

Bacterial leaching of chalcopyrite and bornite with native bioleaching microorganism

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Abstract: A native mesophilic iron-oxidizing bacterium, *Acidithiobacillus ferrooxidans*, has been isolated (30 °C) from a typical, lead-zinc concentrate of Dachang Mine in the region of Liuzhou located in the southwest of China. Two typical copper sulfide minerals, chalcopyrite and bornite, were from Meizhou Copper Mine in the region of Guangdong Province, China. Variation of pH and cell growth on time and effects of some factors such as temperature, inoculation cell number, and pulp density on the bioleaching of chalcopyrite and bornite were investigated. The results obtained from the bioleaching experiments indicate that the efficiency of copper extraction depends on all of the mentioned variables, especially the pulp density has more effect than the other factors on the microorganism. In addition, the results show that the maximum copper recovery was achieved using a mesophilic culture. The copper dissolution reached 51.34% for the chalcopyrite while it was 72.35% for the bornite at pH 2.0, initial Fe(II) concentration 9 g/L and pulp density 5%, after 30 d.

Key words: bornite; *Acidithiobacillus ferrooxidans*; bioleaching; chalcopyrite

1 Introduction

While world copper consumption has grown fast since 2000, the mining industry is increasingly faced with the necessity to process complex objective, low grade ores and waste tailings, from current mining operations. The economic extraction of copper from low-grade ores requires low-cost processing methods such as biohydrometallurgy[1–3]. Bacterially-assisted heap leaching of low-grade copper sulphides is a developing technology that has been applied successfully to the extraction of copper from secondary sulphide minerals such as chalcocite in a number of operations home and abroad[4–6]. However, the heap-bioleaching of the refractory primary copper sulphide, chalcopyrite, is just in lab experiment or under pilot test. It is a long way to be implemented at commercial scale[7–11].

The bacterial leaching of low grade copper sulfide

is a complex process. Millions of tones of low-grade ore and copper-rich tailings await the development of an efficient and economic bioleaching process for the chalcopyrite (CuFeS_2). The bioleaching of chalcopyrite in-situ and in dumps is a practical option only because the low and slow recoveries are countered by the low processing costs. Not surprisingly, the bioleaching of chalcopyrite, both the most abundant and the most refractory copper sulphide, is a key industry target. However, most of the technological developments have taken place with the bioleaching of chalcocite and other less refractory sulphide minerals[12–13].

In this study, the ability of a native bioleaching microorganism, *Acidithiobacillus ferrooxidans*, to oxidize chalcopyrite and bornite is described. Compared with the other copper sulfide minerals, the Meizhou copper minerals used in this work (chalcopyrite and bornite) contain other metal elements, such as lead and zinc. The work aims to evaluate a bioleaching-processing route for

the treatment of refractory copper minerals. Flask tests were done, followed by continuous analytical tests. A series of tests were carried out to assess the effect of residence time, pulp density and inoculation cell number on the bioleaching performance.

2 Experimental

2.1 Bacterial culture and nutrients

A mesophilic bacterium, iron-sulphur oxidizing bacteria, isolated from a hot, sulphur-rich metal dump near Liuzhou, Guangxi Province, China was used in the study. The bacteria were grown in a mineral salts solution with the following composition: 3.0 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.5 g/L K_2HPO_4 , 0.5 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.1 g/L $\text{Ca}(\text{NO}_3)_2$ [14]. The cultures of *A. ferrooxidans* were incubated in 250 mL Erlenmeyer flasks each containing 100 mL of the medium and 3% (volume fraction) inoculum, on a rotary shaker at 170 r/min at 30°C. The initial pH of the cultures was adjusted to 2.0 using 0.5 mol/L H_2SO_4 . The stock and pre-inoculum cultures were maintained in the same medium under similar conditions. The cultures that were used had been subcultured through several transfers in the concentrate medium in order to adapt the bacteria to the experimental conditions. The stock cultures were subcultured at two-week intervals.

The cell population in this inoculum, determined by direct counting using a Petroff-Hausser chamber, was typically in the range of $(8-10) \times 10^8$ /mL.

2.2 Mineral characteristics

The tests were performed on two copper sulphide minerals, fine-milled in a stirred ball mill. The ore was finally ground to particles of less than 0.5 mm in size. Over 85% of the mineral had a particle size of 0.074 mm for shake flask studies. The chemical compositions of the mineral are listed in Tables 1 and 2.

The X-ray diffraction analysis of mineral

Table 1 Chemical composition of chalcopyrite (mass fraction, %)

Cu	Fe	S	Pb	Zn
31.45	26.74	31.87	0.27	0.14
Al_2O_3	SiO_2	CaO	MgO	As
0.35	2.38	0.32	0.092	0.003

Table 2 Chemical composition of bornite (mass fraction, %)

Cu	Fe	S	Pb	Zn
57.41	10.36	25.27	0.52	0.12
Al_2O_3	SiO_2	CaO	MgO	As
0.51	3.11	0.08	0.01	0.011

chalcopyrite sample showed the presence of chalcopyrite (CuFeS_2) as the main phase, and galena (PbS), sphalerite (ZnS) and silica (SiO_2) as the minor phases. The X-ray diffraction analysis of mineral bornite sample showed the presence of bornite (Cu_5FeS_4) as the main phase, and arsenopyrite (FeAsS), galena (PbS), sphalerite (ZnS) and silica (SiO_2) as the minor phases.

2.3 Flask test

Distilled water was added on a daily basis to compensate for evaporation. The initial pH was set at 2.0 with sulphuric acid. The progress of the leaching was followed by daily measurement of pH levels.

The amount of Fe and Cu released during the leaching was determined by daily liquor analysis. The leaching residue was collected at the end of the run and analysed for the presence of copper, iron, silicate, elemental sulphur, sulphide sulphur and sulphate.

2.4 Analytical methods

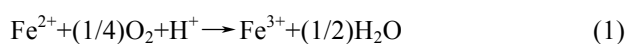
Quantity of free bacteria in the solution was counted by direct counting, using a Thoma chamber of 0.1 mm in depth and 0.0025 mm^2 in area with an optical microscope. Copper and total iron concentrations in the solution were measured with an atomic absorption spectrophotometer (Z-8000 PE). The ferrous ion concentration was ascertained by a volumetric method by titration with potassium dichromate. The pH of the supernatant at room temperature was also measured with a pH meter (PHSJ-4A).

3 Results and discussion

3.1 Bacterial oxidation of ferrous iron and elemental sulfur

Effects of temperature on the growth of *Acidithiobacillus ferrooxidans* in the shake flasks at pH=2.0 are shown in Fig.1 and Fig.2. Two stages can be identified: an increase of the bacteria number detected during the first 50 h (first stage), and a death phase during which the growth of *A. ferrooxidans* decreased. The first phase corresponds to the biooxidation of ferrous ions initially present in the medium. A growth limitation occurred because the supply of an essential nutrient (ferrous iron) in the medium was decreased.

The main mechanism of bacterial catalysis in the dissolution of sulfide minerals is based on the bacterial oxidation of ferrous iron, with oxygen as electron acceptor, according to reaction (1):



It is known that ferrous iron oxidized by *Acidithiobacillus ferrooxidans* rapidly decreases at pH larger than 2.5 [8]. In most reports of ferrous iron oxida-

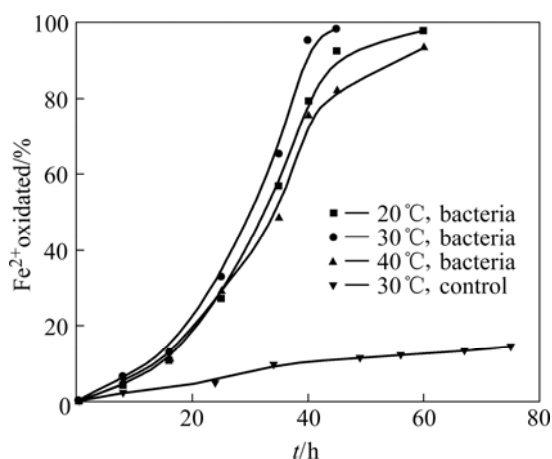


Fig.1 Effect of temperature on Fe^{2+} oxidation rate (pH 2.0, initial $\text{Fe}(\text{II})$ concentration 9 g/L)

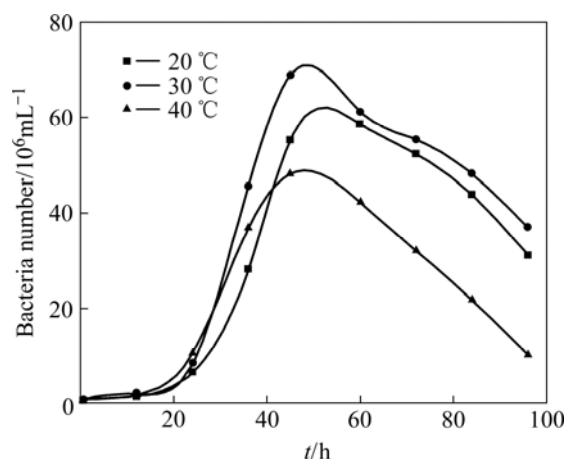


Fig.2 Variation of cell number vs time at different temperatures (pH 2.0, initial $\text{Fe}(\text{II})$ concentration 9 g/L)

tion by acidophiles, bacterial catalysis is significant only up to $\text{pH}=3.5$ [8, 15]. According to the chemiosmotic theory, a decrease in the ferrous iron oxidation activity of *A. ferrooxidans* is expected when the pH increases[16]. Some authors have suggested that the formation of ferric iron precipitates can also have an inhibiting influence in this pH range[15], though there is no clear evidence to support this suggestion.

The results of the calculated rates of ferrous iron oxidation for the experiment with 1 g/L initial ferrous iron concentration are shown in Fig.1 (abiotic oxidation: 30 °C control and biologically enhanced oxidation at 20, 30 and 40 °C).

The data represented correspond to values of instantaneous oxidation rates as a function of the pH which continuously decreases with time from the initial value of 2.0.

The results in Fig.1 for abiotic conditions show that, at this low pH, there is no significant rate of chemical ferrous iron oxidation. Only 14.51% ferrous iron was

oxidized after 75 d.

In every experiment, a continuous pH increase and decrease was observed, which was triggered by the oxidation of elemental sulfur by microbiologically mediated mechanism. A typical trend is shown in Fig.4, which corresponds to the case of an inoculated basal medium solution containing an initial elemental sulfur concentration of 5 g/L. The experimental results from Figs.1–4 indicated that the optimum temperature for the growth of *Acidithiobacillus ferrooxidans* was 30 °C. This corresponds with other report[17].

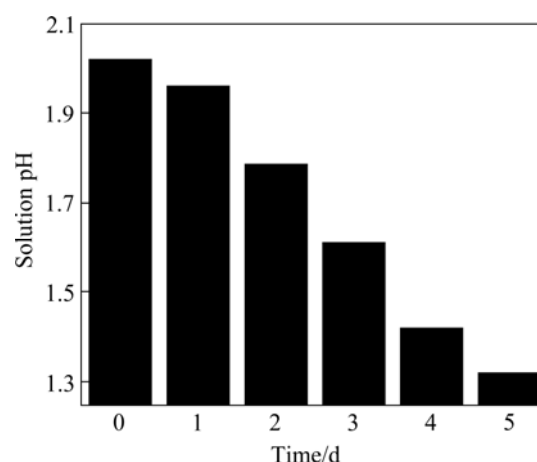


Fig.3 Variation of pH on time in solution (30 °C)

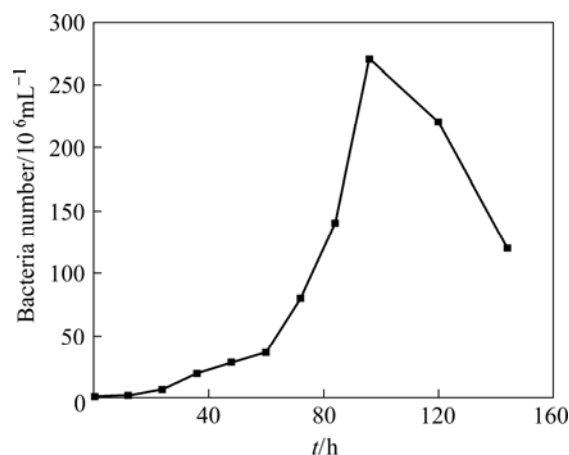


Fig.4 Variation of cell number vs time (30 °C)

3.2 Bioleaching in presence and absence of *Acidithiobacillus ferrooxidans*

Bioleaching curves of chalcopyrite and bornite in the presence and the absence of *Acidithiobacillus ferrooxidans* (30 °C, 5% pulp density) are shown in Fig.5 and Fig.6.

From Fig.5 it can be seen that for chalcopyrite copper extraction reached 6.32% after 30 d in sterile control. While in bacterial leaching copper extraction reached 51.34% after 30 d. The results shown in Fig.6 indicated that for bornite copper extraction reached 8.51% after 30 d during sterile control. While in bacterial

leaching copper extraction reached 72.35% after 30 d. Fig.5 and Fig.6 also illustrate that bornite can be more easily biooxidized than chalcopyrite by *Acidithiobacillus ferrooxidans*. While chalcopyrite can be easily oxidized under extremely thermophilic condition[18].

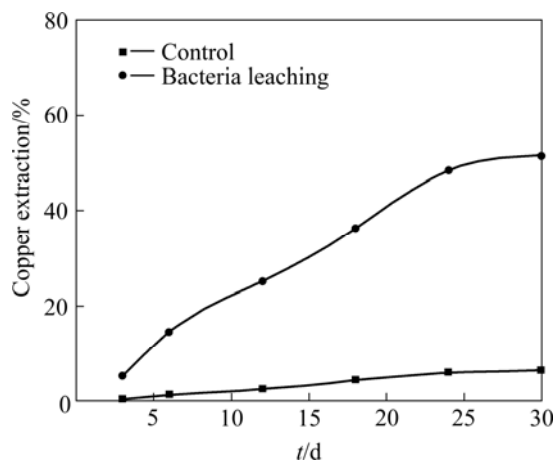


Fig.5 Bioleaching of chalcopyrite in presence and absence of *Acidithiobacillus ferrooxidans* (30 °C, 5% pulp density)

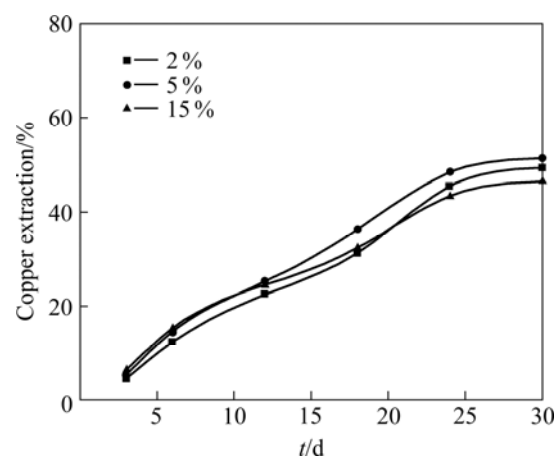


Fig.7 Effect of pulp density on bioleaching of chalcopyrite (30 °C, 3% inoculation)

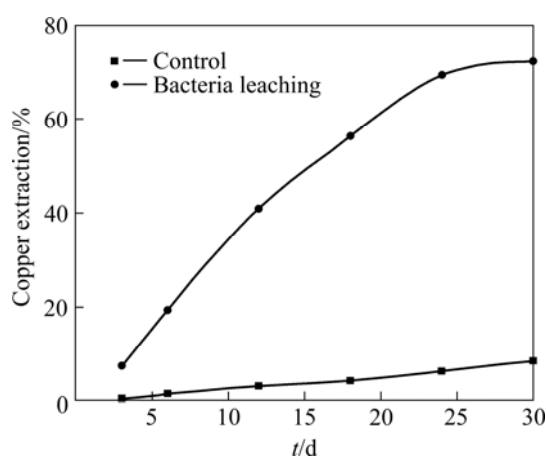


Fig.6 Bioleaching of bornite in presence and absence of *Acidithiobacillus ferrooxidans* (30 °C, 5% pulp density)

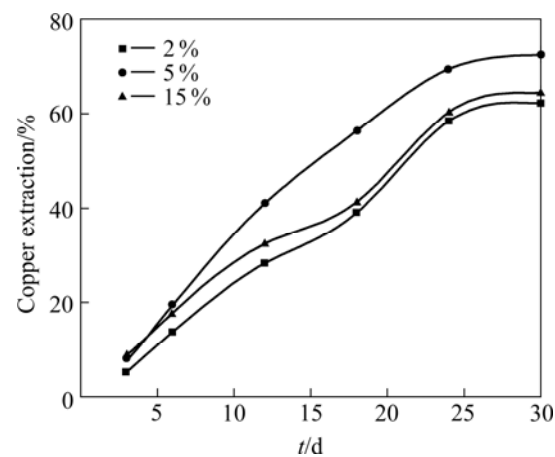


Fig.8 Effect of pulp density on bioleaching of bornite (30 °C, 3% inoculation)

3.3 Effect of pulp density

Fig.7 and Fig.8 indicated that other than the sterile controls, the dissolution of chalcopyrite and bornite was influenced markedly by pulp density when inoculating 3% *Acidithiobacillus ferrooxidans*. The results showed that the maximum copper recovery was achieved when the pulp density is 5%. Copper dissolution reached 51.34% for chalcopyrite while it was 72.35% for bornite at pH 2.0, initial Fe(II) concentration 9 g/L and pulp density 5%, after 30 d.

3.4 Effect of inoculation cell number

Fig.9 and Fig.10 indicated that the dissolution of chalcopyrite and bornite was marginally influenced by inoculating cell amount with 5% pulp density. The results showed that the maximum copper recovery was

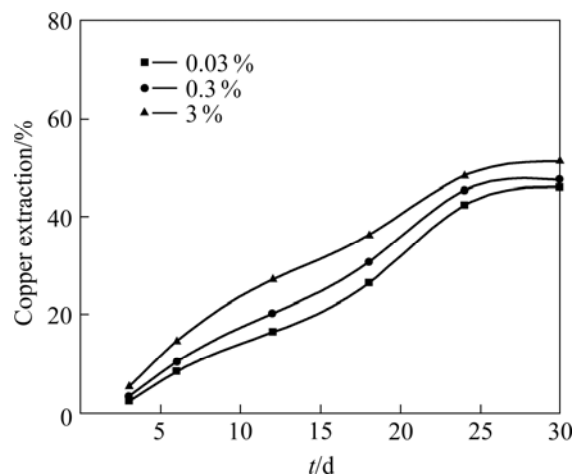


Fig.9 Effect of cell number on bioleaching of chalcopyrite (30 °C, 5% pulp density)

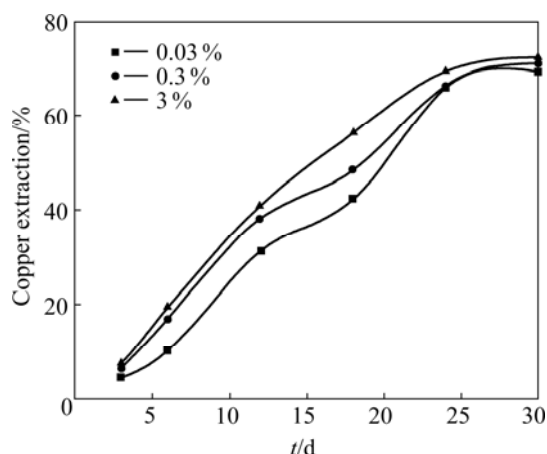


Fig.10 Effect of inoculation cell number on bioleaching of bornite (30 °C, 5% pulp density)

potential[19].

In addition, SEM observations indicated that the surface features of leaching residues were different under different leaching conditions. XRD and EDX analyses showed that a mass of elemental sulfur formed during the bioleaching process of the copper minerals although the bacteria were able to oxidize elemental sulfur into SO_4^{2-} . Chalcopyrite and bornite were dissolved preferentially in the bioleaching process. The result is accordant with other reports about chalcopyrite and bornite bioleaching [20–21].

4 Conclusions

1) The results of bioleaching experiments indicate that the efficiency of copper dissolution depends on the pH, pulp density and inoculation cell number, especially the pulp density has more effect than other factors for the microorganism.

2) Bioleaching results show that the maximum copper recovery is achieved using a mesophilic culture. Copper dissolution reached 51.34% for chalcopyrite while it was 72.35% for bornite at pH 2.0, initial Fe(II) concentration 9 g/L and pulp density 5%, after 30 d.

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