A comparison of bioleaching of chalcopyrite using pure culture or a mixed culture

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Abstract

The aim of this investigation was to determine the efficacy of chalcopyrite bioleaching using pure cultures of Acidithiobacillus ferrooxidans or Acidithiobacillus thiooxidans and a mixed culture composed of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans. The experiments were carried out in shake flasks with [Fe 2+] 4 g L⁻¹ and S 1 g L⁻¹ at pH 1.80, 130 rpm and 30 °C. Inocula of both iron-oxidizing bacteria were obtained from cultures with Fe 2+ as the sole energy source, whereas Acidithiobacillus thiooxidans inoculum was taken from a culture growing on sulphur. Tests showed that the copper extraction in a mixed culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans was higher than in pure cultures. On the other hand, an important potential of Acidithiobacillus thiooxidans to leaching chalcopyrite was indicated. It can prevent jarosites accumulation on the substrate and allow further copper solubilization through the action of ferric ion. The selection of the suitable pH during the bioleaching processes would be important.

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1. Introduction

Chalcopyrite (CuFeS₂) is the most important copper mineral in the world (Dutrizac, 1978). Unlike many other ores, chalcopyrite is known to be particularly recalcitrant to hydrometallurgical processes. Researchers have been striving for decades to accelerate the speed of chalcopyrite in the biological leaching reactions. The selection of the suitable microorganisms applied to leaching tests is one of important factors. Thiobacillus ferrooxidans and Thiobacillus thiooxidans are the most widely involved in bioleaching operations (Lundgren and Silver, 1980).

However, the most important role in bacterial leaching is played by Thiobacillus ferrooxidans. This bacterium was first isolated by Colmer and Hinkle (1947) from acid coal mine drainage. In 2000, it was reclassified as Acidithiobacillus ferrooxidans by Kelly and Wood (2000). Acidithiobacillus ferrooxidans is a mesophilic microorganism and is able to catalyze the oxidation of metallic sulphides to sulphate through a multi-step mechanism in which oxygen is the terminal electron acceptor (direct mechanism) through the oxidation of Fe²⁺ to Fe³⁺ (indirect mechanism) (Torma, 1977).

Thiobacillus thiooxidans, isolated in 1922 by Waksman and Joffe (1922), is well known for its rapid oxidation of elemental sulphur. It was also reclassified as Acidithiobacillus thiooxidans by same researchers in 2000. It is able to oxidize reduced sulphur compounds but not Fe²⁺ that is believed to be responsible for faster dissolution of metallic sulphides. For this reason, the action of Acidithiobacillus thiooxidans on metallic sulphides has only been studied partially.
Although bacterial populations composed of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans showed high copper recoveries during leaching of copper ores, up to now there has not been a correlation between the dominant bacterial species and the efficiency of the bioleaching process. Even if some papers are concerned with it, these papers are scarce and the results obtained are also ambiguous (Khalid and Malik, 1988; Falco et al., 2003). Thus, it is interesting to compare the behaviour of Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and a mixed culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans in the bioleaching of a model system consisting of a pure metallic sulphide.

The aim of this investigation was to determine the efficacy of copper bioleaching from chalcopyrite using pure cultures of Acidithiobacillus ferrooxidans or Acidithiobacillus thiooxidans and a mixed culture composed of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans and find out a way to enhance copper recoveries.

2. Materials and methods

2.1. Bacteria

A strain of Acidithiobacillus ferrooxidans from a discarded ores at Yongping mine (China) was used through out these experiments. The strain of Acidithiobacillus ferrooxidans was cultured on 9K medium (Silverman and Lundgren, 1959) with pH 1.50, 130 rpm and 30 °C through numerous serial cultures with chalcopyrite (10% W/V) as the sole substrate. It was adapted to chalcopyrite as the sole energy source. The 9K medium contained 3 g (NH₄)₂SO₄, 0.1 g KCl, 0.5 g K₂HPO₄, 0.5 g MgSO₄·7H₂O and 0.01 g Ca(NO₃)₂ L⁻¹, adjusted to pH 1.80 with sulphuric acid.

A strain of Acidithiobacillus thiooxidans was also from a discarded ores at Yongping mine (China). It was grown in 9K + S medium with pH 1.80, 130 rpm and 30 °C through numerous serial cultures with chalcopyrite (10% W/V) as the sole substrate. It was also adapted to chalcopyrite as the sole energy source. The 9K + S medium contained 3 g (NH₄)₂SO₄, 0.1 g KCl, 0.5 g K₂HPO₄, 0.5 g MgSO₄·7H₂O, 0.01 g Ca(NO₃)₂ and 1 g S L⁻¹, adjusted to pH 2.00 with sulphuric acid.

The bacterial populations in the two inocula were about 1 × 10⁷ cells mL⁻¹.

2.2. Substrate

The sample of chalcopyrite from Yongping mine (China) was used throughout the study. The copper ores were pulverized in a ring earthen bowl. The fine copper ores with a particle size of less than 1 mm were used for the all leaching experiments. The analytical composition of the copper ores was determined by quantitative X-ray diffraction to be 21.04%Fe, 0.54%Cu, 11.15%S, the remainder being quartz and K, Ca, Mg.

2.3. Leaching experiments

Leaching experiments were carried out in 250 mL flasks with 100 mL 9K medium at pH 1.80. [Fe²⁺] 4 g L⁻¹ and 10 g of copper ores (10% W/V pulp density). Each flask was inoculated with Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans or Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans suspension at 10% (V/V). In mixed cultures, each inoculum was added at 5% (V/V) (5 mL Acidithiobacillus ferrooxidans and 5 mL Acidithiobacillus thiooxidans). Sterile controls were also run by replacing the bacterial inoculum by an equal volume of medium. Flasks were incubated at 130 rpm and 30 °C. All experiments were conducted at least in duplicate.

2.4. Analytical methods

The flasks were periodically analysed for pH and Eh. The pH was measured by a pH probe calibrated with a low pH buffer. The Eh was measured by a silver/silver chloride double reference oxidation–reduction probe. The soluble copper was determined by Atomic Absorption Spectrophotometry (AAS). The soluble iron and the ferrous ion were determined by titration with EDTA (ethylene diamine tetraacetic acid).

3. Results and discussion

In the presence of 4 g L⁻¹ of ferrous ion and 1 g L⁻¹ of sulphur, changes in soluble ferrous ion with time in the bioleaching experiments are reported in Fig. 1.

The Acidithiobacillus ferrooxidans culture and the mixed culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans showed complete oxidation of ferrous ion, although in the Acidithiobacillus ferrooxidans culture test, 8 days were required for all of ferrous ion to be oxidized. In the mixed culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans developed well. It was also indicated that Acidithiobacillus ferrooxidans were adapted to copper ores environment and played an important role in leaching experiment. Ferrous ion oxidation was exclusively chemical for the sterilized control and for the Acidithiobacillus thiooxidans. Ferrous ion oxidation in the Acidithiobacillus thiooxidans culture and in the sterilized control is due to the action of air (no other oxidant is present in leaching solution). On the side, the rate of ferrous ion oxidation in the
Acidithiobacillus thiooxidans culture is slightly higher than in the sterilized control.

Changes in pH with time in the bioleaching experiments are presented in Fig. 2. In the mixed culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans and in pure culture of Acidithiobacillus ferrooxidans, the pH increased between the first 5 and 8 days. After this time, the pH decreased slowly. The pH increased as a result of ferrous ion oxidation reaching the maximum value between 5 and 8 days. After this time, pH decreased progressively as a result of iron hydrolysis and the consequent precipitation of ferric compounds. Jarosite was confirmed as the main phase by X-ray diffraction patterns of the solid residues.

As noted in Fig. 2, pH changes for the pure cultures of Acidithiobacillus thiooxidans and the sterile control were similar in the first 3 days. After 3 days, there was a pH decrease in pure cultures of Acidithiobacillus thiooxidans probably due to the oxidation of sulphur. (Thiobacillus thiooxidans played an important role and produced acid in leaching experiments.) The gradual increase of pH value for the sterilized control was caused by the progressive ferrous oxidation and the acid dissolution of chalcopyrite.

Fig. 3 shows percentages of iron precipitation (estimated as the difference between soluble iron at the beginning and at the end of the leaching experiments). More jarosite precipitation occurred in the presence of iron-oxidizing bacteria perhaps because of the rapid oxidation of iron and the consequent increase of pH. It was also indicated that the iron precipitation decreased significantly in the presence of Acidithiobacillus thiooxidans. Moreover, the pH in leaching experiment would have an important impact on the iron precipitation.

The kinetics of copper dissolution is presented in Fig. 4. Copper extractions after 18 days of bioleaching were 11.25%, 7.75%, 8.00% and 4.25% for mixed cultures of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans, the pure cultures of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans, the pure cultures of Acidithiobacillus ferrooxidans, the pure cultures of Acidithiobacillus thiooxidans and the sterilized control, respectively.
extraction in the mixed cultures of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans was higher than in other pure cultures, probably due to the action of Acidithiobacillus thiooxidans producing sulphuric acid. It can decrease the precipitation of ferric compounds. The high jarosite deposit may limit the rate of the copper solubilization by hindering the diffusion of soluble reactants or products through this layer. Copper extractions in pure cultures of Acidithiobacillus ferrooxidans and in pure cultures of Acidithiobacillus thiooxidans was similar. From this result, it was indicated that Acidithiobacillus thiooxidans played an important role in the leaching experiments. In the sterilized control, copper extraction was little. This result proved that the efficacy of bacterial leaching was better than the efficacy of chemical leaching in another way.

4. Conclusions

In conclusion, we have shown that a mixed culture containing the iron-oxidizing Acidithiobacillus ferrooxidans and the sulphur-oxidizing Acidithiobacillus thiooxidans was better than a pure culture of Acidithiobacillus ferrooxidans or Acidithiobacillus thiooxidans in leaching chalcopyrite. An important potential of Acidithiobacillus thiooxidans to leaching chalcopyrite was indicated. Additionally, its capacity to generate sulphuric acid through sulphur oxidation can lower the pH in leaching solution, decrease the precipitation of ferric compounds and allow further copper dissolution through the action of ferric iron. These results suggested that the mixed cultures of Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans were applied instead of pure culture of Acidithiobacillus ferrooxidans or Acidithiobacillus thiooxidans in the bioleaching chalcopyrite.

On the other hand, we confirmed that the selection of suitable pH in the bioleaching chalcopyrite would be an important factor. In the suitable pH, the decrease of ferric ion precipitation and the development of Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans would all be benefited. Subsequently, it can enhance the recovery of copper from chalcopyrite.

References