thorough understanding of the performance of the reactor. Consider the design of a primary
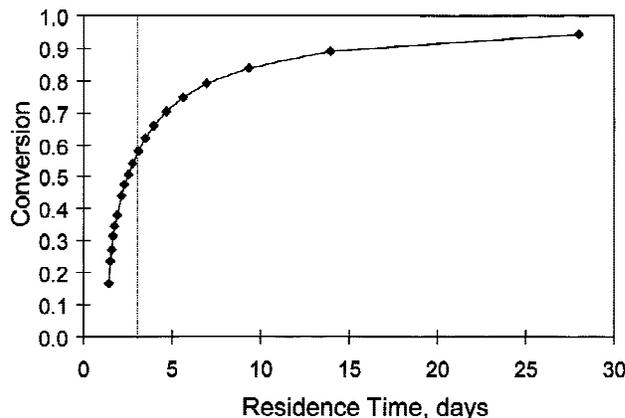
reactor in which there is only one mineral, say pyrite, and the oxidation of ferrous ions by only one type of bacteria, say *Thiobacillus ferrooxidans*. Design parameters for this reactor and the rate constants for each of these reactions are given in Table III. (Note that the term primary reactor is used to denote a reactor in which there are no bacteria in the feed.)

The main performance measurement is the conversion of pyrite achieved, subject to the feed rate of the pyrite, the percentage of solids in the slurry, and the grade of the pyrite in the solids. The effect of changing the residence time on the conversion is shown in Figure 2. At low residence times, the conversion drops to zero at a residence time of about 1.4 days, whereas, at high residence times, the conversion asymptotes to complete conversion at infinite residence times. The cause of the washout at 1.4 days is examined in the section on sensitivity analysis. Typically, each leaching reactor in a series configuration should be designed to achieve a conversion of about 60%.

Because the feed rate of pyrite to the reactor can be changed without changing the residence time (either by changing the solids fraction or the grade of pyrite in the solids), a plot that may be more informative in practice is that of the overall oxidation rate of pyrite, given by $F_{FeS_2} X M_{FeS_2}/V$ (kg/m^3 per day), against the feed rate of pyrite, $F_{FeS_2} M_{FeS_2}$ (kg/day). M_{FeS_2} represents the molecular mass of pyrite. This plot is shown in Figure 3. In addition, the mass balance line for conditions given in Table III is also shown in Figure 3. This plot indicates that, as the feed rate of pyrite increases, the rate of pyrite oxidation goes through a maximum. At the conditions given in Table III, the reactor achieves a conversion of about 60%, and it performs at about 86% of its optimal value. Of course, there is trade-off between overall oxidation rate and conversion, because, even though the overall rate goes through a maximum, the conversion achieved in the reactor drops. The
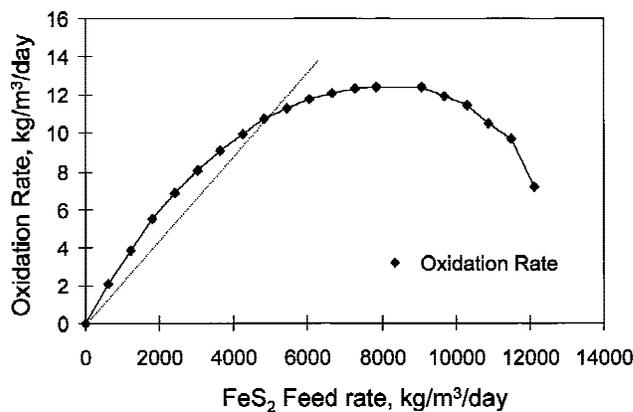

Figure 2. The conversion achieved in the tank reactor as a function of residence time for the values of the parameters given in Table III (excluding the residence time). This set of simulations indicates that the performance of the reactor drops to zero at a residence time of about 1.4 days. The dashed line represents the residence time for the values of the volume and the flow rate given in Table III.

results given in Figure 3 suggest that there is an optimum in the design of the overall leaching plant. This is discussed later.

The concentrations of ferrous and ferric ions and pyrite in the reactor as a function of feed rate are shown in Figure 4. These results indicate that the concentration of ferrous ions in the reactor follows the oxidation rate shown in Figure 3. Also shown in Figure 4 is the concentration of ferric ions, which decreases monotonically with increase in feed rate of pyrite, and the concentration of pyrite. Breed and Hansford (1999) recently concluded that the ratio of ferrous ions to ferric ions is not a function of the amount of pyrite fed to the reactor. The results shown in Figure 4 indicate that the assumptions made by Breed and Hansford (1999) are incorrect.

The shape of the curve for pyrite shown in Figure 4 resembles that for the substrate in a conventional bioreactor;

Table III. Parameters used in the simulation and sensitivity analysis of the bacterial leaching reactor.

Variable	Value	Source
Volume (m^3)	280	
Solids feed rate (tons/day)	20	
Temperature (°C)	40	
Air (Nm^3/min)	25	
% Solids	0.2	
% FeS$_2$	26.2	
% Gangue	73.8	
Mean particle size (μm)	25	
Leaching kinetics		
k_{s,FeS_2} (m/min)	3.7×10^{-9}	Crundwell (1994a)
k (L/mol)	0.0	
Bacterial growth kinetics		Estimate—literature values
μ_{max} (1/min)	0.001	between 0.003 and 0.001
K_s (g/L)	0.073	Harvey and Crundwell (1996)
K_{Fe} (−)	0.094	Harvey and Crundwell (1996)
K_{O_2} (mg/L)	0.64	Huberts (1995)
$K_L a$ (1/min)	2.5	Estimate

Figure 3. The overall oxidation rate, given by $F_{FeS_2} X M_{FeS_2}/V$, against the feed rate of pyrite to the reactor, given by $F_{FeS_2} M_{FeS_2}$. The dashed line represents the residence time for the values of the volume and the flow rate given in Table III.
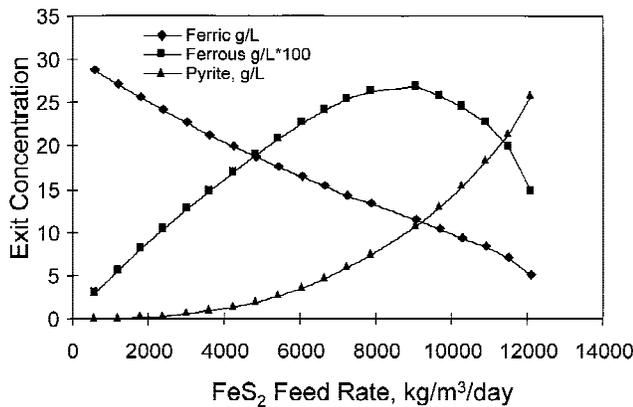
Figure 4. The concentrations of ferric and ferrous ions, and pyrite as a function of pyrite feed rate. The concentration of pyrite behaves in the same manner as that of the substrate in a conventional bioreactor, even though pyrite is not the substrate. The concentrations of ferrous and ferric ions do not change in a fixed ratio.

Figure 5. The sensitivity of the reactor to the dimensionless bacterial growth rate, showing that the conversion rises rapidly to a constant value as N_{Fe} increases from its limiting value of 1. The dashed line indicates the position of the operating point for the parameters given in Table III. Also shown are the corresponding values of the concentration of ferrous ions, showing that the proximity of the washout condition can be monitored by monitoring this concentration.

that is, the concentration increases from zero at zero feed to the feed concentration at washout. This suggests that, even though pyrite is not the direct substrate for bacterial growth in this model, its behavior is similar to that obtained from classic biochemical engineering models in which it is assumed to be the direct substrate. This means that the mechanistic interpretation of bacterial leaching from plant data must be done with much care, or the incorrect conclusion may be easily reached. This is discussed later in further detail.

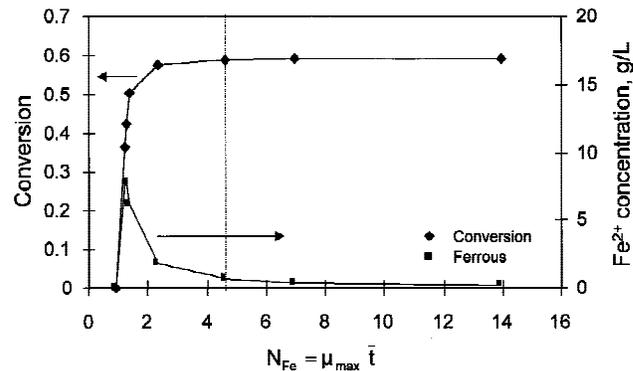## SENSITIVITY (OR RISK) ANALYSIS AND THE CONDITIONS FOR WASHOUT

A sensitivity analysis evaluates the effect of a change in a parameter on the performance of the reactor. For example, sensitivity analysis evaluates the risk to the process that the practitioner may face if the bacterial growth rate changes, or if the sulfide mineralogy changes. The sensitivity of a primary reactor at the operating point given by the parameters in Table III is examined in this section.

There are three dimensionless parameters associated with the three reactions occurring in the reactor. These dimensionless parameters are:

$$N_{Fe} = \mu_{max}\,\bar{t}, \qquad N_{mt} = \frac{k_L\,a\,V}{G_0 H}, \qquad \text{and} \quad N_c = \frac{k_s\,\bar{t}}{\bar{\ell}}$$

where N_{Fe} is the dimensionless parameter associated with bacterial growth. N_{mt} is the dimensionless parameter associated with oxygen mass transfer, and N_c is the dimensionless leaching number discussed previously. G_0 is the total gas flow rate into the reactor in moles per minute, and H is the Henry's law constant for oxygen at the blower delivery pressure and at the reactor temperature in cubic meters per mole.

The effect of changes in N_{Fe} on the performance of a single tank reactor is shown in Figure 5. Normal operation

of the reactor yields values of N_{Fe} between 7 and 15. It is clear from the results illustrated in this figure that the bacteria growth rate does not affect the performance of the reactor when the value of N_{Fe} is >2.33. If the value of N_{Fe} is between 1.0 and 2.33, the performance of the reactor is strongly dependent on the bacterial growth rate, and below a value of 1 washout occurs. This is the washout condition for the classical bioreactor. The range of conditions where the bacterial growth rate affects the performance is relatively small. The point of operation for the parameters given in Table III is shown on the figure. It should be noted that the value of μ_{max} used is the lower limit of the reported range. *Leptospirillum ferrooxidans* and *Thiobacillus ferrooxidans* both have maximum growth rates in excess of 0.001 L/min, which means that the minimum residence time is of the order of 0.7 days, and a residence time of greater than 1.2 days will allow operation in the plateau portion of the curve. This indicates that bacterial washout is not the cause for the conversion dropping to zero at the residence time of 1.4 days, as shown in Figure 2.

Also shown are the corresponding concentrations of ferrous ions. Monitoring the concentration of ferrous ions is an important and accurate indicator of the health of the bacterial population. The practitioner can gauge how close the operation is to this washout condition from the value of this concentration.

The result, shown in Figure 5, that an increase in the bacterial growth rate has little effect on the reactor performance, implies that the substitution of *Thiobacillus ferrooxidans* with, for example, *Leptospirillum ferrooxidans* would make little difference to the conversion achieved in the reactor. Indeed, a change in population would not be detected in the performance of the reactor. It should be noted that the same conclusion will not be reached for batch (or column) culture experiments, particularly when the molar ratio of initial amount of iron in solution to the amount of mineral added is low.

Although the bacteria are sustained by ferrous ions, it is important to note that a higher concentration of ferrous ions in the reactor does not imply better bacterial growth. This is clear from the results shown in Figure 5. The concentration of ferrous ions increases as the bacterial growth rate decreases, whereas the concentration of ferrous ions is lowest for the highest rate of bacterial growth. Instead, it is the continuous supply of ferrous ions that is critical to the sustained growth of the bacteria. This is particularly important in the leaching of minerals that have a slow rate of dissolution, such as chalcopyrite, or minerals that have a low iron content, such as sphalerite. In these cases, washout may occur because the rate of supply of ferrous ions is insufficient to sustain the rate of bacterial growth. If this is the case, a variety of methods may be used to increase the rate of production of ferrous ions. The most constructive of the possible methods is to increase the leaching number, N_C, by either increasing the rate of leaching or by decreasing the mean particle size. Other methods may include the addition of a mineral that has a high rate of dissolution to the feed material, and the recycling of ferric ions from the final tank in a series combination.

The effect of changes in N_{mt} on the performance of a single tank reactor are shown in Figure 6. The shape of the sensitivity curve is similar to that for the bacterial growth rate. At low values of N_{mt}, washout occurs due to a lack of oxygen. As N_{mt} is increased, a critical value is reached where the reactor no longer suffers from washout. The critical value of N_{mt} is equal to the maximum oxygen utilization, defined by the maximum proportion of moles of oxygen in the gas feed that are transferred to the liquid phase. Below this value, washout occurs, because the oxygen partial pressure in the gas bubbles is zero. Above this value, oxygen mass transfer does not have a strong influence on the performance of the reactor during normal operation. Notice that, even though the conversion of pyrite (the performance variable) is unaffected in the plateau region, the concentration of oxygen is not constant. Pinches et al. (1988) reported
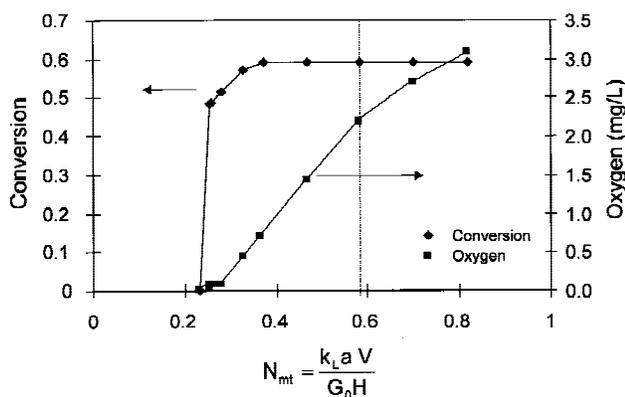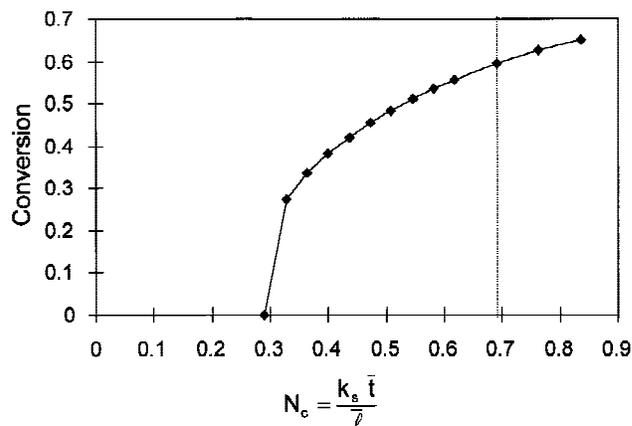
results that are in agreement with those shown in Figure 6 with respect to both the conversion and the oxygen concentration. Monitoring the concentration of oxygen will indicate the proximity of the operation to this washout condition. The maximum value of N_{mt} is 1, which sets the minimum gas flow rate required.

These results indicate that there are essentially only two operating points with respect to both bacterial oxidation rate and oxygen mass transfer: (i) either the reactor is operational and insensitive to these parameters; or (ii) the reactor is not operational due to the insufficient rate of mass transfer or the insufficient rate of oxidation of ferrous ions. This result is not only a characteristic of bacterial leaching reactors. The sensitivity analysis of the pressure oxidation reactor for the leaching of zinc sulfide produced similar results (Crundwell and Bryson, 1992).

The effect of the leaching number, N_c, on the performance of a single tank reactor is shown in Figure 7. This figure indicates that the performance of the reactor is dependent on the leaching number over the whole range. At values of the leaching number below about 0.29, the reactor does not operate because washout occurs. This washout condition is a result of the mineral dissolving so slowly that the rate of supply of substrate (ferrous ions) is insufficient to sustain the rate of bacteria growth. This is the cause of the washout phenomenon shown in Figure 2, and is the most critical condition for the reactor operating with the parameters given in Table III. As the leaching number increases from this critical value, the conversion increases over the whole range.

The results shown in Figures 5, 6, and 7 demonstrate the unique nature of the bacterial leaching reactor: there are three washout conditions dependent on the three dimensionless parameters of the model. The washout condition closest to normal operating conditions found by decreasing the residence time is that due to the leaching number. Washout at this condition can be prevented by decreasing the mean particle size, increasing the temperature, or increasing the

Figure 6. The sensitivity of the conversion and the oxygen concentration to the mass transfer number, N_{mt}. The results show that the conversion rises rapidly to a constant value as N_{mt} increases from the washout condition. The dashed line indicates the position of the operating point for the parameters given in Table III.

Figure 7. The sensitivity of the conversion to changes in the leaching number, N_c. The results show the washout condition related to the leaching rate. The dashed line indicates the position of the operating point for the parameters given in Table III.

residence time. Note that if there is more than one mineral in the system, then there is a washout condition for the N_C for each of these minerals.

The results shown in Figure 7 indicate that the only way to improve the performance of the reactor is to increase the leaching number. This is the strategy adopted in the bioprocessing of chalcopyrite (Kruger and Du Preez, 1999). The kinetics of dissolution of this mineral are too slow at 40°C, the temperature commercially used in bacterial leaching of pyrite and arsenopyrite concentrates. However, at temperatures in excess of 70°C, the rate of leaching increases sufficiently that the leaching number is above the washout condition. This means that acceptable reactor performance is attained (Kruger and Du Preez, 1999). These temperatures require thermophilic organisms, which explains the increase in commercial interest in iron- and sulfur-oxidizing archae. Because another method of increasing the leaching number is to decrease the particle size, chalcopyrite concentrates leached in the presence of thermophiles may be ground to a mean size of between 10 and 20 μm (Kruger and Du Preez, 1999).

THE EFFECT OF ONE MINERAL ON THE LEACHING OF ANOTHER

An interesting observation is that the leaching of one mineral may affect the rate of leaching of another, particularly when the reactor is close to the washout condition due to the leaching number, N_c. Consider a mineral in which the conversion is zero because the rate of dissolution is too slow. The addition of a small amount of a second mineral that has a high rate of dissolution to the feed results in an increase in the amount leached from the first mineral. This is due to the second mineral providing dissolved iron in sufficient quantity to produce significant leaching of the first mineral. For example, if the rate constant of the leaching of pyrite was 1.46×10^{-9} m/min and the other parameters were the same as those in Table III, then the conversion of pyrite is zero. However, the addition of 15 mol% of arsenopyrite with a rate constant of 7.8×10^{-9} m/min causes the conversion of pyrite to increase from zero to 29%. The conversion of the arsenopyrite is 72%. This result may explain many of the observations that have relied on "galvanic interactions" for explanation.

STOICHIOMETRY AND THE DEBATE CONCERNING DIRECT VERSUS INDIRECT MECHANISM

The mathematical description of the reactor presented here is based on the mechanism of bacterial oxidation of ferrous ions to ferric ions, and the oxidation of the minerals by the ferric ions. Thus, there is no direct relationship between the amount of bacteria grown, and the amount of pyrite oxidized. However, the calculations indicate that the number of bacteria produced is linearly proportional to the amount of pyrite oxidized. This is shown in Figure 8. The slope of the
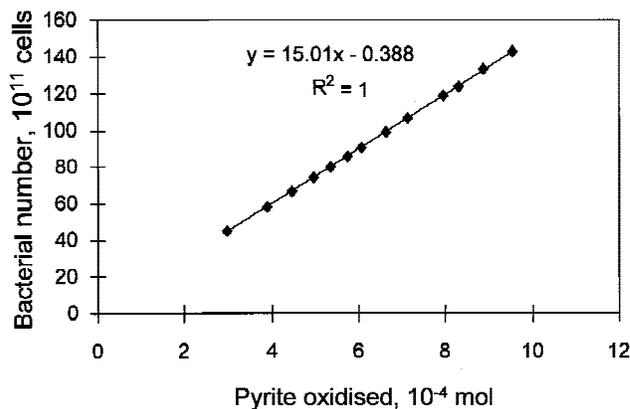
Figure 8. The pseudo-stoichiometry between the number of cells grown in the reactor against the amount of pyrite oxidized in the reactor. The slope of the line is 15, corresponding to the stoichiometry of between ferrous ions and pyrite in Reaction (2).

line in Figure 8 represents a pseudo-yield coefficient between the bacteria and the pyrite in this model. The value of the slope value is 15×10^{11} cells/mol FeS_2, which is exactly 15 times the value of the yield coefficient used, which had a value 1×10^{11} cells/mol Fe^{2+}. The factor of 15 is a direct result of the stoichiometry of Reaction (2), representing the stoichiometric relationship between pyrite and ferrous ions in Reaction (2).

This result shows that stoichiometric analysis cannot distinguish between the direct and the indirect mechanism. Although this is a model of a continuous reactor, similar conclusions are obtained from the analysis of batch experiments. In spite of this conclusion, stoichiometric analysis has been the basis of many studies. For example, Konishi et al. (1994) reported stoichiometric yield coefficients for the growth of bacteria on various substrates. These data were used to argue in favor of the direct mechanism. However, a closer inspection of the data indicates that it reflects the underlying stoichiometry of the leaching reactions, in the same way in which the relationship shown in Figure 8 reflects the underlying stoichiometry of Reaction (2).

OPTIMIZATION OF THE PERFORMANCE OF BACTERIAL LEACHING PLANTS

It has long been realized that bacterial leaching is improved by the operation of a primary reactor followed by smaller secondary reactors in series. Bacterial leaching is an autocatalytic system, and this arrangement of reactors simulates the classical configuration of a CSTR followed by a plug-flow reactor that optimizes the performance of an autocatalytic reaction.

Consider a plant required to treat the material given in Table III. The plant consists of a primary reactor, followed by secondary reactors that are of equal size. Because a plant of the higher capacity will always have a higher conversion than a smaller plant, the overall plant size is (arbitrarily) limited to 560 m^3. How many reactors, and of what size

should they be in order to optimize the amount of pyrite leached from this concentrate?

A number of simulations were performed with different ratios of the size of the primary tank to that of the second tank, and for a differential total number of tanks. The results are shown in Figure 9. It is clear from these results that the greater the number of tanks in series, the greater the overall conversion. In addition, for any given number of tanks in the configuration, there is an optimum ratio of the size of the primary vessel to that of the whole plant. This optimum depends on the number of tanks in the configuration. It is clear that the condition of equally sized tanks is not the optimal arrangement; however, the difference in conversion between equally sized tanks and the optimum is, in most cases, about 1%. In most cases, the size of the primary tank must be between 1.5 and 2 times the size of one of the secondary tank in the series.

CONCLUSIONS

A critical factor in the bacterial leaching process is size distribution of the feed, and the rate of particle shrinkage in the reactor. It is shown that the analysis of these phenomena gives rise to a dimensionless leaching number, N_c. The relationship between bacterial leaching, pressure leaching and leaching after fine grinding is explained by N_c.

The agreement between the predictions of the model and the data from three pilot plants was shown to be excellent.

A detailed sensitivity of bacterial leaching showed that the most critical washout condition under practical operating conditions is associated with N_c, and not with the bacterial growth rate. This analysis also showed that the only way to improve the performance of the leaching reactor is to increase the value of N_c.

The model shows that a pseudo-stoichiometric relationship exists between bacterial growth and mineral leaching. This result shows that the determination of the mechanism of bacterial leaching by stoichiometric argument is invalid. Furthermore, the model shows that the addition of a small 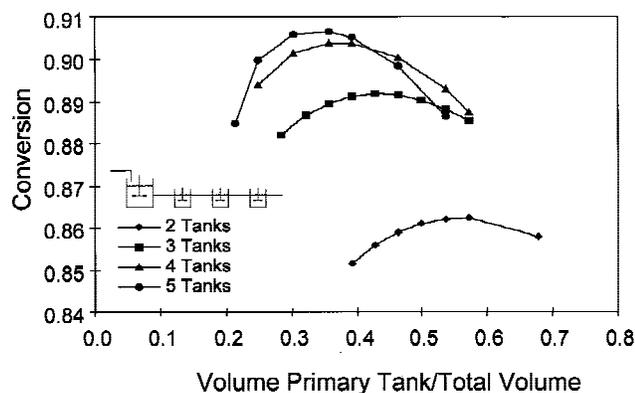amount of a mineral that has a high rate of dissolution can improve the performance of a mineral with a low rate of dissolution. This may account for many of the observations that have relied on "galvanic interactions" for explanation.

NOMENCLATURE

$\tilde{C}$	vector of concentration (mol/L)
$f(C)$	function of concentration (dimensionless)
G_{O_2}	molar flow rate of oxygen in the gas phase (mol/min)
G	molar flow rate of air in the gas phase (mol/min)
H	Henry's law constant for oxygen (L/mol)
k_s	intrinsic rate constant for the leaching reaction (m/min)
K_s	constant in the Monod growth equation (mol/L)
K_{Fe}	constant in the Monod growth equation (dimensionless)
K_i	constant in the Monod growth equation (dimensionless)
K_{O_2}	constant in the Monod growth equation (mol/L)
ℓ	particle size (m)
ℓ^*	dimensionless particle size (m)
$\bar{\ell}$	mean particle size (m)
Q	volumetric flow rate (m³/min)
$n(\ell)$	particle size distribution on a number basis (1/m)
N_C	dimensionless leaching number
N_{mt}	dimensionless mass transfer number
N_{Fe}	dimensionless bacterial growth rate
R	linear leaching kinetics (m/min)
$r_{Fe^{2+}}$	rate of oxidation of ferrous ions (mol/m³ · min)
r_{FeS_2}	overall rate of leaching (of pyrite) (mol/m³ · min)
$\bar{t}$	mean residence time (min)
V	solution, i.e., ungassed, volume of reactor (m³)
X	conversion (dimensionless)
Y	yield coefficient of bacterial cells to moles of ferrous ions (cell/mol)
μ	bacterial growth rate (1/min)
μ_{max}	maximum bacterial growth rate (1/min)

Subscript

0	inlet conditions

Figure 9. The effect of the ratio of the size of the first tank to the size the total plant on the performance of the plant.

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