Comparison on the leaching kinetics of chalcocite and pyrite with or without bacteria

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Received 17 June 2010; received in revised form 4 September 2010; accepted 10 September 2010
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Abstract

The acid leaching, ferric leaching, and bioleaching of chalcocite and pyrite minerals were conducted in two sets of 3L stirred reactors. The dissolution rates of copper and iron were correlated with leaching conditions. In the acid leaching process, the dissolution rate of chalcocite was around 40wt.% while that of pyrite was less than 4%. In the ferric leaching process with high ferric concentration, only 10 wt.% of iron in pyrite was leached out at the same retention time though the copper recovery over 60 wt.% in chalcocite. For the bioleaching process, the chalcocite leaching rate was highly increased, nearly 90 wt.% of copper was leached out, and the iron dissolution of pyrite exceeded 70 wt.%. For the two minerals, the bioleaching shows the highest leaching rate compared with the acid leaching or ferric leaching. In uncontrolled bioleaching process, pyrite could be dissolved effectively. The experimental data were fitted to the shrinking core and particle model. The results show that in all the leaching tests, the chalcocite leaching was mainly controlled by diffusion, while for the pyrite leaching, chemical reaction is the main rate-determining step.

Keywords: chalcocite; pyrite; kinetic model; bioleaching

1. Introduction

Bioleaching of copper sulfides is a very complicated process. Mineral structures, pH values, and concentration of ferric and ferrous ions may affect the leaching process. In China, the first commercial plant of bio-heap leaching with a capacity of 10000 t/a Cu was set up at Zijinshan Copper Mine commissioned by the end of 2005. Due to the relatively high proportion of pyrite in the low grade copper ore, the bioleaching plant suffers from excessive acid and iron ions which decrease the solvent extraction rate and increase the operation cost. Thus understanding the different dissolution mechanisms between chalcocite and pyrite may improve the balance of acid and iron in Zijinshan commercial plant.

Previous researches indicate that pyrite and copper sulfides have different leaching mechanisms. Pyrite dissolution is through thiosulfate pathway while copper dissolution from copper sulfide is through polysulfide pathway [1]. The different degradation pathways indicate different leaching kinetics for the two minerals and thus may be useful to optimize the leaching process which containing both minerals.

For understanding the different leaching kinetics between ferric leaching, acid leaching and bioleaching of chalcocite and pyrite, the shrinking core and particle model proposed by Braun et al. was used [2]. This model has been applied in ZnS leaching and chalcocite leaching [3-4]. According to the model, the particle of copper sulfides is spherical or approximately spherical and the particle size of copper sulfides changes in the bioleaching process [5-6], and the mixed leaching kinetics involving a surface reaction and pore diffusion through a reacted porous zone surrounded by a region of unreacted ore were proposed, thus the reaction may be controlled either by surface reaction or by the pore-diffusion.

In this study, the shrinking core and particle model was applied to the ferric leaching, acid leaching, and bioleaching of chalcocite and pyrite. Different leaching kinetics of chalcocite and pyrite were revealed and these results may help to provide better solution for limiting iron dissolution during copper bioleaching in Zijinshan commercial plant.
2. Experimental

2.1. Bacteria culture

The mesophilic bacterial culture used in laboratory experiments was sourced from the acid mine drainage of Zijinshan Copper Mine. Characterization of the culture by 16S rRNA gene clone library technique indicated that strains of *Leptospirillum* and *Acidithiobacillus* appeared to be the dominant iron/sulphur-oxidising bacteria group. Microbial cultures were maintained in 250 mL orbital shaking flasks with 100 mL of the following medium: 3.0 g/L (NH₄)₂SO₄, 0.5 g/L K₂HPO₄, 0.5g/L MgSO₄·7H₂O, 0.1 g/L KCl, 0.013 g/L Ca(NO₃)₂·4H₂O and double-distilled water. The culture temperature was 30°C, and the culture pH value was adjusted to 1.8 using 6 mol/L sulfuric acid.

2.2. Preparation of mineral

Chalcocite and pyrite mineral samples were obtained from Zijinshan Copper Mine. Mineralogical analysis reveals that the chalcocite samples contain a small amount of covellite and digenite [7], and other composition in pyrite samples is mainly silicate mineral. The size fraction of the samples used was 44-50 μm. The chemical composition of samples was given in Table 1.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocite</td>
<td>72.51</td>
<td>4.64</td>
<td>20.55</td>
<td>2.30</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.32</td>
<td>40.07</td>
<td>42.06</td>
<td>17.55</td>
</tr>
</tbody>
</table>

2.3. Experimental procedure

All the experiments were carried out in sets of 3 L stainless steel tanks at 30°C. An overhead stirrer was used to mix the samples and inoculate microbial consortia at 200 r/min. Reactors were operated under aeration condition. The experimental pH value and temperature were continually monitored. For the acid leaching and ferric leaching, the experiments were performed without bacteria inoculation. Acid leaching tests were conducted at the leaching pH value of 0.5-2.0. In the ferric leaching process, different ferric concentrations from 0.5 to 12.0 g/L were applied to the reactor, and the experiments were carried on under the condition of the initial pH value of 1.3. For the bioleaching tests, 10% inoculums were applied to the reactor, and the experiments were conducted at different ferrous concentrations.

2.4. Model description

Since ferrous ions are biologically oxidized to ferric ions during the leaching process, changes of the [Fe³⁺]/[Fe²⁺] ratio will affect the bioleaching rate of copper sulfides. The bacterial activity is the critical factor for the bioleaching, thus surface chemical reaction of sulfide particles becomes the controlling step of the oxidative process [8-10]. The chemical reaction controlled dissolution kinetics is as follows:

\[ 1 - (1 - \lambda)^{\frac{2}{3}} = k_t \cdot t \]  \hspace{1cm} (1)

where \( \lambda \) is the leaching percent, \( k_t \) is the leaching rate constant \((d^{-1})\), and \( t \) is the leaching time \((d)\).

After the initial stage of bioleaching, the surface of sulfide ores is coated by a loose and porous product layer. The bioleaching kinetics is associated with the surface reaction and the diffusion through a porous product layer which enwraps the un-reacted sulfide cores [11].

Thus, the bioleaching rate of copper sulfides is controlled by the diffusion of [Fe²⁺] and [Fe³⁺] through the porous product layer. Since mineral dissolution was mainly controlled by chemical reaction and diffusion, the mineral surface was assumed as being spherical, the resistance of liquid-film could be omitted [12]. The kinetic behavior can be described as the following equation [13-14]:

\[ 1 - \frac{2}{3} \lambda - (1 - \lambda)^{\frac{2}{3}} = k t \]  \hspace{1cm} (2)
\[ 1 - \lambda = \left( \frac{r_c^2}{R} \right)^3 \]  \hspace{1cm} (3)

where \( r_c \) is a radius of the unreacted sulfide cores and \( R \) is a radius of the initial sulfides. The leaching rate constant \( k \) is associated with the size of sulfide particles and the total surface of sulfides. The leaching data were fitted into Eqs. (1) and (2) to check if the leaching process is controlled by chemical reaction or diffusion.

3. Results and discussion

3.1. Acid leaching of chalcocite and pyrite

The acid leaching of chalcocite and pyrite mineral samples was conducted at different pH values at 30°C. The leaching rates of copper and iron were showed in Fig. 1. Fig. 2 shows kinetic data calculated by Eqs. (1) and (2) when the pH value was 1.5, the dispersive symbols represent the experimental data, and the lines are the simulated results. The results indicated that during acid leaching process, the rate of chalcocite dissolution was around 40 wt.%, and this was consistent with that in the first stage leaching of chalcocite [15], while the pyrite dissolution rate was less than 4% in 21 d at pH 1.0. The experiment data were fitted to the shrinking core and particle model, and the results showed that chalcocite was mainly controlled by diffusion, while the pyrite acid leaching was mainly controlled by chemical reaction.

3.2. Ferric leaching of chalcocite and pyrite

Ferric leaching of chalcocite and pyrite mineral samples