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Mineral

Bioflotation of pyrite with *Thiobacillus ferrooxidans*

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Abstract: Bioflotation of pyrite with bacteria *Thiobacillus ferrooxidans* in the presence or absence of potassium ethyl xanthate was studied on a pure pyrite through microflotation and electrophoretic light scattering measurements. The experimental results showed that in the absence of xanthate, pyrite flotation is slightly enhanced by *Thiobacillus ferrooxidans*. However, with xanthate as a collector, pyrite flotation is strongly depressed after being exposed to the bacteria. The longer is the time when the pyrite is exposed to the bacteria, the stronger the depression is. The mechanism of the depression might be due to the formation of the biofilms of *Thiobacillus ferrooxidans* on pyrite surfaces, preventing the adsorption of xanthate on pyrite surfaces in the form of dixanthogen or xanthate ions.

Key words: bioflotation; pyrite flotation; *Thiobacillus ferrooxidans*; zeta potential

1 Introduction

Bioflotation is a mineral beneficiation process, in which some minerals or reagents are modified with the help of microbes (bacterium or microorganisms), followed by conventional flotation. The history of this process can be traced back 1950s when it was found that *Thiobacillus ferrooxidans* can oxidize certain metal and metalloid sulfides, such as pyrite, chalcopyrite, *etc.* [1]. This finding was then commercially applied to the leaching of uranium ores [2] and refractory gold ores [3], which is well known as bioleaching. In the past decade, this biotechnological processing has been extended to the beneficiation of valuable minerals from ores in the forms of bioflotation and bioflocculation. Because of a high efficiency to beneficiate refractory ores and low environmental pollutions, it has recently attracted an increasing attention worldwide [4,5].

Pyrite, an iron sulfide mineral, is a common coexisting mineral in sulfide mineral flotation and coal flotation. It is usually depressed by adding lime to increase slurry pH in flotation systems. In some case, the depression is also realized through adding stronger depressants, such as sodium cyanide and dextrin, *etc.* Recently, because of the advances of biotechnology in mineral processing, it has been found that some microganisms, for instance, *Saccharomyces cerevisiae* [6] and *Thiobacillus ferrooxidans* [7,8] *etc.*, are also effective depressants for pyrite flotation. The mechanisms of this depression have been suggested to be due to the specific affinity of the microoganisms to pyrite surfaces, resulting in an attaching of the microoganisms to the surfaces in large numbers. Because the microoganisms are hydrophilic, the pyrite covered with the microorganisms is also hydrophilic, and thus is depressed in froth flotation.

In this work, the bioflotation of pyrite with *Thiobacillus ferrooxidans* in the presence or absence of xanthate was studied through microflotation and electrophoretic light scattering measurements. The objective of this work was to obtain a better understanding of the depression of pyrite flotation by means of *Thiobacillus ferrooxidans*.

2 Experimental

2.1 Materials

A natural pyrite sample with 99.3% purity was used in this study. The mineral crystals were crushed by hand hammer, and then classified into the size fraction of −75 μm +45 μm and −10 μm. The former was used for flotation tests, and the later was used for electrokinetic studies.

Potassium amyl xanthate used as a collector in this work was purified in laboratory with the technique described as follows. The xanthate powders were first dissolved in an acetone liquid, followed by a filtration. Next, the filtrate was mixed with amyl ether, and then

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was filtrated. The last filter cake was the purified potassium amyl xanthate. The hydrochloric acid and sodium hydroxide from the J.T. Barker (analyzed purity) were used to adjust the pH value of emulsions. The water used was distilled first, and then treated by passing resin beds and a 0.2 μm filter. The residue conductivity of the water was less than 1 μS/cm.

2.2 Pyrite exposed to bacteria *Thiobacillus ferrooxidans*

A pure strain of *Thiobacillus ferrooxidans* was used in this study. Exposing pyrite particles to *Thiobacillus ferrooxidans* was carried out in a 2 L mechanical mixing tank (bioreactor). 50 g pyrite and *Thiobacillus ferrooxidans* in an initial content of 10^7 cells/mL were added into 1 L cell culture M2, which was a solution containing 1 g/L $(NH_4)SO_4$, 0.4 g/L $MnSO_4$ and 0.4 g/L K_3PO_4. The pH of suspension was adjusted to 1.8 by using H_2SO_4. Then, mechanical agitation at a stirring speed of 450 r/min was employed to the suspension for a given period. The slurry temperature was kept at 30°C throughout the whole treatment. After that, the pyrite slurry was transferred for microflotation tests or electrokinetic measurement.

2.3 Microflotation

The micro-flotation of pyrite treated or untreated by bacteria was performed in a Hollimond flotation tube with nitrogen as a bubble source. Suspensions of pyrite treated or untreated by bacteria *Thiobacillus ferrooxidans* in about 1 g solid were first conditioned with a magnetic agitator while a given dosage of collector potassium amyl xanthate was added and slurry pH was adjusted by adding hydrochloric acid or sodium hydroxide. Then, the suspensions were transferred to the flotation tube and diluted to 130 mL in volume. Next, under a nitrogen gas flow rate of 29.2 mL/min, the flotation was carried out for a given time. The floated and non-floated products were filtered and then dried, respectively. The flotability was obtained by the total mass of the two products divided by the floated product mass.

2.4 Zeta potential measurement

The zeta potentials of pyrite treated or untreated by *Thiobacillus ferrooxidans* were determined by using a Coulter Delsa 440SX instrument, which performs a simultaneous four-angle electrophoretic light scattering measurement using a rectangular capillary cell. A detailed description of the instrument can be found elsewhere [9]. In this study, the measurements were performed using the electric field of 16-19 V/cm and the frequency range of 500 Hz with a duration time of 100 s (2 s on and 1 s off sequence alternating the electric field polarity) at both the upper and lower stationary planes. The temperature through whole measurement was kept at (25.0 ± 0.1)°C.

3 Results and discussions

Figure 1 shows the flotation kinetics of pyrite without any collector after being exposed to *Thiobacillus ferrooxidans* for various hours. The slurry pH in flotation was kept 7.0. As it is noted, in all the cases, the flotability of pyrite increases with increasing the flotation time until reachs plateaus, indicating the maximum flotability. The pyrite exposed with *Thiobacillus ferrooxidans* has a higher flotation rate than that without exposed with the bacteria. At 30 s of flotation time, the difference of flotability is about 12%. However, the difference in maximum flotability is very small. The results suggest that the pyrite flotation is slightly enhanced due to the help of *Thiobacillus ferrooxidans*. In addition, it can be observed that the time exposed with the bacteria only slightly influences the flotability.

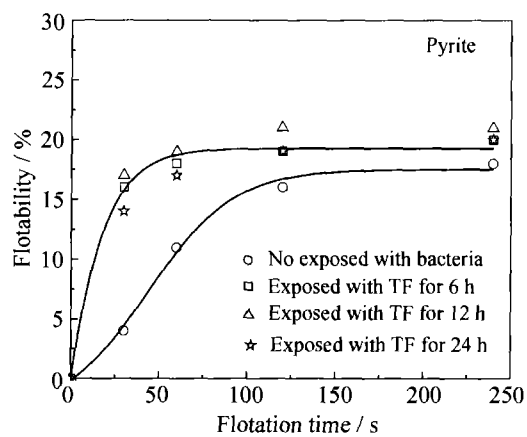

Figure 1 Flotability of pyrite as a function of flotation time without any collector in the absence or presence of *Thiobacillus ferrooxidans* (TF).

It has been experimentally proved that *Thiobacillus ferrooxidans* prefer to attach pyrite surfaces, forming biofilms on the surfaces [10]. The surface area covered by the biofilms depends on bacteria number and reaction time. As Thiobacillus ferrooxidans grow in a pyrite suspension, the bacteria number greatly increases as increasing the reaction time in the bioreactor. Therefore, the longer the reaction time is in the bioreactor, the larger the biofilms on pyrite surfaces are. In the flotation, the pyrite exposed to the bacteria shows the biofilms to nitrogen bubbles, instead of pyrite surfaces. Accordingly, the evidences as shown in figure 1 may indicate that pyrite exposed to *Thiobacillus ferrooxidans* has a higher flotability than natural pyrite.

The flotation kinetics of pyrite by using potassium

ethyl xanthate (PEX) as a collector after being exposed to *Thiobacillus ferrooxidans* for various time is illustrated in **figure 2**. The slurry pH is also kept 7.0. From this graph, it can be seen that without exposed to the bacteria, pyrite shows a high flotation rate, and a big maximum flotability, about 91%. However, after being exposed to the bacteria, the flotation response of the pyrite becomes worse. The flotation rate and the maximum flotability sharply decline. This decline depends on the time exposed to the bacteria. The longer the exposed time of the pyrite to *Thiobacillus ferrooxidans* is, the stronger the decline is. After being exposed to the bacteria for 24 h, the pyrite has the maximum flotability of 40%, lowering 51% in comparison with natural pyrite. Obviously, *Thiobacillus ferrooxidans* indeed strongly depress pyrite flotation when xanthate is used as a collector.

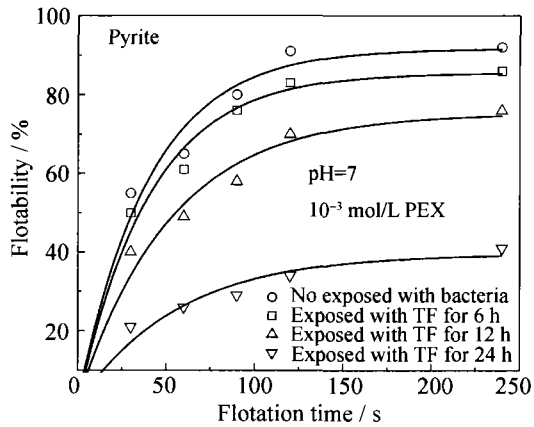

Figure 2 Flotability of pyrite as a function of flotation time with 10^{-3} mol/L potassium ethyl xanthate (PEX) as a collector in the absence or presence of *Thiobacillus ferrooxidans* (TF).

Figure 3 shows the zeta potentials of pyrite as a function of pH in the absence or presence of PEX. As it can be seen, the natural pyrite (in the absence of PEX) has its isoelectrical point (i.e.p.) around pH=5.8. However, in the presence of 10^{-3} mol/L PEX, the zeta potential of pyrite decreases comparably, and the i.e.p. moves to pH=4.9. This observation might be attributed to the adsorption of xanthate ions on the pyrite surfaces, which is in a good agreement with the experimental results as described elsewhere [11]. The adsorption occurs first as dixanthogen on pyrite surfaces on aqueous solutions, and then as xanthate ions on the adsorbed dixanthogen layers. Indeed, it is the adsorption of xanthate ion on pyrite surfaces that causes the considerable increase of the flotability of pyrite in the PEX solution as shown in figure 2.

The zeta potentials of *Thiobacillus ferrooxidans* and pyrite exposed to the bacteria in the absence or presence of PEX as a function of pH are shown in **figure 4**, in which the zeta potential *vs.* pH curve of natural pyrite is also given for a comparison. As it is noted from this graph, the i.e.p. of pyrite changes to pH=3.3 from pH=5.8 after being exposed to *Thiobacillus ferrooxidans* for 24 h, indicating that the pyrite surfaces are modified by means of the bacteria. Furthermore, it can be observed that this zeta potential *vs.* pH curve is similar to that of the *Thiobacillus ferrooxidans*. In other words, the pyrite surfaces exposed to *Thiobacillus ferrooxidans* have a similar electrokinetic property as the bacteria. This result suggests that the pyrite surfaces are mostly covered by the bacteria, forming biofilms on the surfaces. In the presence of PEX, the pyrite exposed to the bacteria has a similar zeta potential *vs.* pH curve as that in the absence of PEX, indicating that there is no or a slight adsorption of xanthate on the pyrite surfaces. Therefore, a very low flotability could be achieved on the pyrite exposed to *Thiobacillus ferrooxidans* for 24 h, as shown in figure 2.

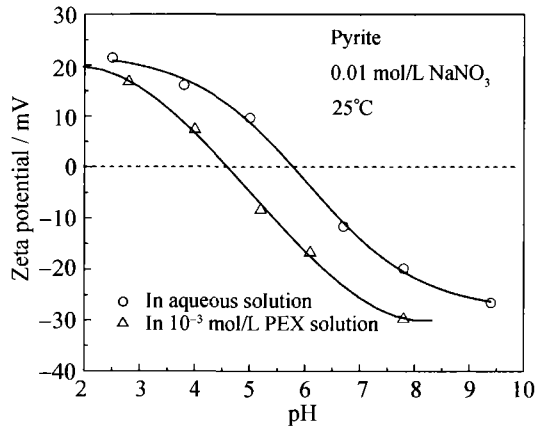

Figure 3 Zeta potentials of pyrite as a function of pH in the absence or presence of 10^{-3} mol/L PEX.

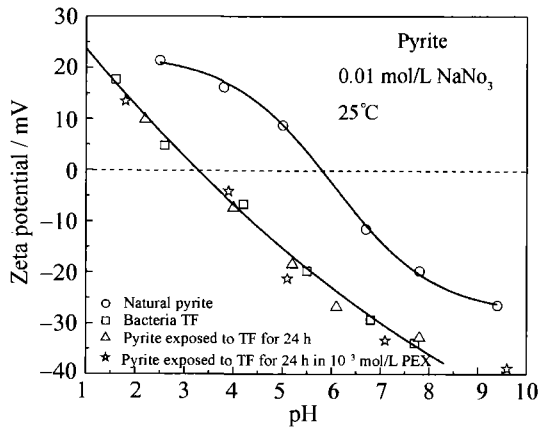

Figure 4 Zeta potentials of *Thiobacillus ferrooxidans* (TF) and pyrite exposed to the bacteria in the absence or presence of 10^{-3} mol/L PEX as a function of pH.

The experimental results described above demonstrate that the depression of pyrite flotation by means of bacteria *Thiobacillus ferrooxidans* might be attrib-

uted to the formation of biofilms on pyrite surfaces, preventing the adsorption of xanthate on the surfaces. The more the pyrite surfaces occupied by the biofilms (or *Thiobacillus ferrooxidans*) was, the stronger was the depression.

4 Conclusions

(1) Pyrite flotation using xanthates as a collector could be strongly depressed by means of *Thiobacillus ferrooxidans*, while the flotation of natural pyrite is slightly enhanced by the bacteria.

(2) The mechanism by which pyrite flotation using xanthates as a collector is depressed by *Thiobacillus ferrooxidans* might be due to the formation of biofilms on pyrite surfaces, preventing xanthate from adsorbing on the surfaces in the form of dixanthogen or xanthate ions.

References

[1] L.C. Bryner, J.V. Beck, B.B. Davis, *et al.*, Microorganisms in leaching sulfide minerals [J], *Ind. Eng. Chem.*, 46(1954), p.2587.

[2] R.A. MacGregor, Uranium dividends from bacterial leaching [J], *J. Min. Eng.*, 21(1969), p.54.

[3] J. Barter, A.J. Carter, N.H.M. Holder, *et al.*, Design and commissioning of 40 tonne per day flotation concentrate biooxidation treatment plant at the harbour light mine, [in] *Extractive Metallurgy of Gold and Base Metals Conference* [C], Australia, 1992.

[4] H.L. Ehrlich, How microbes mobilize metals in ores: A review of current understandings and proposals for further research [J], *Minerals Metall. Process.*, 19(2002), p.220.

[5] P. Somasundaran, N. Deo, and K.A. Natarajan, Utility of bioreagents in mineral processing [J], *Minerals Metall. Process.*, 17(2000), No.2, p.112.

[6] S.K. Kawatra and T.C. Eisele, Depression of pyrite flotation by yeast and bacteria [J], *Minerals Metall. Process.*, 16(1999), No.4, p.1.

[7] A.S. Atkins, Developments in the biological suppression of pyretic sulfur in coal flotation, [in] *Bioprocessing and Biotreatment of Coal* [C], Marcel Dekker, New York, p. 507.

[8] N. Ohmura, K. Kitamura, and H. Saiki, Mechanism of microbial flotation using *Thiobacillus ferrooxidans* for pyrite suppression [J], *Biotechnol. Bioeng.*, 14(1993), p.671.

[9] R. Xu, Metals to resolve mobility from electrophoretic laser light scattering measurement [J], *Langmuir*, 9(1993), p.2955.

[10] C.C. Townsley, Atkins, A.J. Davis, Suppression of pyrite sulfur during flotation by thiobacillus ferrooxidans [J], *Biotechnol. Bioeng.*, 30(1987), p.1.

[11] M.C. Fuerstenau, M. Misra, B.R. Palmer, Xanthate adsorption on selected sulfides in the virtual absence and presence of oxygen [J], *Int. J. Miner. Process.*, 29(1990), p.111.