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Full Length Research Paper

Effect of bacterial conditioning and the flotation of copper ore and concentrate

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In this paper, the effect of bacterial conditioning on KBI Murgul (Turkey) copper concentrate was investigated by the use of *Acidothiobacillus ferrooxidans* (DSM 11477). The various parameters such as bacterial population, conditioning time and particle size were studied. Test results indicated the copper grade increase of about 22% in flotation copper ore through bacterial conditioning of pyrite surfaces resulting in pyrite depression.

Key words: Chalcopyrite, bio-oxidation, bacteria, mineral surface, froth flotation.

INTRODUCTION

Acidothiobacillus ferrooxidans is an aerobic, acidophilic, rod-shaped, autotrophic, gram-negative bacterium. It is approximately 0.5 µm in width and 2 µm in length. This bacterium is active over a pH range of 1.5 to 5 with optimum growth at pH 2.0 (Holt et al., 1993). *A. ferrooxidans* is able to utilize not only inorganic sulfur compounds but also ferrous iron simultaneously as oxidizable inorganic substrates (Nagaoka, 1999; Tributsch, 2001).

Flotation can separate minerals on the basis of differences in surface properties. In the flotation process, hydrophobic minerals attach to air bubble and form a froth phase at the top of the flotation cell. On the other hand, particles with hydrophilic surfaces sink to the bottom of the cell forming tailings. In the flotation system it is necessary to study the chemical and physicochemical properties of mineral surfaces and establish the effect of changes in composition of bulk phases (Luttrell and Yoon, 1987).

Nowadays, it becomes a necessity to process low grade ores with complex mineralogy, particularly for base metals including precious and rare earth minerals. Bio-processing techniques offer alternative ways for such complex ores (Van Aswegen et al., 1991). Additionally, compared to the conventional inorganic reagents such as cyanides, hydrosulfides, dichromate, etc., bacteria are non-toxic and environmentally benign. Many investigations have suggested that certain types of bacterium such as *A. ferrooxidans* may prevent flotation of certain minerals, such as pyrite (Attia and El-Zeky**,** 1989; Misra et al., 1996; Santhiya et al., 2000; Sharma et al., 2001).

Pyrite is one of the well-known minerals, which is mainly associated with all sulphide minerals, especially with chalcopyrite and coal. In the flotation plants, cyanide is used for depressing pyrite. Cyanide is known to be very toxic; much work had been done to depress pyrite with *A. ferrooxidans*, especially in coal flotation (Dogan et al., 1985; Reed, 1990; Atkins, 1990; Gasiorek, 1997). The preconditioning of minerals with bacterial cells reduced the floatability of pyrite and chalcopyrite. The reduction in the floatability is found to be dependent on cell concentration on mineral surfaces which is observed to be a fast process. The sorption and zeta potential studies showed that the substrate-grown cells have more affinity toward a pyrite surface than chalcopyrite surface. The cells sorption inhibited the xanthate flotation of pyrite without any effect on chalcopyrite. However, this micro organism could also affect the chalcopyrite surface during flotation (Sharma et al., 1999).

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Table 1. Chemical analysis of chalcopyrite.

Element	%	Element	%
Cu	30.56	Al	0.007
Fe	30.25	Na	0.003
S	23.76	K	0.01
Mg	0.03	Ca	0.01
Ti	0.002	P	0.059

Fewer studies have been conducted on chalcopyrite, as compared to pyrite after conditioning with bacteria. In this paper, the effect of bacterial conditioning on chalcopyrite surface was investigated (Tarkan, 2003).

EXPERIMENTAL

Chalcopyrite sample

In the experiments, chalcopyrite concentrate was used and obtained from KBI Murgul Copper Concentrator. The chemical analysis of chalcopyrite sample is given in Table 1.

Reagents and Bacteria

All the reagents used in the experiments were analytical grade and were used as received. *Acidothiobacillus ferrooxidans* (DSM 11477) used in the experiments is provided by DSMZ-Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Braunschweig (Germany). *A. ferrooxidans* was cultivated, in Buhler type compactor KS 15A with incubator head TH 15, with Erlenmeyer flasks at pH 2, at 30.5°C in 9K medium with the following composition: $(NH_4)_2SO_4$ 3.0 g, K_2HPO_4 0,5 g, KCl 0.1 g, $MgSO_4.7H_2O$ 0,5 g, $Ca(NO_3)_2$ 0,1 g, $FeSO_4.7H_2O$ 44,2 g in 1000 ml water. In order to prevent toxicity of metal ions on bacteria, the bacteria were adapted to copper. When bacteria were cultivated, 10^{-2} g/l chalcopyrite sample was added to 9K medium. Amount of copper in 9K was increased up to 1 g/l, at end of the adaptation process.

Flotation Tests

The flotation tests were carried out in a Hallimond tube and Denver type flotation machine. In Hallimond tube tests, 1 g sample was used having –210+38 µm. In the study of the effect of particle size, different sizes were used. Air flow rate of 6 ml/min was maintained. In all tests, potassium amyl xanthate ($2x10^{-5}$ M KAX) and methyl isobutyl carbonyl (0.5 cc MIBC); 1% (w/v) were applied as a collector and frother respectively. pH was adjusted by HCl and NaOH additions. The parallel tests were carried under two identical conditions with or without bacteria. In the tests, the effect of number of bacteria, conditioning time, and particle size were investigated. In all experiments, the flotation time was 45 s and stirred flask speed was 200 rpm. The results were evaluated by the following:

Recovery, % = Weight of floated fraction (g) / Weight of the feed (g)

In Denver flotation tests, the sample was -210 µm in size, with 1/5 (w/v) solid/water ratio. Chemical analyses were made by the use of X-ray fluorescence (XRF).

RESULTS

Hallimond tube tests without bacteria

The tests were carried out with and without collector in the absence of bacteria with 5 min conditioning time. The results are given in Figure 1. It is seen in the figure that chalcopyrite has some floatability. This has been established previously (Gardner and Woods, 1979; Heyes and Trahar, 1977). Using KAX as a collector, the best chalcopyrite recovery was obtained at pH 9.5 which coincided with the result of previous studies.

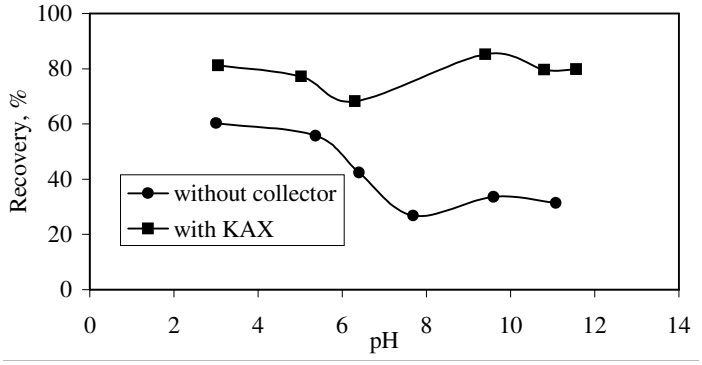

Figure 1. Chalcopyrite flotation with and without KAX.

Hallimond tube tests with bacteria

The bacterial conditioning and flotation tests were carried out at pH 2 and 9.5 respectively.

Effect of conditioning time: The effect of bacterial conditioning on flotation recovery is given in Figure 2. The bacterial population was fixed at 10^6 cells/ml during tests. Figure 2 shows that the flotation recovery of chalcopyrite is decreased sharply to about 28% in first hour. This is continued to the end of 2 h and then the recovery is ceased at 20%. For the study of other parameters, conditioning time was set at 2 h.

Effect of bacterial population: The bacterial population was determined by counting under microscope. The tests were made in four different bacteria concentrations (10^1,

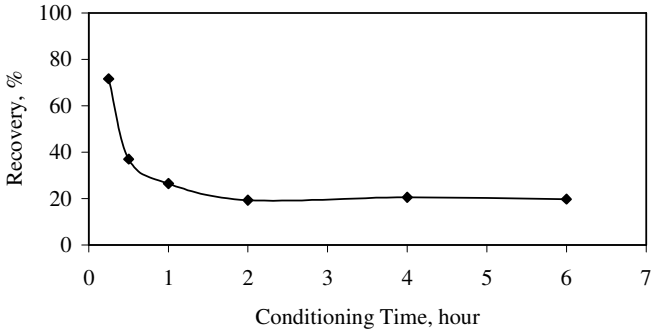

Figure 2. Effect of conditioning time on chalcopyrite flotation.

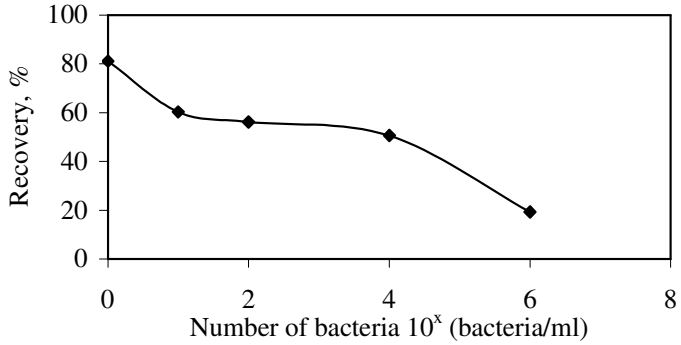

Figure 3. Effect of bacterial concentration on chalcopyrite flotation.

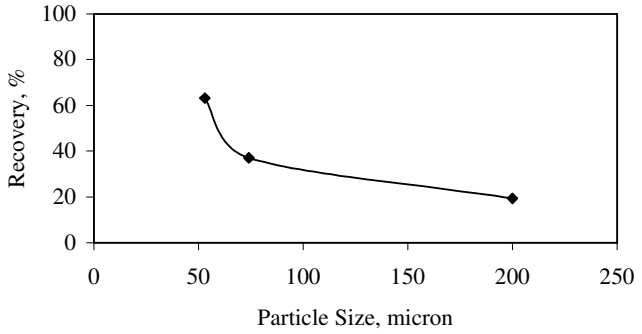

Figure 4. Effect of flotation recovery on particle size.

10^2, 10^4 and10^6 cells/ml). Results are shown in Figure 3. The figure indicates that even a small number of bacteria (10^1 cells/ml) caused a significant decrease in flotation recovery. This decrease was slower between 10^1 and 10^4 cells/ml, but a gradual decrease in chalcopyrite recovery started again when bacterial population exceeded over 10^4 cells/ml.

Effect of particle size: The effect of particle size in -210+38 m; -74+38 m and -53+38m fractions was investigated. In these tests, the bacterial population was kept at 10^6 cells/ml. The results are given in Figure 4. It is clear that the decrease in particle size causes an increase in surface area of the mineral. As shown in Figure 4, chalcopyrite recovery decreases in the size fraction of -53+38 µm due to the smaller bacterial activity to surface area ratio. The effect of agitation rate (150; 200 and 250 rpm) was also studied without any significant change in flotation recovery.

Denver cell flotation tests

The Denver cell flotation tests were performed in order to justify the results obtained in Hallimond Tube tests. In these experiments, concentrate with 15.79% Cu was used. Two identical tests on this concentrate were carried out with and without bacteria. In this tests, the concentration of KAX and MIBC used were the same, pH adjustment was made by lime addition. Conditioning time was 5 min. Bacteria concentration was 10^6 bacteria/ml. The results are given in Table 2. As seen from Table 2, Fe and S contents in the tailings was more than in the tests without bacteria while Fe and S contents in the tailings with bacteria increased. Cu content in the concentrates with bacteria shows increase. The stochiometry calculations support this idea. Once the stoichiometric percentage of Fe, Cu and S in chalcopyrite ($CuFeS_2$), and Fe and S in pyrite (FeS_2) are calculated, it is found that the ratio of Fe in chalcopyrite (30.4%) is less than that of Fe in pyrite (46.6%). This ratio indicates that the differences in Fe grade and recovery in the tailings are due to the depression of pyrite. The same calculations can also be made for S. Consequently; the Denver Cell flotation tests show that pyrite was depressed without copper loss.

DISCUSSION

It is found that a copper concentrate with 22.23% Cu content is obtained through bacterial conditioning, followed by flotation. Whereas copper concentrate with 18.20% Cu resulted in conventional flotation. Consequently copper grade of flotation concentrate subjected to bacterial conditioning is increased by 22%. *A. ferrooxidans* can affect mineral surfaces by direct (intimate contact) or indirect (no intimate contact) as shown in Figure 5.

In both mechanisms, the bacteria eliminate the occurrence of oxidized sulfur which has hydrophobic properties and induce higher floatability to minerals (Heyes and Trahar, 1977), so that hydrophobicity of pyrite is decreased.

The mechanisms explained above, bacteria much more effective on pyrite surface than chalcopyrite surface. Because, at low pH values, the oxidation of pyrite is much more pronounce than that of chalcopyrite (Majima and Peters, 1966; Rao and Leja, 2004). In addition *A.*

Table 2. The Denver cell flotation tests.

Test	Product	Weight	Cu		Fe		S	
		%	Grade,%	Rec,%	Grade,%	Rec,%	Grade,%	Rec,%
With bacteria	Concentrate	58.0	22.23	81.6	40.70	64.4	45.84	67.5
	Tailings	42.0	6.95	18.4	31.03	35.6	30.41	32.5
	Feed	100.0	15.81	100.0	36.64	100.0	39.36	100.0
No bacteria	Concentrate	72.7	18.20	83.9	41.79	82.9	48.42	89.4
	Tailings	27.3	9.29	16.1	22.91	17.1	15.23	10.6
	Feed	100.0	15.77	100.0	36.64	100.0	39.36	100.0

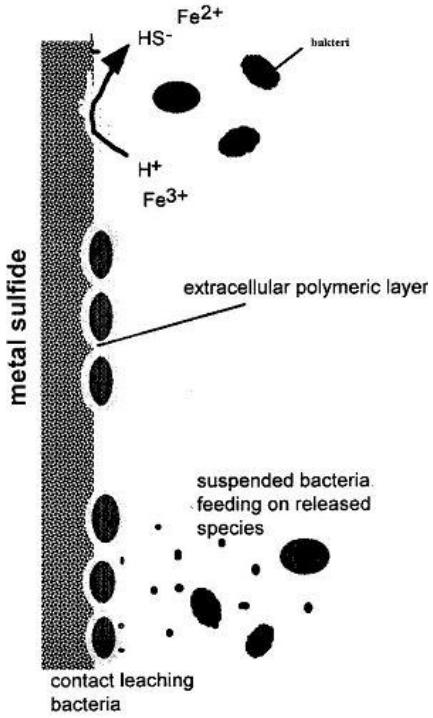

Figure 5. Direct and indirect mechanism of bacterial activity on mineral surface (Tributsch, 2001).

$$4\ FeSO_4 + 15\ O_2 + 2\ H_2SO_4 \xrightarrow{bacteria} 2\ Fe_2(SO_4)_3 + 2\ H_2O \quad \text{(Eq. 2)}$$

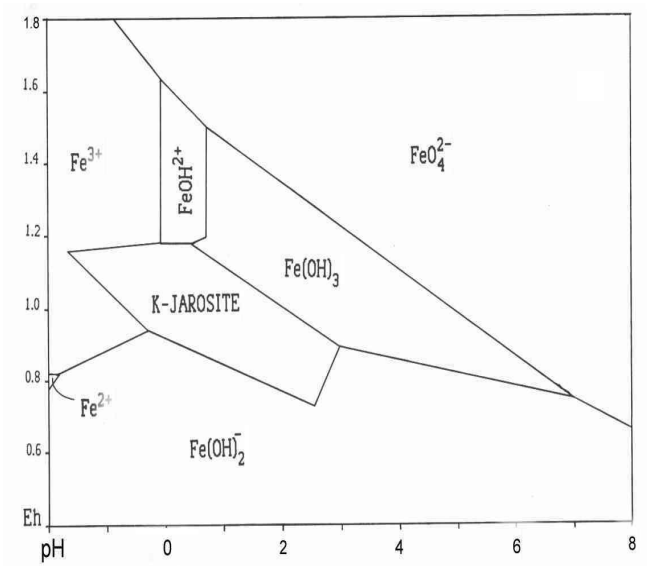

Figure 6. Eh-pH plot of jarosite (Arslan and Arslan, 2002).

ferrooxidans increases the oxidation rate of pyrite gradually (Bryner et al., 1967). In these systems, the formation of jarosite layer takes place at low pH values as illustrated in Figure 6.

The jarosite formation is problematic in bacterial leaching. Once jarosite is formed, it precipitates on mineral surfaces and decreases the effectiveness of reagent/mineral surface interaction in flotation resulting in pyrite depression. Once bacteria oxidize iron to ferric state indicated in equation 1 or equation 2, a jarosite, (K^+, Na^+) $Fe_3(SO_4)_2$, layer is formed on the mineral surface.

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O \xrightarrow{bacteria} 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad \text{(eq. 1)}$$

The formation of ferric iron precipitates, especially jarosite is highly dependent on pH. According to the pH, it can be observed yellowish brown color precipitate in the solution pH between 1.8 and 2.0 while amorphous Fe^{3+} precipitate giving light brown, orange or yellow color in the solution pH between 2.2 and 5.5. Furthermore precipitation in the form of jarosite is more pronounced at pH between 1.9 and 2.2.

In conclusion, the bacterial conditioning followed by flotation tests of Cu concentrate with 22.23% Cu the optimum parameters were 2 h conditioning time, 10^6 cells/ml bacterial population and -53+38 µm particle size. Copper concentrate with 15.79% Cu was floated after bacterial conditioning, resulted in a concentrate with 22.23%. This represents 22% increase in grade of Cu

concentrate without any bacterial treatment. *A. ferrooxidans* appears to be a good depressant for pyrite in selective flotation of chalcopyrite from pyrite. Low recovery figures can be ascribed to the formation of jarosite in the bacterial conditioning of Cu ore and concentrate.

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