

Modeling and Simulation of Enargite Bioleaching*

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Abstract A mathematical model for enargite bioleaching at 70°C by *Sulfolobus* BC in shake-flasks has been constructed. The model included (1) the indirect leaching by Fe³⁺ and Fe³⁺ regeneration by suspended *Sulfolobus*, and (2) the direct leaching by the attached *Sulfolobus*. The model parameters were optimized using genetic algorithm (GA). Simulations of the ferric leaching and bioleaching processes were done using this model. The dynamic changes of the concentrations of Cu²⁺, As³⁺, As⁵⁺, Fe³⁺ and/or Fe²⁺, as well as ferric-arsenate precipitation were accurately predicted.

Keywords bioleaching, ferric leaching, enargite, modeling, arsenic, redox potential

1 INTRODUCTION

Bioleaching is more economical and environmental friendly than the traditional metallurgy technologies, such as pressured oxidation and roasting, especially for low-grade and/or arsenic-bearing refractory ores [1–3]. However, in order to make the bioleaching process completely successful, the operation parameters that affect the bioleaching processes need to be optimized. Therefore, mechanistically based kinetic models are required for the design, optimization and control of bioleaching processes [4].

Bioleaching efficiency is strongly affected by the types of the ores. The sensitivities of different types of sulfide minerals to bioleaching are quite different [5]. Enargite, which is known to be refractory, is the main arsenic-bearing mineral in copper ores [6, 7]. Enargite has been less studied than other well-known sulphur minerals [8]. Only a few studies on the bioleaching of enargite are available [9], and few of them are on the process modeling. In this study, a comprehensive mathematical model for bioleaching of enargite is developed, and the bioleaching process is analyzed using the mathematical model and simulation.

2 THEORETICAL BASIS

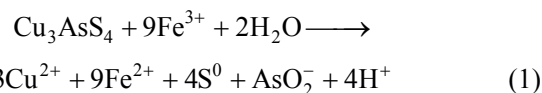
Enargite ferric leaching was performed in shake-flasks using 2.0 g mineral samples of a granulometric size of 104–147 μm in 100 ml of basal medium with 1.00 g·L⁻¹ Fe³⁺ at pH 1.6 and 70°C, reported by Escobar *et al.* [10]. The flasks were periodically analyzed for pH and *E_h*. Ferrous and total irons were analyzed using the ophenanthroline colorimetric method. Total arsenic and copper concentrations in the leaching solution were determined using atomic absorption spectrophotometry. It was regarded that arsenic in enargite was solubilized to produce As³⁺ at first, and then oxidized to As⁵⁺ [11, 12], while sulfur in enargite was initially oxidized to produce S⁰ other than

sulfide [9, 11, 12]. The enargite ferric leaching model includes four reactions [Eqs. (1), (3), (4) and (6)], four rate equations [Eqs. (7)–(9) and (15)], and seven mass balance equations [Eqs. (16)–(22)]. $r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}}$ in Eqs. (16), (18) and (20), and $r_{\text{Fe}^{2+}}$ in Eqs. (17) and (22) were set to zero in the enargite ferric leaching model.

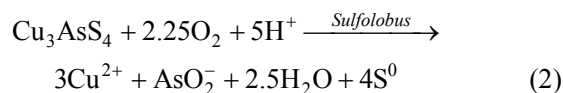
Enargite bioleaching was performed using 2.0 g mineral samples of a granulometric size of 104–147 μm in 100 ml of basal medium with 1.00 g·L⁻¹ Fe³⁺ and 5 ml *Sulfolobus* BC [10] culture broth at pH 1.6 and 70°C, reported in the same article by Escobar *et al.* [10]. Concentrations of bacteria in solution were determined microscopically by direct counting using Petroff-Hauser chamber. The model of enargite bioleaching includes two kinds of mechanisms, which are ferric leaching of enargite (indirect leaching mechanism) and bioleaching of enargite (direct leaching mechanism), six reactions, nine rate equations [Eqs. (7)–(15)], and nine mass balance equations [Eqs. (16)–(24)].

2.1 Reactions

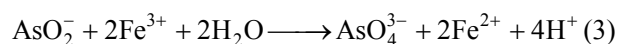
Ferric leaching of enargite:



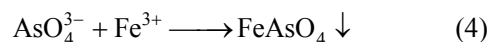
Direct bioleaching of enargite by attached *Sulfolobus*:



Oxidation of As³⁺ to As⁵⁺:



Precipitation of ferric arsenate:

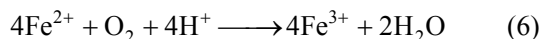
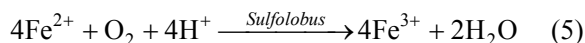


Oxidation of Fe²⁺ to Fe³⁺ by *Sulfolobus* or oxygen:

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2.2 Rate equations

Enargite leaching by ferric:

$$V_{\text{Cu}_3\text{AsS}_4} = \frac{-r_{\text{Cu}_3\text{AsS}_4}}{C_{\text{Cu}_3\text{AsS}_4}} = \frac{V_{\text{Cu}_3\text{AsS}_4}^{\max}}{1 + B_1 \cdot \frac{C_{\text{Fe}^{2+}}}{C_{\text{Fe}^{3+}}}} \cdot \frac{C_{\text{Fe}^{3+}}}{K_{\text{Fe}^{3+}} + C_{\text{Fe}^{3+}}} \quad (7)$$

Oxidation of As^{3+} to As^{5+} by Fe^{3+} :

$$V_{\text{AsO}_2} = \frac{-r_{\text{AsO}_2}}{C_{\text{AsO}_2}} = \frac{V_{\text{AsO}_2}^{\max}}{1 + B_2 \cdot \frac{C_{\text{Fe}^{2+}}}{C_{\text{Fe}^{3+}}}} \quad (8)$$

Precipitation of ferric arsenate:

$$r_{\text{precip}} = k_{\text{precip}} \cdot C_{\text{AsO}_4^{3-}} \cdot C_{\text{Fe}^{3+}} \quad (9)$$

Growth of suspended *Sulfolobus*:

$$\mu = \frac{\mu_{\max}}{1 + \frac{K_s}{C_{\text{Fe}^{2+}}}} \cdot \left(1 - \frac{C_{X_{\text{liquid}}}}{C_{X_{\text{liquid}}}^{\max}}\right) \cdot \left(1 - e^{-\frac{t}{t_L}}\right) \quad (10)$$

Fe^{2+} consumption by suspended *Sulfolobus*:

$$q_{\text{Fe}^{2+}} = \frac{-r_{\text{Fe}^{2+}}}{C_{X_{\text{liquid}}}} = \frac{\mu}{Y_{\text{Fe}^{2+}, X}^{\max}} + m_{\text{Fe}^{2+}} \quad (11)$$

Growth of attached *Sulfolobus* [13]:

$$r_{X_{\text{adsorb}}} = k_{\text{dl}} \cdot C_{X_{\text{adsorb}}} \cdot C_{\text{Cu}_3\text{AsS}_4} \cdot (1 - \theta) \quad (12)$$

where,

$$\theta = \frac{C_{X_{\text{adsorb}}}}{C_{X_{\text{adsorb}}}^{\max}} \quad (13)$$

Direct bioleaching of enargite by attached *Sulfolobus* [13]:

$$r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}} = \frac{-r_{X_{\text{adsorb}}}}{Y_N} \quad (14)$$

Oxidation of Fe^{2+} to Fe^{3+} by oxygen:

$$r_{\text{Fe}^{3+}}^{\text{O}_2} = k_{\text{Fe}^{3+}}^{\text{O}_2} \cdot C_{\text{Fe}^{2+}} \quad (15)$$

The specific enargite oxidation rate [Eq. (7)] and the specific As^{3+} oxidation rate [Eq. (8)] were modeled using a modified Michaelis-Menten-type equation, which was used in pyrite bioleaching [17]. Eq. (7) was expressed in terms of ferric iron concentration, which was the substrate of the reaction, and ferric/ferrous iron ratio, which was related to the redox potential. Eq. (8) was controlled by the ferric/ferrous iron ratio.

The specific growth rate of bacteria in liquid [Eq.

(10)] was described using a modified Monod-type equation with ferrous iron as the substrate. Both the lag growth phase and the stationary growth phase can be described using Eq. (10). Ferrous iron consumption was owing to both bacteria growth and maintenance. The specific ferrous iron consumption rate [Eq. (11)] was described using Pirt equation.

Equations 12–14 were proposed by Asai [13]. The rate of ferric arsenate precipitation [Eq. (9)] was assumed to be proportional to the concentrations of AsO_4^{3-} and ferric iron. The rate of Fe^{2+} oxidation by oxygen [Eq. (15)] was assumed to be proportional to the concentration of ferrous iron in solution.

2.3 Mass balances

$$\frac{dC_{\text{Cu}_3\text{AsS}_4}}{dt} = r_{\text{Cu}_3\text{AsS}_4} + r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}} \quad (16)$$

$$\frac{dC_{\text{Fe}^{3+}}}{dt} = 9 \cdot r_{\text{Cu}_3\text{AsS}_4} + 2 \cdot r_{\text{AsO}_2} - r_{\text{precip}} - r_{\text{Fe}^{2+}} + r_{\text{Fe}^{3+}}^{\text{O}_2} \quad (17)$$

$$\frac{dC_{\text{Cu}^{2+}}}{dt} = -3 \cdot r_{\text{Cu}_3\text{AsS}_4} - 3 \cdot r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}} \quad (18)$$

$$\frac{dC_{\text{As, total}}}{dt} = -r_{\text{Cu}_3\text{AsS}_4} - r_{\text{precip}} - r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}} \quad (19)$$

$$\frac{dC_{\text{As}^{3+}}}{dt} = -r_{\text{Cu}_3\text{AsS}_4} + r_{\text{AsO}_2} - r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}} \quad (20)$$

$$\frac{dC_{\text{As}^{5+}}}{dt} = -r_{\text{AsO}_2} - r_{\text{precip}} \quad (21)$$

$$\frac{dC_{\text{Fe}^{2+}}}{dt} = -9 \cdot r_{\text{Cu}_3\text{AsS}_4} - 2 \cdot r_{\text{AsO}_2} + r_{\text{Fe}^{2+}} - r_{\text{Fe}^{3+}}^{\text{O}_2} \quad (22)$$

$$\frac{dC_{X_{\text{liquid}}}}{dt} = C_{X_{\text{liquid}}} \cdot \mu \quad (23)$$

$$\frac{dC_{X_{\text{adsorb}}}}{dt} = \frac{r_{X_{\text{adsorb}}}}{C_{\text{Cu}_3\text{AsS}_4}} \quad (24)$$

3 RESULTS AND DISCUSSIONS

3.1 Ferric leaching of enargite

The seven first-order differential equations [Eqs. (16)–(22)] were solved using the fourth ordered Runge-Kutta method. The values of the model parameters were optimized by minimizing the sum of the relative squared errors between the model predictions and the experimental data using GA [14, 15]. The results of the parameter optimization are shown in Table 1. The results of the simulation of the enargite ferric leaching process are shown in Figs. 1–3.

Table 1 Kinetic parameters for the ferric leaching of enargite

B_1	B_2	$K_{\text{Fe}^{3+}} / \text{mmol} \cdot \text{L}^{-1}$	$k_{\text{precip}} / \text{L} \cdot \text{h}^{-1} \cdot \text{mmol}^{-1}$	$k_{\text{Fe}^{3+}}^{\text{O}_2} / \text{h}^{-1}$	$V_{\text{Cu}_3\text{AsS}_4}^{\max} / \text{h}^{-1}$	$V_{\text{AsO}_2}^{\max} / \text{h}^{-1}$
19.8	3.59	14.5	2.07×10^{-3}	2.90×10^{-3}	6.09×10^{-2}	8.16×10^{-2}

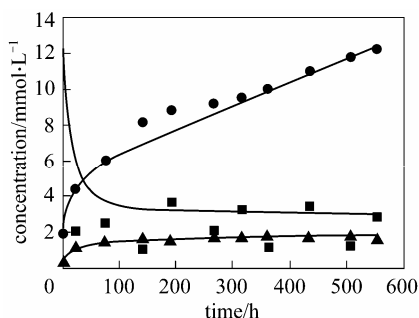


Figure 1 The concentrations of Fe^{3+} , Cu^{2+} , and total dissolved arsenic during the ferric leaching (Lines represent model simulations, and symbols represent experimental data)

■ Fe^{3+} ; ● Cu^{2+} ; ▲ total dissolved arsenic

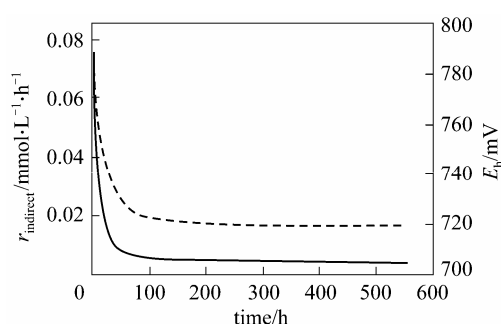


Figure 2 The plots of E_h versus indirect leaching rate (r_{indirect}) during the ferric leaching of enargite

— r_{indirect} ; --- E_h

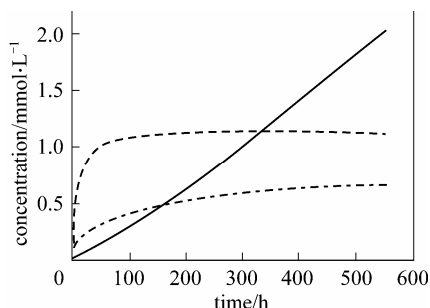


Figure 3 The time course of As^{3+} , As^{5+} and precipitated ferric arsenate concentrations during the ferric leaching of enargite

--- As^{3+} ; As^{5+} ; — precipitated arsenic

The ferric leaching kinetic equation, Eq. (7), was expressed in terms of both the concentration of ferric iron and the redox potential (expressed by ferric/ferrous-iron ratio) of the leaching solution. Ferric iron, the leaching agent, played a key role in the leaching of sulfide minerals. The pyrite oxidation rate was controlled by the ferric iron concentration when ferric iron was in low concentration [16]. It was also reported that only the presence of ferric iron was not sufficient for leaching of sulfide minerals if the redox potential was not sufficiently oxidizing [5]. Therefore, ferric/ferrous-iron ratio was also used in describing the ferric leaching rate of sulfide minerals [17–19].

Figure 1 shows the concentrations of Cu^{2+} , Fe^{3+} and total arsenic in the leaching solution during the ferric leaching process. The results show that the

model fitted the experimental data very well. The simulation results show that As^{3+} is more easily oxidized by Fe^{3+} than enargite. From Table 1, it is seen that the value of $V_{\text{Cu}_3\text{AsS}_4}^{\text{max}}$ is larger than the reported value of

$V_{\text{pyrite}}^{\text{max}}$ ($4.8 \times 10^{-3} - 6.7 \times 10^{-3} \text{ h}^{-1}$) [12], while the value of B_1 is smaller than the reported saturation constant (2200–3300) for pyrite oxidation [12]. The above results indicate that the enargite dissolution rate in the initial leaching stage is high (Fig. 1). The constant $V_{\text{AsO}_2}^{\text{max}}$ ($8.16 \times 10^{-2} \text{ h}^{-1}$) is larger than $V_{\text{Cu}_3\text{AsS}_4}^{\text{max}}$ while

the constant B_2 (3.59) is smaller than B_1 , which indicates that Fe^{3+} prefers to oxidize As^{3+} when the leaching system contains both enargite and As^{3+} . This can also be confirmed by Nernst equation, in which the solution redox potential (E_h) of the H_3AsO_4 - HAsO_2 system at 298 K and pH 1.6 can be described in the form: $E_h = 0.574 - 0.0592 \text{ pH} - 0.0296 \lg \alpha(\text{HAsO}_2) + 0.0296 \lg \alpha(\text{H}_3\text{AsO}_4)$, where α is the activity constant of the species. It can be calculated from the above equation that As^{3+} can be oxidized to As^{5+} at above 479 mV. However, enargite was leached at about 700 mV, which makes the leaching of enargite difficult [5]. The above results explain the reason for the kinetic constant B_2 being smaller than B_1 . It was found in the bioleaching of pyrite-arsenopyrite ores that the reactions of arsenopyrite and As^{3+} oxidation by ferric were competing, and were influenced by the concentrations of Fe^{3+} , As^{3+} and As^{5+} [12]. At low concentration of Fe^{3+} and high concentration of As^{3+} , oxidation of As^{3+} to As^{5+} was the dominant reaction, while at low concentration of Fe^{3+} and low concentration of As^{3+} , chemical leaching of minerals was the dominant reaction; however, at high concentration of Fe^{3+} , both As^{3+} and minerals were oxidized, resulting in the low As^{3+} and high As^{5+} concentrations in the late leaching stages [12].

Figure 2 shows the predicted E_h and r_{indirect} (leaching rate of enargite by ferric, which is $r_{\text{Cu}_3\text{AsS}_4}$ in rate equations) during the leaching process. A close correlation between E_h and r_{indirect} was seen. During the initial 24 h, E_h was between 782 and 742 mV and r_{indirect} was between 0.0810 and 0.0150 $\text{mmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$. After 124 h of leaching, E_h decreased to about 720 mV, and as a result, r_{indirect} decreased to a very low level of 0.00400 $\text{mmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ and then remained at this level. The above results indicate that enargite should be leached at least above 700 mV, which is in agreement with the Ref. [5].

Figure 3 shows the predicted concentrations of As^{3+} , As^{5+} and precipitated ferric arsenate during the ferric leaching process of enargite. During the initial 24 h, enargite dissolved quickly indicated by the quick increase of As^{3+} concentration (Fig. 3) owing to the high ferric concentration and the high E_h (Figs. 1 and 2). With the increase of As^{3+} concentration, the oxidation rate of As^{3+} to As^{5+} by Fe^{3+} exceeded the production rate of As^{3+} from enargite dissolution at about 358 h, which resulted in the slight decrease of As^{3+} concentration at that time (Fig. 3). At the same time, the increased concentration of As^{5+} increased the precipitation rate of ferric arsenate rapidly (Fig. 3). After 552 h of leaching using 1.00 $\text{g} \cdot \text{L}^{-1} \text{Fe}^{3+}$, the ratio of $\text{As}^{3+}/\text{As}^{5+}$ was 1.69 : 1 according to the simulation (Fig. 3), from

Table 2 Parameter values of the enargite bioleaching model

$K_s/\text{mmol}\cdot\text{L}^{-1}$	k_d/h^{-1}	$m_{\text{Fe}^{2+}}/\text{mmol}\cdot\text{h}^{-1}$	t_l/h	$C_{X_{\text{ad}}}^{\text{max}}/\text{mmol}\cdot\text{L}^{-1}$	$C_{X_{\text{liq}}}^{\text{max}}/\text{ml}^{-1}$	$Y_{\text{Fe}^{2+},X}^{\text{max}}/\text{mmol}^{-1}$	Y_N/mmol^{-1}	$\mu_{\text{max}}/\text{h}^{-1}$
21.3	0.0170	5.50×10^{-9}	94.0	3.322×10^9	8.6×10^7	1.002×10^6	1.069×10^{11}	8.41×10^{-2}

which As^{3+} was calculated to be 62.8% of the total dissolved arsenic. Escobar *et al.* [9] reported that As^{3+} was about 50% of the total dissolved arsenic in enargite leaching using $3.00\text{ g}\cdot\text{L}^{-1}\text{ Fe}^{3+}$. At high concentration of Fe^{3+} of $3.00\text{ g}\cdot\text{L}^{-1}$, more As^{3+} was oxidized to As^{5+} so that the proportion of As^{3+} in total dissolved arsenic was lower than that at low concentration of Fe^{3+} of $1.00\text{ g}\cdot\text{L}^{-1}$, which was the reason for the portion of As^{3+} in total dissolved arsenic being higher in this simulation than that reported by Escobar *et al.* [9].

According to the experimental results, 8.4% of the copper and 3.9% of the arsenic in enargite were dissolved in the ferric leaching experiment [10], from which it could be calculated that 53.6% of the leached arsenic transformed into ferric-arsenate precipitation, which was in close agreement with the model predicted result of 53.1% (Fig. 3).

From the simulation results presented above, it is apparent that the model has successfully predicted the dynamics and all the major facts of enargite ferric leaching.

3.2 Bioleaching of enargite

The nine differential equations [Eqs. (16)–(24)] of the enargite bioleaching model were solved using the fourth ordered Runge-Kutta method. The parameter values of the ferric leaching model in Table 1 were directly used in the bioleaching model and were set fixed during the optimization of the other parameter values of the bioleaching model using GA [20]. The optimized model parameters are shown in Table 2. Simulation and prediction of enargite bioleaching were done using the bioleaching model with the parameter values in Tables 1 and 2, and the results are shown in Figs. 4–6.

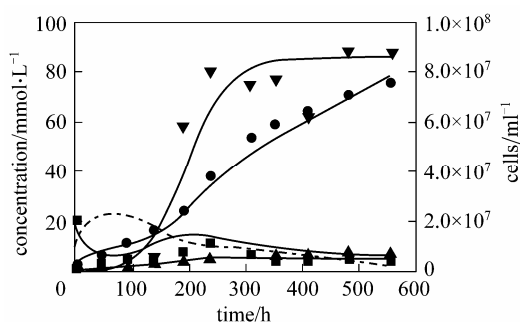
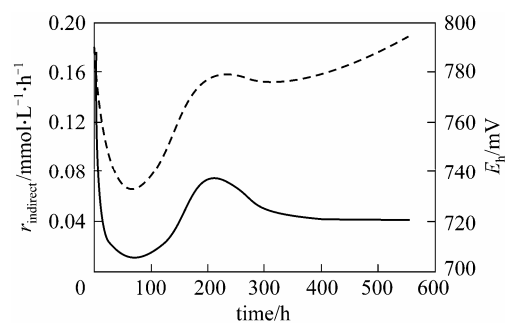


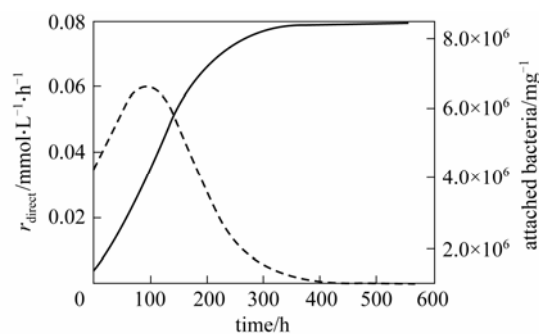
Figure 4 The time course of concentrations of Fe^{3+} , Fe^{2+} , Cu^{2+} , total dissolved arsenic, and suspended *Sulfolobus* cells during enargite bioleaching

(Lines represent model simulations, and symbols represent experimental data)
 ▲ total dissolved arsenic; ▼ bacteria in solution; ■ Fe^{3+} ;
 ● Cu^{2+} ; ---- Fe^{2+}



(a) E_h versus indirect leaching rate

— r_{indirect} ; --- E_h



(b) Attached *Sulfolobus* cells versus direct leaching rate

--- r_{direct} ; — attached bacteria

Figure 5 The plots of E_h versus indirect leaching rate and attached *Sulfolobus* cells versus direct leaching rate during the bioleaching of enargite

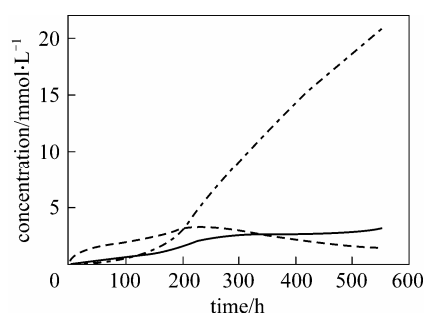


Figure 6 The time courses of As^{3+} , As^{5+} and precipitated ferric arsenate concentrations during enargite bioleaching
 --- As^{3+} ; — As^{5+} ; ---- precipitated arsenic

The simulation results of the concentrations of Fe^{3+} , Fe^{2+} , Cu^{2+} , total dissolved arsenic, and suspended *Sulfolobus* cells during the enargite bioleaching process are shown in Fig. 4. Good agreements between the model predictions and the experimental data were obtained (Fig. 4). During the initial 48 h, both Fe^{3+} and the enargite dissolution rates decreased rapidly owing to the consumption of Fe^{3+} in the oxidation of enargite to produce Fe^{2+} . Then, the suspended

Sulfolobus cells entered into the exponential growth phase to oxidize Fe^{2+} to Fe^{3+} quickly, and therefore, the enargite dissolution rate gradually increased (Fig. 4). In the meantime, a significant amount of precipitation was produced from the reaction of Fe^{3+} with As^{5+} [Eq. (4)] and the concentration of Fe^{3+} decreased, which leads to the decrease of the enargite dissolution rate (discussed later).

r_{indirect} decreased from 0.182 to 0.0240 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ with the decrease of E_h from 789 to 747 mV during the initial 24 h [Fig. 5 (a)]. E_h decreased to 733 mV at 68 h, and as a result, r_{indirect} decreased to 0.0120 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$. With the regeneration of Fe^{3+} by *Sulfolobus* cells, E_h increased to 779 mV and r_{indirect} increased to 0.0740 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ at 218 h. After 220 h of leaching, suspended *Sulfolobus* cells entered into stationary growth phase and E_h decreased slightly to 775 mV. Then, owing to the formation of a significant amount of ferric-arsenate precipitation (Fig. 6), the total iron in the leaching solution decreased. The decreasing rate of Fe^{2+} was quicker than that of Fe^{3+} (Fig. 4), and resulted in the gradual increase of E_h to the final value of 794 mV [Fig. 5 (a)]. Even if E_h increased gradually after 320 h, r_{indirect} decreased slightly as shown in Fig. 5 (a), which could also be confirmed by the decreased production rate of Cu^{2+} after 320 h (Fig. 4). The reason was that the concentration of Fe^{3+} was lower than 10.0 $\text{mmol}\cdot\text{L}^{-1}$ in the late leaching stage and became the limiting factor to r_{indirect} , which indicated that it was necessary to include the concentration of Fe^{3+} besides the ferric/ferrous-iron ratio in Eq. (7) as discussed earlier.

r_{direct} (the direct leaching rate of enargite by attached *Sulfolobus* cells, which is the $r_{\text{Cu}_3\text{AsS}_4}^{\text{dl}}$ in rate equations) increased with the increase of attached *Sulfolobus* cells during the initial 96 h. However, r_{direct} decreased after 96 h even if the number of attached cells still increased [Fig. 5(b)]. The nonlinear relationship between r_{direct} and the number of attached cells was reported by Porro *et al* [21].

In bioleaching of sulfide minerals, the contributions of direct or indirect leaching are different from case to case. In some cases, mineral dissolution is mainly a chemical process in which ferric iron and protons are responsible for carrying out the leaching reactions, and the role of microorganisms are to regenerate the leaching chemical of Fe^{3+} [22]. The simulation results of this study are in agreement with the above point of view. From Fig. 5, it is apparent that r_{indirect} is considerably larger than r_{direct} , and E_h is almost proportional to r_{indirect} before the Fe^{3+} concentration being decreased to a very low value to become the limiting factor. It was calculated using this model that the proportions of enargite dissolved by indirect and direct leaching were 95.52% and 4.48%, respectively.

Figure 6 shows the predictions of As^{3+} , As^{5+} and the precipitated ferric arsenate concentrations during the bioleaching process. During the initial leaching stage, there was a rapid increase of As^{3+} concentration resulting from enargite oxidation. As Fe^{3+} preferred to oxidize As^{3+} producing As^{5+} than to oxidize enargite as discussed earlier, the produced As^{5+} from As^{3+} oxidation reacted with Fe^{3+} to produce ferric-arsenate precipitation, which resulted in the increases of both

As^{5+} and precipitated ferric-arsenate concentrations and the gradual decrease of As^{3+} concentration. Similar results were reported by Breed *et al.* [12] on the bioleaching of pyrite-arsenopyrite ores. The formation of ferric-arsenate precipitation greatly reduced the toxicity to the microorganisms.

4 CONCLUSIONS

A comprehensive mathematical model was constructed for modeling the bioleaching of enargite. The simulation results fitted with the experimental data reasonably well. The following important conclusions were drawn and/or confirmed from the analyses using the bioleaching model. The indirect leaching rate (r_{indirect}) was controlled by both E_h and ferric iron concentration. The indirect leaching was effective when E_h was above 700 mV and the ferric iron concentration was not very low. The oxidation reactions of enargite and As^{3+} by Fe^{3+} were competing and As^{3+} was preferentially oxidized. The contributions of indirect and direct leaching of enargite were 95.5% and 4.5%, respectively. Large amounts of ferric-arsenate precipitation were produced, which greatly reduced the toxicity to microbial cells. The mathematical model developed in this study is confirmed to be a useful tool for analysis and optimization of the bioleaching process. This model can also be used in optimizing the scaling up of the bioleaching process. The results of the up-scaled bioleaching process can be predicted by simulation using this model under various cultivation conditions, reactor characteristics, and/or operation modes, so as to increase the reliability of the scaling-up and decrease the experimental numbers and costs.

NOMENCLATURE

B_1	kinetic constant in chemical enargite oxidation
B_2	kinetic constant in As^{3+} oxidation
C	concentration, $\text{mmol}\cdot\text{L}^{-1}$
$C_{X_{\text{adsorb}}}$	cell concentration attached on enargite, (mmol enargite) $^{-1}$
$C_{X_{\text{liquid}}}$	cell concentration in the liquid, ml^{-1}
E_h	redox potential, mV
$K_{\text{Fe}^{3+}}$	saturation constant for ferric iron, $\text{mmol}\cdot\text{L}^{-1}$
K_s	saturation constant for ferrous iron, $\text{mmol}\cdot\text{L}^{-1}$
k_{dl}	direct leaching rate constant for attached <i>Sulfolobus</i> cells, h^{-1}
$k_{\text{Fe}^{2+}}^{\text{O}_2}$	rate constant of Fe^{2+} oxidized to Fe^{3+} by oxygen, h^{-1}
k_{precip}	rate constant of ferric-arsenate precipitation, $\text{L}\cdot\text{h}^{-1}\cdot\text{mmol}^{-1}$
$m_{\text{Fe}^{2+}}$	maintenance coefficient of the cells on ferrous iron, $\text{mmol}\cdot\text{h}^{-1}$
r	reaction rate, $\text{mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$
$r_{X_{\text{adsorb}}}$	adsorbing rate of cells to enargite, $\text{L}^{-1}\cdot\text{h}^{-1}$
t_L	time delay in lag growth phase, h
$V_{\text{AsO}_2}^{\text{max}}$	maximum specific As^{3+} oxidation rate, h^{-1}
$V_{\text{Cu}_3\text{AsS}_4}^{\text{max}}$	maximum specific enargite oxidation rate, h^{-1}
$Y_{\text{Fe}^{2+}, X}^{\text{max}}$	maximum <i>Sulfolobus</i> cell yield on ferrous iron, mmol^{-1}
Y_N	yield of <i>Sulfolobus</i> cells on enargite, mmol^{-1}
μ_{max}	maximum specific growth rate of suspended <i>Sulfolobus</i> cells, h^{-1}

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