USE OF BIOREACTORS IN THE LEACHING OF AN OXIDIZED COPPER ORE

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***Abstract*— Copper recoveries using two methodologies of acid leaching of a low-grade ore are reported in this work. The ore, abounding in oxidized species, was from Barda González reservoir in Neuquén province, Argentina. In the first methodology, cells of *Acidithiobacillus thiooxidans* were inoculated into a column containing the ore and sulfur as energy source. In the second one, a bioreactor with immobilized cells of *Acidithiobacillus thiooxidans* placed on small pieces of elemental sulfur was used to generate acid medium. This medium was then transferred to another column containing the ore. In the first methodology low cell counts and also low copper recovery were obtained. However, in the other, about 56 % of copper was recovered after four loads of fresh medium.**

***Keywords*— Bioreactors, copper, oxidized ore, *Acidithiobacillus thiooxidans*.**

I. INTRODUCTION

Acidithiobacillus thiooxidans (*A. thiooxidans*) is a chemolithotrophic bacterium frequently associated with sulfide ores. It plays a major role in metal solubilization processes from minerals, in a direct or indirect way, together with another microorganisms (Rawlings, 1997). This bacterium is able to catalyze the oxidation of reduced inorganic sulfur compounds using oxygen as the terminal electron acceptor. Elemental sulfur can be also used as substrate (Gourdon and Funtowicz, 1998; Konishi *et al.*, 1995) according to the following process:

$$S + 3/2\ O_2 + H_2O \longrightarrow H_2SO_4 \qquad (1)$$

Precisely, the previous equation probably shows the most significant contribution of this bacterium to the solubilization of metals, specially when they are associated with oxidized species easily assailable through acid leaching (Bhatti *et al.*, 1997; Donati *et al.*, 1995*)*.

Sulfuric acid can be continuously produced in bioreactors with *A. thiooxidans* where the cells are attached to elemental sulfur (Donati *et al.*, 1995; Pich Otero *et al.*, 1995).

The aim of this work was to study the sulfuric acid production in a bioreactor with immobilized *A. thiooxidans* cells and the use of this acid in the leaching of an ore. The mineral is from Neuquén province and its copper content is present mainly as oxidized compounds easily solubilized by low-concentration acid solutions.

II. METHODS

Culture

A. thiooxidans DSM 11478 routinely cultured at 30 °C in 9 K medium (Silverman and Lundgren, 1959) without ferrous sulfate, named 0 K, with sulfur as energy source, was used in all experiments.

Sulfur Bioreactor

Bioreactors were flooded columns of 29 cm height and 4 cm diameter, containing 300 ml of 0 K medium adjusted to pH 5.0 and 100 g of sulfur (particle size about 1-2 mm). Cultures of *A. thiooxidans* were harvested in exponential growth phase and used as inoculum. Air was continuously fed to the solution at a flow of 2.5 VVM (air volume/liquid volume/minute). When the pH about 1.0 was reached, the liquid into the reactor was replaced by the same volume of fresh medium, without new inoculation. The bioreactor was loaded five times in order to reach a constant sulfuric acid production (five steps of biofilm generation). During these growth phases, pH, proton concentration and bacterial numbers in suspension were determined. Scanning electron micrographs of the cells were taken in a Philips 515 equipment. A drop of liquid culture was dried

on a slide and covered with a thin gold layer for SEM observation.

Ore

The analyzed samples belong to the clastic-hosted copper deposits exposed at Barda González reservoir, Confluencia mining district, Neuquén province, Argentina (Angelelli and Schalamuk, 1978). Analytical and mineralogical studies on copper bearing samples were carried out in order to establish the best strategies of metal recovery. X-ray diffraction patterns on powdered samples were carried out before and after the leaching process. A Rigaku DII-Max automated diffractometer was used between 5-70º 2 θ with Cu-Kα radiation at 2º/min rate.

Bioleaching Experiments

Leaching experiments were carried out using two different methodologies. In the first one, *A. thiooxidans* cells, from a culture at exponential growth phase, were inoculated into a column containing 100 g of the ore, 100 g of sulfur and 250 ml of 0 K medium at initial pH 5.0. This experiment attempted to simulate "in situ" bioleaching conditions. In the second methodology, sulfuric acid was produced in a bioreactor as previously described, and then used in another column containing 100 g of ore. Acid was replaced in the column with ore when pH of the system reached the value of 3.0. This operation was called "load of the bioreactor". Four loads were carried out during the experiment.

Bacterial populations in suspension were determined using a Bausch & Lomb microscope with contrast phase attachment in a Petroff-Hausser counting chamber. Proton concentration was measured by titration with sodium hydroxide solution. Soluble copper was determined by atomic absorption spectrophotometry.

III. RESULTS

Ore mineral characterization

The mineralogical composition of the ore was determined from X-ray diffraction analysis. It was possible to confirm that the ore sample consists of quartz, feldspar and copper compounds. The main sulfide and oxidized species were:

Chalcocite	(CuS_2)
Malachite	($Cu_2(CO_3)(OH)_2$)
Azurite	($2CuCO_3.CuO.H_2O$)

The knowledge of mineralogical composition of the ore suggested the possibility of applying acid leaching techniques. Oxidized species and chalcocite (Schippers and Sand, 1999) can be easily leached with low concentration acid medium extracting copper from the ore. Total copper concentration in the samples (5.2%) was higher than the average value reported for the reservoir (Danielli and Giusiano, 1992). The characteristics of the selected sampling place and the milling process contributed to the copper enrichment in the sample.

Biofilm generation and acid production

Figures 1 and 2 show the evolution of proton concentration in the solution and the acid productivity in different steps of the biofilm generation during five loads of the sulfur bioreactor.

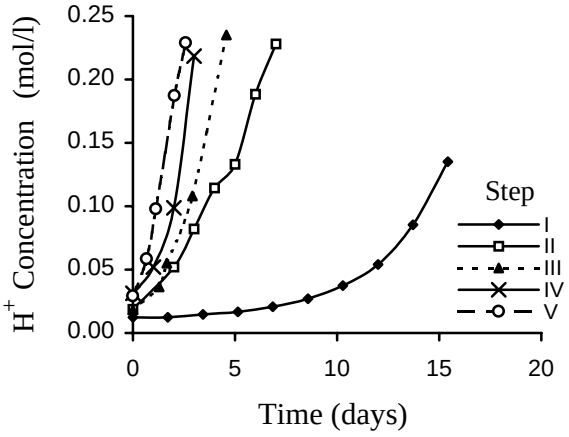

Figure 1. Proton production during the first five steps of the biofilm formation in the sulfur bioreactor.

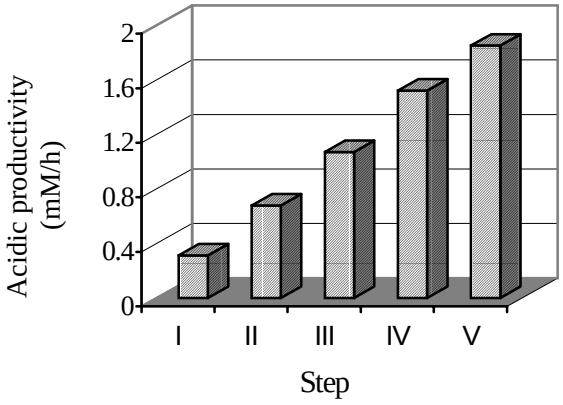

Figure 2. Sulfuric acid productivity in a sulfur bioreactor during the first five steps of biofilm generation.

Figure 3 shows the bacterial population in suspension during the different steps. A scanning electron micrograph of a sample of this culture, prepared as it is described in methods, is illustrated in Fig. 4. It shows typical morphology of *A. thiooxidans* cells.

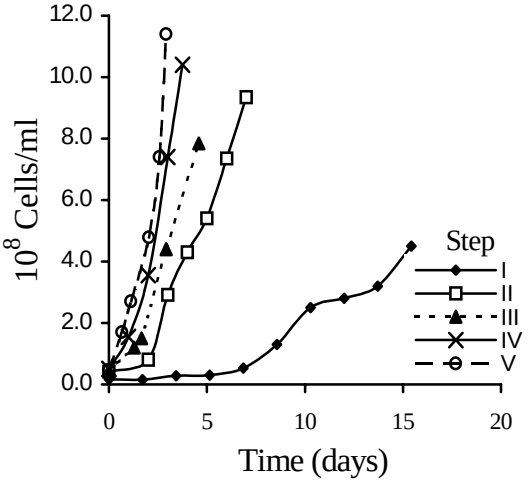

Figure 3. Cell population in suspension in each of the five steps carried out in the sulfur bioreactor.

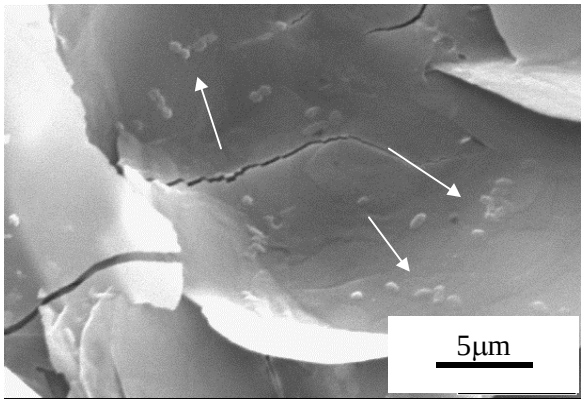

Figure 4. Scanning electron micrograph of *A. thiooxidans* cells present in a dried drop of 0 K medium from the sulfur bioreactor.

During the process of *A. thiooxidans* biofilm formation, proton production rate increases in each load reaching a constant value after the fourth step. This constant proton production rate is probably reached when:

a) A monolayer of cells was formed on sulfur surface avoiding higher cell attachment and higher proton production rate.
b) The bacterial growth and the subsequent proton production are limited by oxygen and/or carbon dioxide diffusion rate.

The first option is in agreement with electron micrographs (not shown) indicating the formation of biofilms on the sulfur. Acid production average rate in each step can be expressed as global productivity and it is depicted in Fig. 2. The change of the productivity value in each new step decreases and tends to be zero, this meaning that the acid production has reached a constant rate.

Although total bacterial population could not be determined, the model reported by Espejo and Romero (1987) for the growth of *A. ferrooxidans* on sulfur was assumed. In that study, sulfur surface becomes saturated with cells without further increase of adsorbed bacteria after a few days. Then, the progeny is released to the solution where it is unable to duplicate unless soluble compounds susceptible to further oxidation were released into the medium. In that way, bacterial population in the suspension is an indirect measure of the growth of attached cells. Figure 3 shows that the bacterial population in suspension continues increasing in each step before the fifth one in agreement with the acid productivity obtained. This means that after each step cells have less surface to attach to and were released to the suspension immediately. According to Espejo and Romero (1987), it is also possible that some regions which remained intact in the first stages were finally colonized by the cells producing higher bacterial growth and acid production. However, after the fifth step, cells had covered completely the available surface and the limiting step in the acid production (due to the bacterial growth on the surface) could be attributed to both oxygen and nutrient diffusion and not to either the cell number or the available surface.

Bioleaching experiments

Soluble copper concentration during direct bioleaching by *A. thiooxidans* can be seen in Fig. 5. Results show very low copper extraction -less than 1 %- in agreement with the negligible growth of bacterial population and the evolution of the medium pH. At the beginning, pH increased to 7.0 and then decreased to 4.5 tending to be constant at this value till the end of the experiment. This performance can be explained considering that initial biological acid production is consumed during the initial copper solubilization of oxidized species. It makes pH quickly increase and inhibits bacterial growth. In order to check this interpretation, a new experiment was done but initial pH was 3.0 and it was maintained constant during a period of time to let bacteria grow. However, no cell growth was observed.

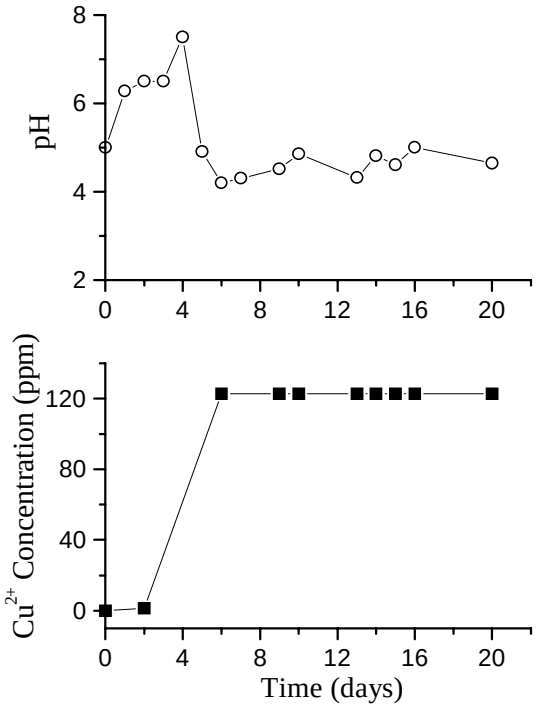

Figure 5. Copper solubilization in the direct inoculated bioleaching system.

Another bacterial strain, *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) DSM 11477, was used in a new series of experiments. The results obtained in pH evolution and copper extraction were similar to those ones using *A. thiooxidans*, while bacterial growth was slightly higher. The increase in cell population may be due to a direct action of *A. ferrooxidans* on insoluble sulfides present in low quantity in the ore. This action is not possible for *A. thiooxidans*.

Low copper recovery obtained in the direct inoculation with *A. thiooxidans* could be attributed to the following considerations, although they have not been confirmed yet:

- Attachment to the surface is an essential step in the biooxidation of elemental sulfur. Because of this, it is possible that an important adsorption could have occurred on the ore surface avoiding their attachment to the sulfur particles.
- Acid solubilization of minor but toxic species present in the ore. These species could have inhibited the bacterial growth. This explanation is supposed to be the most probable one.

In the indirect leaching using acid medium generated in a bioreactor with immobilized cells, higher copper dissolution than in the experiment with direct inoculation was observed (Fig. 6).

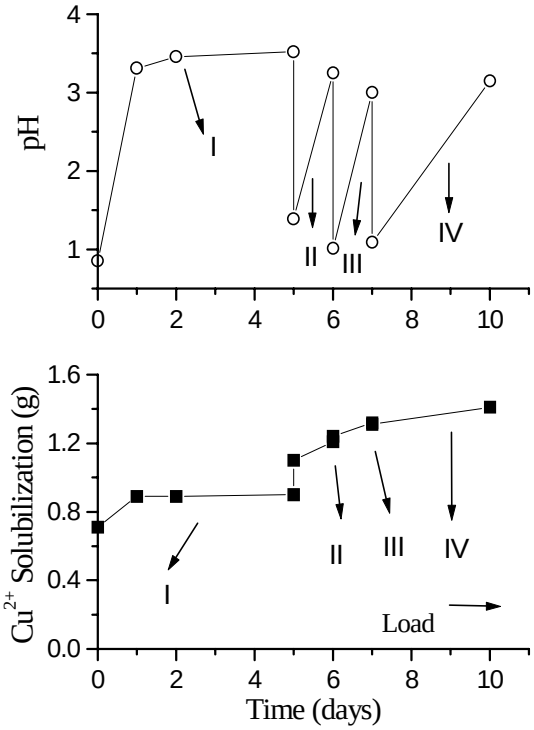

Figure 6. Copper solubilization during indirect bioleaching of the ore. Each load represents the replacement of medium by fresh sulfuric acid solution generated in the sulfur bioreactor.

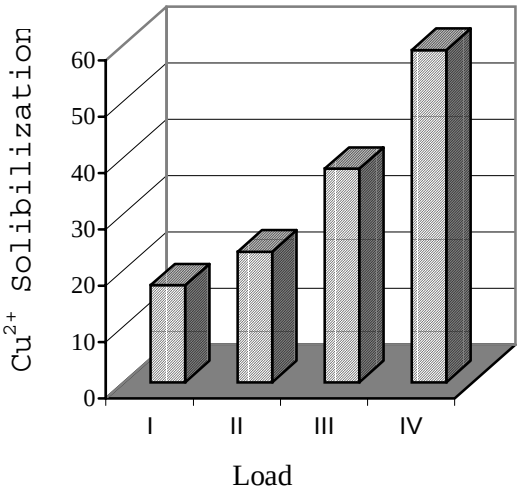

Figure 7. Copper percentage obtained at the end of each load during the indirect leaching. These values were calculated taking into account the amount of metal accumulated in the previous load.

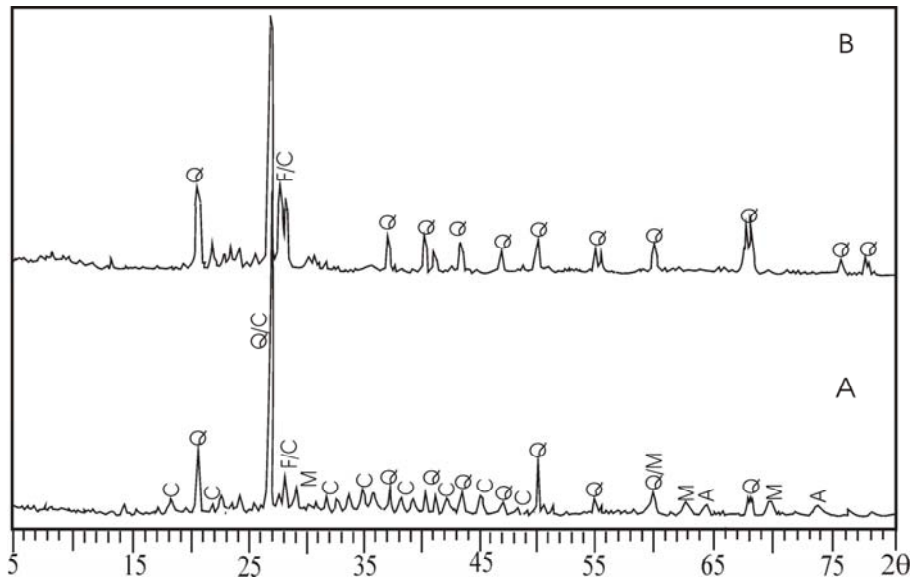

Figure 8. X-ray diffraction patterns of the original sample (A) and after treatment (B). M=malachite; A=azurite; Q=quartz; C=chalcocite; F=feldspar.

In Fig. 6, the slow increase of pH in the last load can be observed; it suggests that the solubilization of the species that can be directly recovered in acid medium is decreasing. Nevertheless, copper extraction was increasing in the last loads (Fig. 7) suggesting that it would be possible to obtain greater recoveries in next stages independently of the extraction rate. However, as the experiment was stopped after four loads, the final copper recovery was about 56 % of the original content in the ore sample.

In Fig. 8, X-ray diffraction patterns, before and after the treatment, are compared. X-ray diffraction patterns of leached residues revealed that oxidized copper compounds present in the original sample were absent in the solid residues after acid treatment, whereas some sulfides (like chalcocite) were partially removed. These results are consistent with the copper extraction observed in the leaching experiments. Quartz and feldspar were not removed.

Although this methodology seems to be effective, its industrial application needs further studies. Among others, we have to probe this methodology operating in a closed circuit, which is more adequate within an industrial context. These studies should evaluate the necessity to insert the partial copper recovery from the leachate (or the elimination of possible toxic substances for the cells) before recirculating the effluent solutions.

IV. CONCLUSIONS

In the present study, we demonstrated that copper recovery from Barda González ore is feasible through a leaching process by using sulfuric acid produced in a reactor with immobilized *A. thiooxidans*. Our results also indicate the advantage of the use of combined bioreactors instead of "in situ" leaching. However, its application at commercial level implies further studies.

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