

Technical Note

Kinetic modeling for the bacterial leaching of chalcopyrite catalyzed by silver ions

M. Wang *, Y. Zhang, T. Deng, K. Wang

College of Materials and Bioengineering, Chengdu University of Technology, Chengdu 610059, PR China

Received 23 May 2003; accepted 28 November 2003

Abstract

The mechanism of bacterial leaching of chalcopyrite catalyzed by silver ions is studied in this paper. The copper and iron ions in the chalcopyrite crystal lattice are replaced by the silver ions, the silver ions then combining with the sulfur to form silver sulfide. The ferrous ions are oxidized to ferric ions by the *thiobacillus ferrooxidans*. The ferric ions can convert the silver sulfide into silver ions. Using this mechanism, a new kinetic model of bacterial leaching of chalcopyrite in the presence of silver ions was established. The model accurately predicts the copper recovery rate in the bacterial leaching of chalcopyrite in the presence of silver ions.

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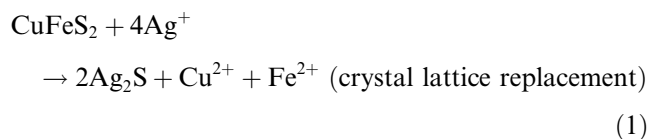
Keywords: Hydrometallurgy; Bioleaching; Modeling; Sulfide ores; Particle size

1. Introduction

Bioleaching metallurgy is attracting ever more attention in mineral processing. The extraction of valuable metal from sulfide ores by bacterial leaching is widely used in many countries (Qiu, 1995). The kinetic process of bacterial leaching of chalcopyrite has been well studied, and many mathematical models of the bacterial leaching of chalcopyrite have been established (Bhattacharya et al., 1990; Neuburg et al., 1991). In order to improve the copper leaching rate and recovery rate, the studies have concentrated on enhancing bacterial leaching through chemical and physical methods, e.g. by adding a small quantity of silver ions (Coto et al., 1993), or by applying a magnetic field (Wang et al., 2000). Studies on the kinetic mechanism of bioleaching catalyzed by metallic ions are rare, and articles on bioleaching catalyzed by silver ions are non-existent. In this paper, the kinetic modeling of bacterial leaching of chalcopyrite catalyzed by silver ions has been studied, and a new kinetic model has been established.

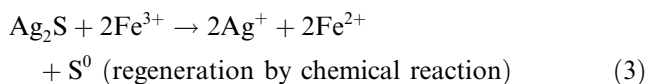
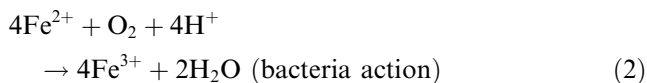
The bioleaching recovery rate of chalcopyrite in the presence of silver ions is far larger than that of bacterial

leaching free of silver ions. The authors consider that the covalent radius value of the silver ions is similar to that of the copper and ferrous ions which are leached in the system (Wang et al., 1997). Furthermore, the outer electrons distribution structures of silver, copper and ferrous ions, such as $nd^{6-10}(n+1)s^0$, are also similar to one another. The electronegativity of catalyzing silver ions and the leached metallic ions is also similar (between 1.7 and 2.0), and both the catalyzing and leached ions can combine easily with sulfur to form a covalent structure. The nature and structure of these metallic ions are similar enough that the silver ions can replace the copper and ferrous ions in chalcopyrite and then form a flat, loose silver sulfide film on the surface of the mineral grain. Ferrous ions are oxidized to ferric ions through the bacterial action. The silver sulfide can then be transformed back to silver ions by the action of the ferric ions oxidation. The silver ions can replace the copper in the chalcopyrite by circulation. Therefore, the silver ions-catalyzing-bacterial leaching can be considered as the indirect bioleaching mechanism, and the major reactions are as follows (Hu et al., 2001; Wang et al., 1997):



* Corresponding author. Tel.: +86-28-84079015; fax: +86-28-84079074.

E-mail addresses: wmh@cdut.edu.cn (M. Wang), dtl@cdut.edu.cn (T. Deng).



G	grade of sulfide mineral
β	kinetic factor (constant)
$C(\text{Fe}^{3+})$	concentration of ferric ions
t	leaching time
ρ	density of the sulfide
ϕ	shaping factor of sulfide particle
σ	chemometrics constant
D_{eff}	efficient diffusing coefficient
K_c	resistance constant

2. Description of the model

One of the main controversies in bioleaching concerns the bioleaching mechanism and kinetic modeling, i.e. whether the direct bioleaching mechanism or the indirect bioleaching mechanism has been considered. If the modeling is based on the direct bacterial leaching mechanism, it is therefore based on the sulfides acting as nutriment for the bacteria, and the presumption that the growth character of the bacteria should accord with the Monod equation (Herrera et al., 1989). For example, Bhattacharya et al.'s mathematical modeling of the bioleaching of chalcopyrite (Bhattacharya et al., 1990). However, some models assume that the character of the bacteria, both on the surface of chalcopyrite and in the leaching solution, should accord with the Langmuir adsorption isothermal equation (Asia et al., 1992).

According to the direct bioleaching mechanism, the bacteria are adsorbed onto the surface of the sulfides minerals and can oxidize the sulfides. However, according to the indirect bioleaching mechanism, the bacteria oxidize the ferrous ions into ferric ions and then the ferric ions oxidize the sulfides. During the process of the bioleaching of chalcopyrite catalyzed by silver ions, Eq. (1) presents the process of silver ions crystal lattice replacement, where silver ions replace copper and ferrous ions in the chalcopyrite. The main role of the bacteria is to oxidize the ferrous ions into ferric ions, so the bacteria's role cannot be neglected. The lixiviating solvent is ferric ions during the oxidation of sulfides without silver ions, whereas in the bioleaching of chalcopyrite catalyzed by silver ions the lixiviating solvent is silver ions.

During the bioleaching process, where ferric ions act as the lixiviating solvent, the radius change of the mineral particle with leaching time can be expressed by the following equation (Herrera et al., 1989):

$$\frac{-dr_i}{dt} = \frac{M_S}{\rho G \phi} \frac{C(\text{Fe}^{3+})}{\left[\frac{1}{G\beta} + \frac{\sigma}{D_{\text{eff}}} \frac{r_i}{r_{i0}} (r_{i0} - r_i) + \frac{\sigma}{K_c} \left(\frac{r_i}{r_{i0}} \right)^2 \right]} \quad (5)$$

The denotions of the symbols are as follows:

r_i	radius of sulfide particle
M_S	molecular weight of the sulfide
r_{i0}	initial radius of sulfide particle

It is suggested that the behavior of silver ions in the bioleaching of chalcopyrite catalyzed by silver ions is the same as that of ferric ions in the bioleaching process of chalcopyrite without silver ions, and that the kinetic equation be expressed as follows:

$$\frac{-dr_i}{dt} = \frac{M_S}{\rho G \phi} \frac{C(\text{Ag}^+)}{\left[\frac{1}{G\beta} + \frac{\sigma}{D_{\text{eff}}} \frac{r_i}{r_{i0}} (r_{i0} - r_i) + \frac{\sigma}{K_c} \left(\frac{r_i}{r_{i0}} \right)^2 \right]} \quad (6)$$

Compared with Eq. (5), only $C(\text{Fe}^{3+})$ is replaced by $C(\text{Ag}^+)$ in Eq. (6). The physical meaning of the remaining parameters in Eq. (6) is the same as those in Eq. (5), and some of the parameter's values should be adjusted correspondingly.

The first item in the square brackets in the denominator of Eq. (6) denotes the shape factor of the mineral particles and the kinetics of the dissolution. The second item in the square brackets denotes the diffusion of the leaching solution in the mineral particles and the third item denotes the resistance when silver ions in the leaching solution diffuse into the particles. It is not convenient to measure the radius of the mineral particles during the process of bioleaching. The change in particle radius can be expressed by Eq. (7)

$$\alpha = 1 - \left(\frac{r_i}{r_{i0}} \right)^3 \quad (7)$$

the α in Eq. (7) is the leaching rate, Eq. (8) can be gained after integral disposal when Eq. (6) is combined with Eq. (7):

$$\begin{aligned} \frac{d\alpha}{G\beta(1-\alpha)^{\frac{2}{3}}} + \frac{\sigma r_{i0}}{D_{\text{eff}}} \frac{d\alpha}{(1-\alpha)^{\frac{2}{3}}} + \left(\frac{\sigma}{K_c} - \frac{\sigma}{D_{\text{eff}}} \right) d\alpha \\ = \frac{3M}{\phi_{i0} G r_{i0} \rho} C(\text{Ag}^+) dt \end{aligned} \quad (8)$$

Eq. (8) is the mathematical model of the bioleaching of chalcopyrite catalyzed by silver ions and this model can predict the recovery rate of copper in the chalcopyrite bioleaching process.

The $C(\text{Ag}^+)$ in the right of the Eq. (8) denotes the concentration of silver ions in the bioleaching solution. However, the concentration in the experiment is very low, and does not remain constant throughout the bioleaching process, so the concentration of silver ions should be further disposed in the model.

After the silver ions were added, the silver ion concentration decreased rapidly during the initial stage of bioleaching. The silver ion concentration then increased slowly during the rest of the bioleaching stage. The main reason for the silver ion concentration “drop” is that the silver ions can combine easily with sulfide or the elemental sulfur into a silver sulfide deposit. In fact, during the initial stage the copper recovery rate was very low because time was needed for the *thiobacillus ferrooxidans* to adapt themselves to the new conditions. Assuming the silver ions played a tiny role in this stage, the initial value of the concentration of silver ions was approximately equal to zero. The silver ion concentration can be disposed by linearity regression, the factors, such as the leaching time X_1 , the initial concentration of silver ions X_2 , the initial particles radius of chalcopyrite X_3 and the bacteria inoculation being considered. The silver ion concentration linear regression equation in the leaching solution is as follows, with Y being the concentration of silver ions.

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 \quad (9)$$

Integrate and simplify Eq. (8), and a new mathematical model can be gained after linearity regression disposal of the concentration of silver ions.

$$\frac{3}{G\beta} \left[1 - (1 - \alpha)^{\frac{1}{3}} \right] + \frac{3\sigma r_{i0}}{2D_{\text{eff}}} \left[1 - (1 - \alpha)^{\frac{2}{3}} \right] + \left(\frac{\sigma}{K_c} - \frac{\sigma}{D_{\text{eff}}} r_{i0} \right) \alpha = \frac{3Mt}{\phi_{i0} Gr_{i0} \rho} \left(\frac{a}{2} t + b \right) \quad (10)$$

Y is equal to $(\frac{a}{2}t + b)$, and the a and b in Eq. (10) denote the coefficient only related to time.

3. Roots of the equations

Eq. (10) is an equation about the fractional exponent, and it is a complicated equation. There are two variables in this equation, leaching rate α and time t . To gain the roots of this equation, the displacement and Newton iterative methods should be used.

4. Experiments

4.1. Chalcopyrite analysis

The chalcopyrite concentrate used in this study was sampled from a copper mine in Pengzhou, Sichuan Province, China. The chalcopyrite was analyzed by X-ray diffraction. The main ingredients were pyrite, chalcopyrite, and quartz. The total copper content reached 0.97%. The ore was analyzed by phase analysis and the copper content in the free copper oxide minerals reached 1.65% of the total copper content. The copper content of the combined copper oxide minerals reached 17.34% of

the total content. The copper reached 75.13% in the primary copper sulfides, 5.88% in the secondary copper sulfides. The following elements were found by chemical analysis: Cu 0.97%, Fe 17.32%, SiO₂ 35.14%, CaO 8.12%, Al₂O₃ 6.48%, MgO 5.21%.

4.2. Experimental method

All experiments were carried out in 250 ml bottom baffled Erlenmeyer flasks containing 5.0 g concentrate sample and 90 ml of the iron-free 9 K liquid substrate, and were inoculated with a 10 ml solution of *thiobacillus ferrooxidans*. The concentration of the bacterial inoculum was 2×10^7 singles/ml. The pH value of the solution was kept to 2 using 1:1 H₂SO₄. Silver ions were added, then the sample was weighed. The leaching solution was placed in a shaking flask, with a surging speed of 120 rpm and a temperature of 30 °C. The pH value of the solution was determined periodically and adjusted to pH 2. Evaporated water was replaced periodically by the addition of distilled water. One milliliter of clarified solution was removed from the leaching solution and the copper ion concentration was determined. Nine kelvin liquid substrate was added to offset against the sample loss.

4.3. Analysis methods

The numbers of *thiobacillus ferrooxidans* were counted with a hemocyte classifying counter under a biology microscope. The pH value of the sample solution was determined with a pH meter.

5. Validation of the kinetic modeling

The mineral leaching experiments were performed using 50, 100, 200 mesh particles. The parameter values for the different particle sizes are as follows. Comparisons between the modeling data and the experimental data are illustrated in Figs. 1–3.

It is shown in Fig. 1 that the kinetic model data is in good agreement with the experimental data for leaching

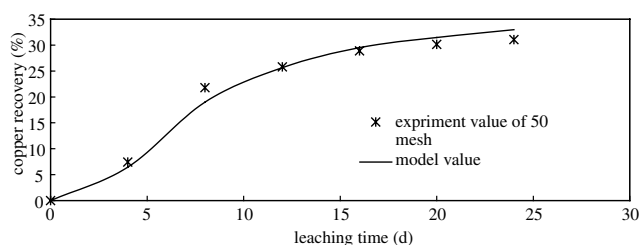


Fig. 1. Comparison between the modeling data and experimental data for leaching of minerals of particle size of 50 mesh.

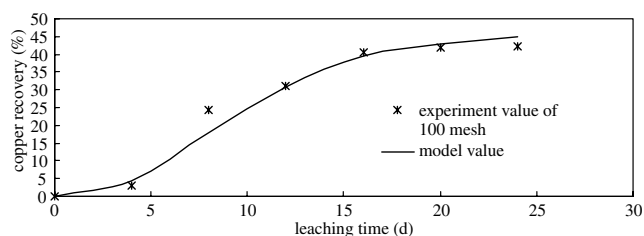


Fig. 2. Comparison between the modeling data and experimental data for leaching of minerals of particle size of 100 mesh.

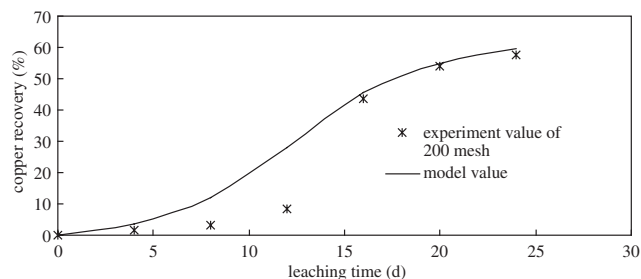


Fig. 3. Comparison between the modeling data and experimental data for leaching of minerals of particle size of 200 mesh.

of minerals of a particle size of 50 mesh. The increase in copper recovery with leaching time of the experimental data also agrees with that of the kinetic model data. The parameter values will vary with the particle size of the sulfides. Several parameter values that are affected by particle size are listed in Table 2, and the unchangeable parameter values are shown in Table 1.

Fig. 2 also shows that the kinetic model data is in good agreement with the experimental data. The fact that the experimental values for chalcopyrite of particle size of both 50 and 100 meshes are in good agreement with the modeling values shows that the modified kinetic model for the bacterial leaching of chalcopyrite cata-

Table 1
Modeling parameters value for particle size of 50 mesh

Name	Symbol	Value	Origination
Chalcopyrite grade	G	0.02	Determined
Initial particle radius	r_{i0}	0.0355 cm	Determined
Density of ore	ρ	2.7 g/cm ³	Neuburg et al. (1991)
Factor of kinetics	β	7.4×10^{-8} cm s ⁻¹	Herrera et al. (1989)
Particle shape factor	ϕ_{i0}	1.0	Herrera et al. (1989)
Stoichiometrical factor	σ	4	Calculated
Resistance constant	K_c	1.1×10^{-4}	Estimated
Diffusing coefficient	D_0	8.82×10^{-6} cm ² s ⁻¹	Neuburg et al. (1991)
Initial particle	ε_0	1.5×10^{-2}	Determined

Table 2
Modeling parameters value for particle size of 100 mesh

Name	Symbol	Value	Origination
Initial particle radius	r_{i0}	0.015 cm	Determined
Kinetic factor	β	6.5×10^{-8}	Determined
Mass transfer resistance constant	K_c	9.2×10^{-3}	Estimated

Table 3
Modeling parameters value for particle size of 200 mesh

Name	Symbol	Value	Origination
Initial particle radius	r_{i0}	0.0076 cm	Determined
Kinetic factor	β	3.7×10^{-8}	Determined
Mass transfer resistance constant	K_c	7.2×10^{-3}	Estimated

lyzed by silver ions conforms well to the leaching mechanism (Table 3).

It can be seen from Fig. 3 that the kinetic model values are in good agreement with the experimental values after day 15. However, during the period prior to day 15 there is much difference between the experimental values and the kinetic model values. In particular, the experiments performed on day 8 and day 12. This could indicate that the lag phase of the bacterial growth is fairly long compared to the smaller particle size of chalcopyrite during the prior period of bioleaching. As a result, the recovery rate of the experiment is lower than that of the kinetic model.

6. Conclusion

Based on the shrinking core model, a modified kinetic model is established in this paper for chalcopyrite bioleaching catalyzed by silver ions. The copper recovery obtained from the experiments accords well with that calculated from the kinetic model. The modified model can explain the phenomena occurring in the bioleaching solution. Both the theoretical studies and experimental results have shown that the rate-controlling step during the bioleaching is the silver ions replacement of metallic ions in the chalcopyrite. The diffusion of silver ions in the chalcopyrite particle is a key step. The modified kinetic model clearly shows that silver ions play an important role in chalcopyrite bioleaching catalyzed by silver ions.

Acknowledgements

A key subject project financial contribution from the Ministry of National Land Resources of PR China to Prof. M.H. Wang is gratefully acknowledged.

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