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Arsenic precipitation in the bioleaching of enargite by *Sulfolobus* BC at 70 °C

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Abstract

Enargite (Cu_3AsS_4) was leached at 70 °C by *Sulfolobus* BC in shake-flasks. The highest copper dissolution (52% after 550 h of leaching) was obtained with bacteria and 1 g l^{-1} ferric ion. In the absence of ferric ion, *Sulfolobus* BC catalyzes the bioleaching of enargite through a direct mechanism after adhesion onto the mineral surface. In ferric bioleaching, arsenic precipitated as ferric arsenate and arsenic remained associated to the solid residues, preventing the presence of a high dissolved arsenic concentration in the leaching solution. About 90% inhibition of bacterial growth rate and activity was observed for dissolved arsenic concentrations above 600 mg l^{-1} for As(III) and above 1000 mg l^{-1} for As(V). Arsenic-bearing copper ores and concentrates could be leached by *Sulfolobus* BC in the presence of ferric iron due to the favourable precipitation of arsenic ion as ferric arsenate, avoiding significant bacterial inhibition.

Introduction

Bioleaching is an attractive technology from an economical and environmental point of view to process determined low copper sulfide ores and refractory gold concentrates (Jo *et al.* 1991, Lawrence 1990). Enargite, a copper and arsenic sulfide (Cu_3AsS_4), is present in several Chilean copper deposits (Alvarez 1992) and generates hazardous atmospheric contaminants during the processing of the copper sulfide concentrates in smelting plants. Accordingly, efforts are directed to develop alternative processes to recover copper and eliminate arsenic from these arsenic bearing ores and concentrates. In spite of the extensive publications related to copper sulfide bioleaching (Rossi 1990), few studies on chemical (Dutrizac & MacDonald 1972) and biological leaching of enargite in sulfuric acid media have been reported (Ehrlich 1964, Hao *et al.* 1972). More recently, studies on the bioleaching of enargite-pyrite gold concentrate have been published (Acevedo *et al.* 1998, 1999). A previous work on leaching and bioleaching of pure enargite at 30 °C with *T. ferrooxidans* indicated that this sulfide is highly refractory and that, even in the presence of mesophilic bacteria, it dissolves very slowly in a sulfuric acid medium with ferric sulfate (Escobar *et al.* 1997). Previous comparative studies of bioleaching on sulfide concentrates have shown that faster rates can be obtained with thermophilic bacteria than with *T. ferrooxidans* (Lawrence & Marchant 1987, Escobar *et al.* 1993). *Sulfolobus* species, isolated from different high temperature environments (Brierley 1978), can oxidize metal sulfides, sulfur or ferrous iron at 65–75 °C. However, the presence of arsenic in ores and concentrates could limit the use of bioleaching due to the toxicity of dissolved arsenic on living organisms. Lindström & Sehlin (1989) determined that As(III) in solution can be detoxified through biological oxidation to As(V) by *Sulfolobus* BC and that toxic levels of As(V) were between 10–20 mM.

The aim of this work was to study the mechanisms and compare the kinetics of the chemical and bacterial leaching of enargite using *Sulfolobus* BC at 70 °C.

Material and methods

Mineral

An enargite sample was ground and separated into different granulometric fractions. The mineral was analyzed chemically by atomic absorption (flame) and mineralogically by microscopic observation under reflected light. X-ray analyses were also performed. The sample contained mainly enargite with some very small inclusions of chalcopyrite and a few particles of quartz. The chemical analysis of this sample showed the following metal content: Cu: 46.2%, As: 16.3%, Fe: 0.55%.

Bacteria

A thermophilic strain of *Sulfolobus* BC was grown at 70 °C in a basal medium with the following composition $(NH_4)_2SO_4$ (0.4 g l^{-1}), $MgSO_4 \cdot 7H_2O$ (0.5 g l^{-1}), KH_2PO_4 (0.2 g l^{-1}), Fe(II) iron (0.5 g l^{-1}) and enargite (1.0 g) as energy source, acidified to pH 1.6; 5.0 ml of the final leach solution were used as inoculum for the bacterial leaching experiments.

Leaching conditions

Leaching experiments were performed in 250 ml Erlenmeyer flasks using 2.0 g mineral samples of a granolometric size between 104 μm and 147 μm (-100 $+150$ mesh) in 100 ml of basal medium pH 1.6 as leaching solution. The flasks were shaken at 100 rpm in a rotary shaker at 70 °C. Chemical leaching experiments were performed in basal medium pH 1.6 without iron or with 1.0 g l^{-1} of Fe^{3+} l^{-1} added as ferric sulfate. Bacterial leaching was performed under the same conditions but with 5.0 ml of bacterial culture added initially as inoculum.

Analysis

The flasks were periodically analyzed for pH and Eh; ferrous and total iron were analyzed by the o-phenanthroline colorimetric method (Muir & Anderson 1977, Herrera *et al.* 1989). Total arsenic and copper concentrations in the leaching solution were determined by atomic absorption spectrophotometry. Total bacteria concentration was determined microscopically by direct counting in a Petroff–Hauser chamber.

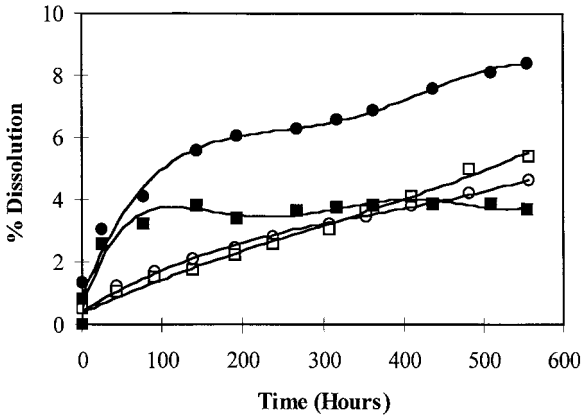

Fig. 1. Copper and arsenic dissolution in the chemical leaching of 2.0 g of enargite at 70 °C in 100 ml medium pH 1.6 with and without ferric sulfate (3.0 g Fe^{3+} l^{-1}); acid leaching ○: Cu, □: As; ferric leaching ●: Cu, ■: As.

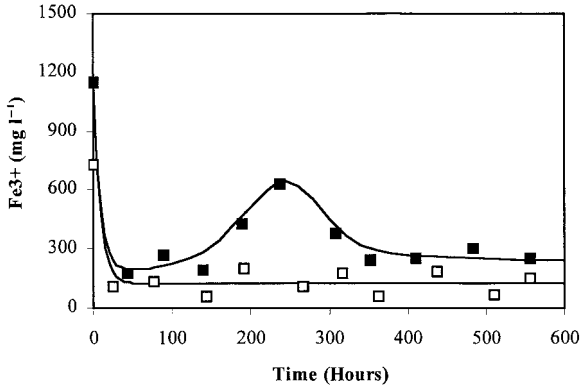

Fig. 2. Copper and arsenic dissolution in the bacterial leaching of 2.0 g enargite at 70 °C in 100 ml medium pH 1.6 with and without ferric sulfate (3.0 g Fe^{3+} l^{-1}); bacterial leaching ○: Cu, □: As; ferric/bacterial leaching ●: Cu, ■: As.

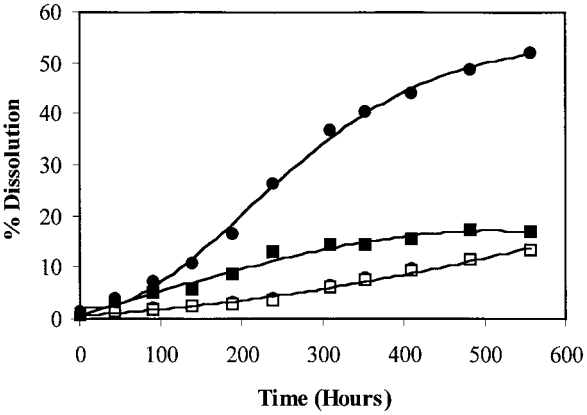

Fig. 3. Ferric ion concentration in the solution during the ferric and bacterial ferric leaching of enargite at 70 °C □: ferric leaching; ■: ferric/bacterial leaching.

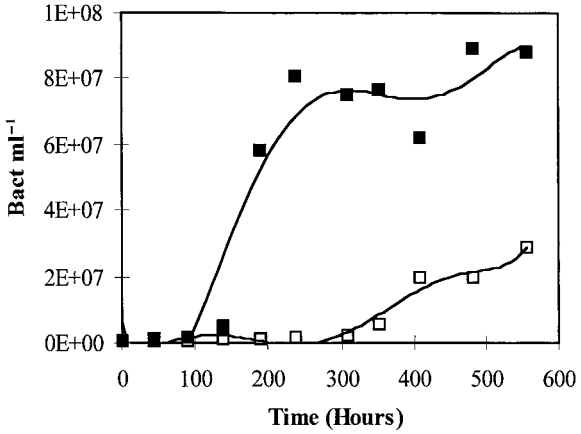

Fig. 4. Changes in bacterial numbers in the solution during the bacterial leaching of enargite at 70 °C; □: bacterial leaching; ■: ferric/bacterial leaching.

Results and discussion

Leaching and bioleaching of enargite

Enargite is a highly refractory sulfide that dissolves very slowly in sulfuric acid medium, even in the presence of ferric sulfate. Chemical acid leaching of enargite without iron only produced a small and constant dissolution rate of copper and arsenic, reaching after 552 h a dissolved fraction of 4,6% for copper and of 5.4% for arsenic (Figure 1).

The rate of chemical leaching of enargite with ferric iron was also slow and decreased significantly during the first 200 h of leaching. Then, the dissolution proceeded at a constant rate similar to that observed in the acid leaching without iron. After 552 h of leaching, only 8.4% of the copper initially present in enargite was dissolved. The decrease observed in the leaching rate could be partially explained by a decrease of the ferric ion concentration and, accordingly, an increase of the ferrous to ferric ratio (Figure 2). Nevertheless, even at the end of the leaching test, the ferric iron in the solution was not exhausted; therefore this low dissolution rate must be due to the refractory character of this mineral.

In this ferric leaching experiment, arsenic dissolution showed initially a kinetic similar to copper; however, due to the formation of ferric arsenate precipitates, final arsenic concentration in the leaching solution corresponded only to 3.9% of the arsenic initially present in enargite (Figure 1).

As observed in Figure 3, the copper dissolution in the ferric bioleaching was higher than in chemical ferric leaching. During the first 48 h, in both experiments ferric iron decreased (from 1200/700 to 200/100 mg l^{-1}) by reduction to ferrous iron on the enargite surface (Figure 2). The bacteria that initially attached to the mineral did not produce any significant oxidation of the ferrous iron. Ferrous ion concentration increased in the solution and the leaching was initially similar to the abiotic ferric experiment. However, the bacteria population started to grow significantly in the solution and reoxidized the ferrous iron to ferric iron (Figures 2 and 4). Then the rate of copper dissolution increased strongly until the ferric iron concentration decreased again due to the co-precipitation with arsenic. After 350 h of leaching, only about 200 mg l^{-1} of dissolved ferric iron remained in the solution. As a result of the precipitation, the difference between the apparent leaching of copper and arsenic was very significant. In this case, copper dissolution rate was much higher than the corresponding increase of dissolved arsenic, reaching (after 552 h) a copper concentration equivalent to 52% of dissolution calculated from the copper content of enargite. Dissolved arsenic concentration increased more slowly and tended to a constant value equivalent to only 17% of dissolution, probably due to ferric arsenate precipitation. X-ray diffraction analysis, performed on precipitates produced under similar conditions in a ferric bacterial leaching experiment, did not allow the identification of any crystallized products. In the absence of ferric iron, the bioleaching of enargite was slow, reaching only 12% of dissolution after 552 h for both copper and arsenic ions.

Arsenic effect on bacterial activity

Dissolved arsenic is known to be very toxic for organisms and its presence in solution could negatively affect the bioleaching of enargite. Therefore, the effect of increasing concentrations of dissolved As(III) and As(V) on bacterial growth was studied using pyrite as energy source instead of Fe(II) and in presence of arsenic concentrations between 200 and 1000 mg l^{-1}. For this strain of *Sulfolobus*, a concentration of 600 mg As(III) l^{-1} caused 90% decrease of the growth rate; the toxicity of As(V) was lower and significant only at 1000 mg l^{-1}. These values are similar to those obtained by Lindstrom & Selihn (1989), who grew a *Sulfolobus* strain in thiosulfate and by Ngubane & Baecker (1990), who obtained a complete inhibition of their strain grown in pyrite with 700 mg As l^{-1}. In our experiments, the maximum arsenic concentration

was 370 mg l^{-1} in the bacterial leaching solution and 420 mg l^{-1} in the ferric bioleaching.

According to Escobar *et al.* (1997), at 30 °C enargite dissolves stoichiometrically with similar copper and arsenic dissolution rates. Assuming that, in the present case, enargite leaching is also stoichiometric and supposing that all the leached arsenic would remain in solution, arsenic concentration equivalent to the enargite dissolution (calculated from soluble copper) would reach a final value of ~2000 mg l^{-1}, much above the inhibitory level determined for this bacteria. However, the results of these experiments show that co-precipitation of arsenic with ferric iron decreases arsenic concentration in solution. Therefore, this ferric-arsenic precipitation, enhanced by the high temperature used in these experiments, prevents bacterial inhibition in the bioleaching of enargite by leveling arsenic concentration in the leaching solution. It should be noted that the precipitation of ferric arsenate or ferric arsenite did not affect the kinetics of the sulfide dissolution.

Bacterial leaching mechanisms

Changes in bacterial numbers in the leaching solution during bacterial leaching with and without ferric iron are shown in Figure 4. In both cases, after an initial decrease of bacteria numbers (initial concentration was 3×10^7 bacteria ml^{-1}) due to attachment into the mineral surface, an increase was observed, suggesting that bacterial growth proceeded without inhibition. In the case of the ferric bioleaching, dissolved ferrous iron produced by the reduction of ferric iron at the mineral surface is reoxidized to ferric iron by the bacteria, which enhances bacterial growth. No significant inhibition by the presence of arsenic in the solution was observed.

A comparison between the copper dissolution rates obtained in the bacterial and chemical leaching experiments clearly shows the catalytic effect of bacteria (Figure 5). In the presence of bacteria, the rate of copper dissolution increased during the first 250 h, as did the bacterial numbers. In the bacterial leaching experiment without initial addition of ferric iron, the iron concentration in the leaching solution reached a maximum value between 5 and 10 mg l^{-1}, due to the dissolution of some iron containing contaminant of the mineral sample, probably chalcopyrite. This low concentration was not enough to sustain a long distance indirect mechanism and suggested that *Sulfolobus* BC catalyzes the dissolution of the sulfide by mechanisms

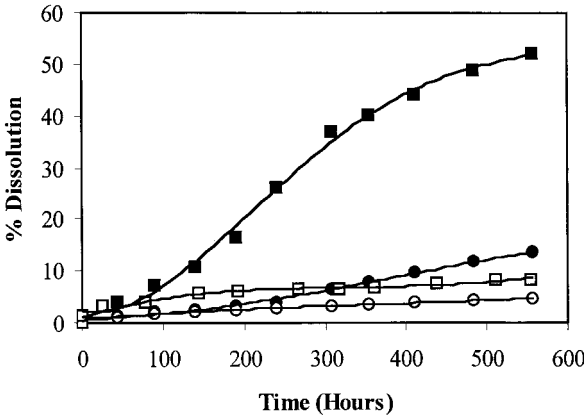

Fig. 5. Copper dissolution in the chemical and bacterial leaching of 2.0 g of enargite at 70 °C in 100 ml medium; ○: acid leaching; □: ferric leaching; ●: bacterial leaching; ■: ferric/bacterial leaching.

related to attached bacteria. Recent works suggest that the direct enzymatic oxidation of metal sulfides does no exist but that the bacteria catalyses the sulfide dissolution through different indirect mechanisms (Sand *et al.* 1999). In the case of metal sulfides like enargite that are amenable to a proton attack, the bacterial catalysis can be related to both elemental sulfur and ferrous ion oxidation. *Sulfolobus* can remove elemental sulfur produced during the chemical oxidation of enargite. Even at very low dissolved iron concentration, ferrous iron oxidation by attached bacteria is also an effective mechanism of leaching. Extracellular polymeric substances related to bacterial attachment to sulfide surface form an exopolymeric layer containing complexed ferric ions in a reaction space in which the dissolution process takes place (Sand *et al.* 1999). This is in agreement with the strong initial attachment of bacteria to the mineral surface, more than 86% in the first 30 min (Figure 4). The final copper dissolution obtained in the bacterial leaching without iron (12%) is higher than those obtained in the chemical ferric leaching (8%). In the ferric bioleaching experiment, both attached and free bacteria catalyzed the dissolution of enargite. Unattached bacteria reoxidize dissolved ferrous iron to ferric iron that in turn oxidizes the mineral.

Conclusions

The results of this study show that enargite is effectively solubilised by ferric bioleaching with *Sulfolobus* BC, with a high copper dissolution but a lower dissolution of arsenic because a fraction of the ar-

senic remains in the solid residues, probably as ferric arsenate.

Sulfolobus BC bacteria attached to the sulfide are able to catalyzed enargite dissolution, even at very low dissolved iron concentration. The bacterial dissolution rate of enargite is higher than chemical dissolution in the presence of ferric iron. In these bioleaching experiments, due to the high temperature and to the continuous regeneration of ferric iron, arsenic precipitates as ferric arsenate, which reduces its dissolved concentration and therefore its negative effects on bacteria.

The above results suggest that, due to the precipitation of ferric arsenate, bioleaching of arsenic bearing copper ores and concentrates in the presence of *Sulfolobus* BC and ferric ion could be considered as an alternative, in spite of arsenic inhibition of bacterial activity at high dissolved arsenic concentrations.

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