PRE-TREATMENT OF A REFRACTORY GOLD SULFIDE ORE BY MEANS OF *ACIDITHIOBACILLI* CELLS

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***Abstract*— Cyanidation is a relatively simple and cheap technology to treat gold-containing ores. However, this process is not completely effective in refractory gold-bearing sulfide ores. In the case of very low-grade ores, biooxidation is an attractive alternative pre-treatment to render the gold amenable to extraction. This process utilizes the ability of acidophilic bacteria to oxidize the sulfide matrix, physically freeing the gold. The aim of this work is to evaluate the recovery of other available metals (Fe, Mn, Cu and Zn) during the biooxidation pre-treatment of an ore from Andacollo with low gold recovery (less than 50 %). This pre-treatment was carried out in shaken flasks using pure cultures of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and a mixed culture with both bacteria.**

***Keywords*— *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans,* metal recovery, biooxidation.**

I. INTRODUCTION

The autotrophic bacteria *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) and *Acidithiobacillus thiooxidans* (*A. thiooxidans*) are frequently associated with sulfide minerals (Rawlings, 1997; Kelly and Wood, 2000). Both bacteria obtain their energy from the oxidation of reduced sulfur compounds. The major difference between those species is fundamentally that *A. ferrooxidans* is also capable of oxidizing iron(II).

These bacteria are capable of acting directly or indirectly on metallic sulfides, oxidizing the sulfides till sulfate and thus leaching the metals if the respective sulfates are soluble. For this reason, these microorganisms have been used for bioleaching of low-grade ore on a commercial scale (Donati *et al.*, 1992; Donati *et al*., 1996).

Other recent application of these microorganisms is in the pre-treatment of gold ores in order to increase the subsequent gold recovery during cyanidation processes. In several gold ores, gold is trapped in the matrix of metallic sulfides, mainly pyrite (FeS_2) and arsenopyrite (FeAsS). In such cases, ore must be pre-treated in order to release the gold physically and to make the ore amenable to cyanidation. The traditional methods of pre-treatment include oxidation by nitric acid, roasting or pressure oxidation. Roasting produces off-gases containing sulfur dioxide and arsenic trioxide, which requires later expensive treatment. The other methods require high pressure, high temperature and/or corrosion-resistant materials. Biological oxidation (biooxidation) as pre-treatment of refractory gold ores is based on the ability of acidophilic microorganisms to oxidize and dissolve pyrite and arsenopyrite, thus releasing the entrapped gold particles (Longhans *et al*., 1995; Komnitsas and Pooley, 1989). Although the rate is low, biooxidation is considered to be cheaper (specially in very low-grade ores) and more environmentally friendly than other methods (Poulin and Lawrence, 1996; Deng *et al.*, 2000; Climo *et al.*, 2000; Ubaldini *et al.*, 2000, Karamanev *et al.*, 2001). During the biooxidation process, other available metals can be recovered, thus avoiding overconsumption of cyanide (due to the presence of cyanicides like iron or zinc). At the same time, this process avoids the possible coating of gold particles with precipitates (specially iron hydroxides) during the cyanidation under alkaline conditions.

Andacollo is a gold sulfide ore coming from Andacollo area in the northwest of Neuquén province (Argentina). Gold is present in that ore as submicroscopic particles contained in a pyrite matrix. This ore is partially refractory (about 50 % of the gold was extracted even without pre-

treatment). The aim of this work is to evaluate the recovery of other available metals (Fe, Mn, Cu and Zn) during the biooxidation of that ore. This pre-treatment was carried out in shaken flasks using pure cultures of *A. ferrooxidans* and *A. thiooxidans* and a mixed culture with both species in order to compare bacterial mechanisms (Nestor *et al.*, 2001). Finally, the effect of this pre-treatment in gold extraction was evaluated on the bioresidue from the culture with the best extraction of other metals. This last fact suggested high oxidation of the sulfides and high release of the gold trapped within the sulfide matrix.

II. METHODS

A. Microorganisms and media

Pure cultures and mixed cultures of *A. ferrooxidans* (DSM 11477) and *A. thiooxidans* (DSM 11478) were used throughout this study. *A. ferrooxidans* was cultivated routinely in 9K medium of initial pH 1.80 (Silverman and Lundgren, 1959). Cells were harvested by filtering through a 0.22-micron filter when 90 % of the iron(II) had been oxidized. Previously, culture was filtered through blue ribbon filter paper to retain jarosite (basic iron(III) sulfates). Cells were washed at least twice with iron-free medium and suspended in the same medium (pH=2.0). *A. thiooxidans* was cultivated routinely in the same basal medium with sulfur instead iron(II) as energy source. Cells were collected when the pH descended below 1.0 and the procedure for harvesting was similar to that applied for *A. ferrooxidans*. These suspensions (with bacterial populations of approximately $2x10^8$ cells/ml) were used as inoculum at the 10 %v/v.

B. Mineral

Gold ore from Andacollo in the northwest of Neuquén province (Argentina) was used in this study. The mineralogical composition was sphalerite 0.71 %, galena 0.76 %, pyrite 9.51 %, chalcopyrite 0.16 %, arsenopyrite 0.08 % and iron oxides 0.13 %. The chemical composition was 10 g/t Au, 238 g/t Cu, 2975 g/t Zn, 0.39 % MnO and 6.53 % Fe_2O_3. The particle size was under 200 mesh.

C. Experiments

500-ml flasks containing 270 ml of iron-free 9K medium (pH=2.0) and 30 ml of inoculum (15 ml of each inoculum in mixed cultures) were used throughout these experiments. 15 g of the mineral were added to the flasks. The flasks were incubated on a shaker at 180 rpm and 30 ± 0.5 ºC.

Sterile controls were prepared replacing the inoculum by the same volume of 2 % w/v thymol solution in methanol. Moreover, they were prepared as the uninoculated control systems.

After biooxidation, cyanidation of the bioresidue was carried out in shaken flasks for 24 h (solid/liquid 1/2.5) with sodium cyanide (1.5 kg/t of mineral) at pH 11.

D. Analytical methods

Total iron, manganese, copper and zinc in solution were determined by atomic absorption spectrophotometry. Iron(II) concentration was determined by permanganimetry. Bacterial populations in solution were determined using a Petroff-Hausser camera in a microscope with a contrast phase attachment. Redox potential and pH were measured each one with an electrode. The sulfuric acid formed was analyzed by titration with 0.01N sodium hydroxide solution. The mineralogical analysis was performed with a chalcographic microscope and confirmed by microanalysis with EDAX.

III. RESULTS

In preliminary experiments it was verified that the contact of the mineral with the medium caused an immediate increase of the pH until values near the neutrality where the bacterial activity is completely inhibited. For that reason, previous to biooxidation experiment it was necessary the pH stabilization by successive sulfuric acid additions. During this stabilization, 21.0 % of Mn, 12.5 % of Cu and 6.2 % of Zn were solubilized. Before inoculation, sulfuric acid consumption was 67.5 g H_2SO_4/kg ore average indicating the presence of high alkaline gangue contents such as carbonate minerals. The amount of acid generated by the microorganisms could not be enough to maintain the initial pH 2.0.

Figure 1 presents the evolution of sulfuric acid concentration in each culture during the bioleaching process. Values lower than the original in each system indicate that there was acid consumption in the process, while higher values suggest an acid production.

Figures 2, 3, 4 and 5 show the evolution of some metals in solution (Fe, Mn, Cu and Zn, respectively) during the biooxidation process.

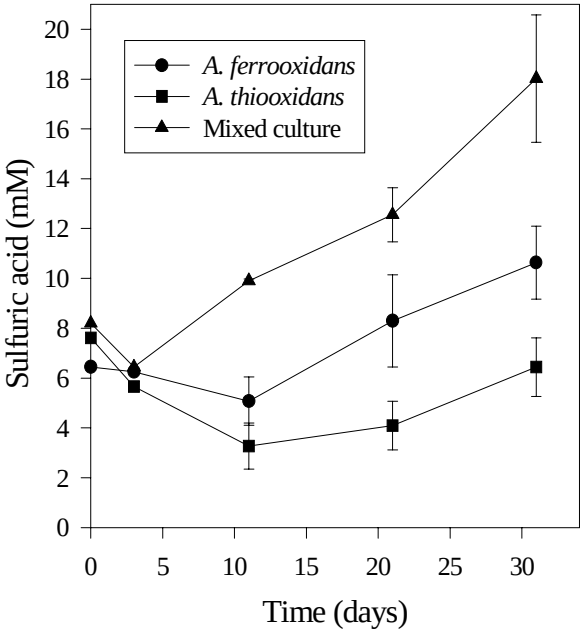

Figure 1. Evolution of sulfuric acid concentration.

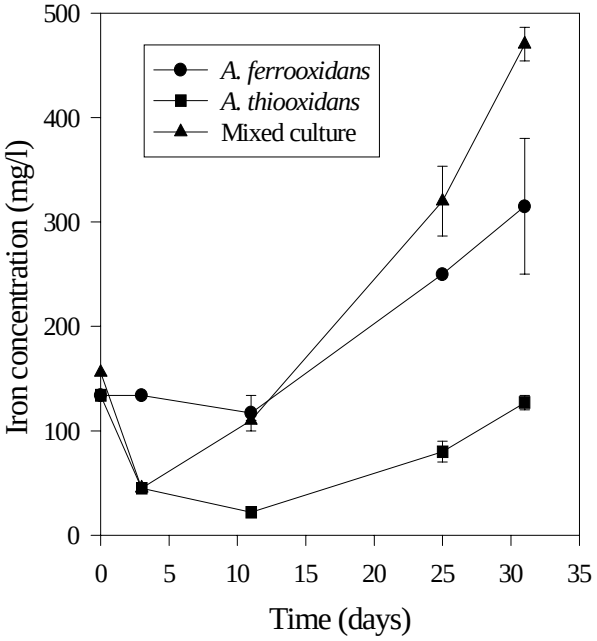

Figure 2. Total iron concentration.

IV. DISCUSSION

Figure 1 shows an initial acid consumption probably due to the solubilization of some oxidized species. The highest acid consumption was found in *A. thiooxidans* culture. After that, an increase of sulfuric acid concentration can be observed. This fact suggests a bacterial action on the sulfides producing sulfur and a later sulfur oxidation to sulfuric acid. Both cultures including *A. ferrooxidans* produced more sulfuric acid showing a larger activity of this bacterium. This is in agreement with previous results indicating that *A. thiooxidans* cells do not present significant activity on insoluble sulfides such as pyrite or covellite (Donati *et al*., 1996; Donati *et al*., 1995). Mixed culture shows an activity clearly larger than that of the pure cultures suggesting that the activity of both species was complementary. Probably, the role of *A. ferrooxidans* was the attack of sulfides while the role of *A. thiooxidans* was the production of sulfuric acid by the oxidation of the sulfur generated during the first process.

In Fig. 2 it can be observed that the iron evolution in solution is similar to the observed in the acid production. Thus, although *A. ferrooxidans* culture continues being the best pure culture, it extracts less iron than the mixed culture. Except for *A. thiooxidans* culture, iron in solution was detected mainly as iron(III) indicating the activity of *A. ferrooxidans.* This agrees with high Eh values.

Figure 3 shows the percentage of manganese recovery during bioleaching processes. There were not significant differences between the different cultures although *A. thiooxidans* culture reached the largest extraction (26.6 %) while in the sterile control manganese recovery was 23.8 %. Thus, the presence of these bacteria did not enhance manganese recovery significantly. This behavior is probably due to the fact that manganese was as carbonate in the ore and this compound is easily solubilized in acid media even in the absence of microorganisms.

Copper extraction reached values near 50 % in the mixed culture (Fig. 4). The extraction in the culture of *A. thiooxidans* began to be important towards the last periods of the experiment and probably it was due to an indirect mechanism of bioleaching in the presence of iron(III) as it has been previously reported (Donati *et al*., 1995). 20.0 % was extracted in the sterile control.

The kinetics of zinc extraction (Fig. 5) was similar to that found in the case of copper and iron extractions. Zinc recovery in the sterile control was 11.0 % . Thus, microbial action allowed to increase significantly the extractions of Fe, Cu and Zn which were essentially as sulfides in the ore.

According to previous studies (Spencer, 2001), the best metal extraction was found using a mixed culture. Although it is almost impossible to use pure cultures in any commercial application, the comparison between results in the biooxidation using mixed or pure cultures allowed to obtain some evidence about the role of each bacterial species.

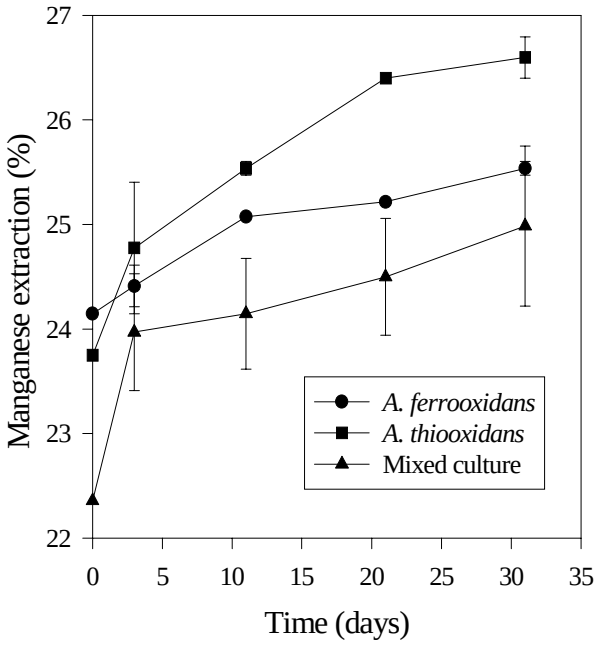

Figure 3. Percentage of manganese recovery.

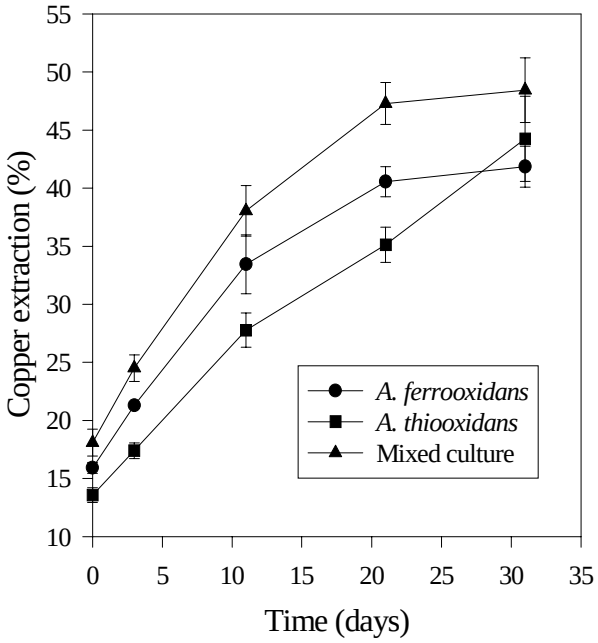

Figure 4. Percentage of copper recovery.

After bacterial pre-treatment, the residue from the mixed culture was exposed to cyanidation and 74.0 % of the gold was extracted (20 % higher than that extracted using the ore without pre-treatment) confirming that the sulfide matrix had been partially oxidized.

V. CONCLUSIONS

The biooxidation of Andacollo ore allowed us a large extraction of iron, manganese, copper and zinc specially when a mixed culture was utilized probably through the combination of two processes (sulfide dissolution by *A. ferrooxidans* and sulfur oxidation by *A. thiooxidans*).

Moreover, gold recovery by cyanidation was enhanced significantly after the bacterial oxidation confirming the partial destruction of the sulfide matrix surrounding the gold.

Summarizing, it is possible to use biooxidation of Andacollo ore as pre-treatment not only to increase the final gold recovery but also to recover other available metals contained in the ore.

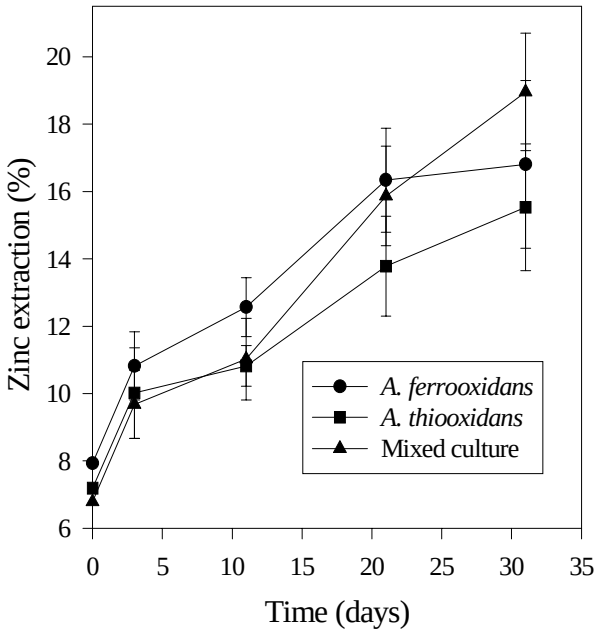

Figure 5. Percentage of zinc recovery.

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