ABSTRACT

The bioleaching or bio-assisted leaching of flotation concentrate was begun, many years ago, with the use of microorganisms present, naturally, in the acid mine drainages. With the use of acidophilic microbial consortia, it was sought to speed up the digestion of metallic sulphides. The copper sulphides flotation concentrate used in this study is constituted of 30% of bornite \((\text{Cu}_5\text{FeS}_4)\) and 70% of chalcopyrite \((\text{CuFeS}_2)\), being this last one highly refractory sulphide mineral to the conventional leaching processes. Following, in the oxidative process of column sulphides, the parameters such as copper extraction, the redox potential, pH, ferrous and ferric ions and total iron concentrations, were monitored and/or adjusted. Nearly 79% of copper was extracted in 60 days of leaching process, showing that the bioleaching was an efficient route for opening sulphide minerals releasing the metals of interest.

RESUMEN

La bio-lixiviación o lixiviación bio-asistida, de concentrados de flotación fue iniciada hace muchos años con la utilización de microorganismos presentes naturalmente en el agua ácida de mina, producto de drenaje ácido. Con la utilización de consorcios microbianos acidófilos se pretendió agilizar la abertura de los sulfuros metálicos. El concentrado de flotación de sulfuros de cobre utilizado en este estudio estuvo compuesto de 30% de bornita \((\text{Cu}_5\text{FeS}_4)\) y 70% de calcopirita \((\text{CuFeS}_2)\), siendo este último un mineral altamente refractario, es decir, más resistente a los procesos convencionales de lixiviación. Para el acompañamiento del proceso oxidativo de los sulfuros, en columnas, fueron monitoreados o ajustados los parámetros de concentración de cobre en la lixiviación, los valores de potencial redox, el pH, las concentraciones de iones ferrosos, iones férricos y el hierro total. Se logró una extracción de cerca del 79% de cobre en 60 días de operación, mostrando que la bio-lixiviación fue una ruta eficiente para la abertura de los sulfuros y la solubilización del metal de interés.
INTRODUCTION

The copper production from flotation concentrate follows conventional technological routes as a function of mineralogical species that compose such concentrate. In the case of flotation concentrate, the copper sulphides are converted into blister copper (impure metallic copper) after using previous pyrometallurgical processes, through flash smelting process and electrolytically refined afterwards. Although the pyrometallurgical process presents the advantage of transforming different copper sulphides of those concentrates into metallic copper, it presents, otherwise, inconveniences of generating sulphur dioxide (SO$_2$) together with heavy metals issues, as cadmium, arsenic, mercury, bismuth, selenium etc.

The copper sulphides concentrate under study was constituted, mainly, of chalcopyrite (CuFeS$_2$) and bornite (Cu$_5$FeS$_4$) with tenors, approximately, of 70 and 30%, respectively.

The heap bioleaching process is important in the metals extraction from sulphide minerals can be used in wide scale, with low operational costs. The bioleaching is a biotechnological process based in the use of microorganisms capable to solubilise metals through the oxidation of sulphide minerals [Garcia Jr., 2001].

Most of the studies accomplished at lab-scale considered that the metal extraction process was only reached with the use of bacteria of Acidithiobacillus ferrooxidans species. However, those experiences did not correspond to the natural situation and, during the last years, other microorganisms, involved in the leaching process, were discovered and characterized (Leptospirillum ferrooxidans, Acidithiobacillus thiooxidans, thermophilic, anaerobic and heterothrophic bacteria) [Norris, 1990].

Bio-leaching Mechanism

It is well known that the temperature, stirring speed, particle size (surface area), acidity, nutrients and addictive affect the dissolution rate of the sulphide minerals through microorganisms. There are two mechanisms involved in the bacterial attack of those sulphides: the direct and indirect ones. In the direct mechanism, the bacterium acts directly in the sulphide mineral. In the indirect mechanism, the bacterium converts, simply, Fe$^{2+}$ to Fe$^{3+}$ and elemental sulphur into sulphate, while the Fe$^{3+}$ ions act directly in the oxidation of the sulphide minerals [Smith & Misra, 1991].

![Figure 1 Bio-leaching mechanisms: Direct and indirect ones [Smith & Misra, 1991]](image)
The use of mixed cultures of acidophilic microorganisms, acting in different temperature ranges, aims at speeding up the digestion of the sulphide minerals bearing flotation concentrate produced by Caraíba Mining Company, with an attractive processing.

**EXPERIMENTAL**

**Flotation Concentrate**

The sulphide concentrate used in the experiments is the result of the copper sulphides flotation process from a primary ore (underground mining). That concentrate contains about 30% of bornite ($\text{Cu}_5\text{FeS}_4$) and 70% of chalcopyrite ($\text{CuFeS}_2$). The particle size analysis was made by wet sieving, using Tyler series standardized sieves (0.106 to 0.043 mm). The copper concentration in the liquor was measured by atomic absorption spectrometry, while the Fe$^{2+}$ and Fe$^{3+}$ concentrations by spectrophotometry in the UV-visible range.

**Coating of Support Rock with Flotation Concentrate**

The definition of the support rock is necessary bearing in mind that the copper extraction process from the flotation concentrate will be accomplished in a heap and, therefore, the finely divided sulphides concentrate should be coating the support rock surface so that the bioleaching takes place. The support rock used was the marginal copper ore, with 0.3% copper content in particle size ranging from 2 to 20 mm.

The support rock coating procedure was accomplished (marginal ore of low copper content) with flotation concentrate so as to start the bioleaching process in semi-pilot columns, in order to simulate, in that scale, the heap bioleaching process.

A crushed, screened support rock is thinly coated with sulphide concentrate slurry, stacked on a lined pad, and allowed to bio-oxidize. The coating operation is accomplished by spraying the concentrate slurry onto the support rock as it discharges from the end of a stacking conveyor onto the bio-oxidation heap [Harvey et al., 2002].

The coating solids density is highly dependent on the slurry viscosity and densities of 50–65% have been successfully coated at scale. The support rock is relatively uniformly sized, in the range of 6–25 mm in diameter and the concentrate coating is relatively thin, less than 1 mm in thickness [Harvey et al., 2002].

In agreement with the technology holder, Geobiotics, LLC, the amount of concentrate coating the surface of the mineral substrate can reach up to 10% of the total mass of the material (support rock + sulphides concentrate) constituting the final heap.

**MKM Culture Medium**

For the propagation of the microbial inoculum, the MKM culture medium was used, with small modifications [Olson et al., 2006]. The composition of the aforementioned medium can be seen in the Tables 1.
Table 1 Nutrients solution composition of MKM medium

<table>
<thead>
<tr>
<th>Nutrients</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>0.4 g/L</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>0.04 g/L</td>
</tr>
<tr>
<td>MgSO$_4$*7H$_2$O</td>
<td>0.4 g/L</td>
</tr>
</tbody>
</table>

Microorganisms Cultivation

**Mesophile Microorganisms (A. ferrooxidans and A. thiooxidans)**

The microorganisms *A. ferrooxidans*-S and *A. thiooxidans*-FG01 [Garcia, 1991] used were cultivated in room temperature, in shaking table at 150 rpm, using the MKM culture medium with double concentration [Olson, 2006]. The pH of the culture medium was adjusted to 1.8 for *A. ferrooxidans* and 2.8 for *A. thiooxidans*, adding H$_2$SO$_4$ 10N.

**Consortium of thermophile microorganisms**

The consortia of moderate and extreme thermophile microorganisms used were cultivated in temperature of 50°C (moderate) and 68°C (extreme), in incubator with rotation speed of 150 rpm, using MKM culture medium with double concentration [Olson, 2006]. The pH adjustment for 1.7 was accomplished adding H$_2$SO$_4$ 10N. The daily monitoring of redox potential and pH was accomplished, being H$_2$SO$_4$ added when necessary for keeping the pH below 1.8.

It was used 33.33 g/L of FeSO$_4$*7 H$_2$O for cultivating *A. ferrooxidans*, and 1% of elemental sulphur for cultivating *A. thiooxidans*. For the cultivation of thermophile microorganisms, 1% of flotation concentrate was used, 1% of pyrite and 0.2 g/L of yeast extract.

**Counting of microorganisms**

The counting of microorganisms in Thoma Chamber was the adopted method. This camera is a compartment with defined dimensions: 0.0025mm$^2$ of area and depth of 0.1 mm, endowed with square divisions. The cells number was counted in optical microscope, with the aid of a Thoma Chamber.

**Bioleaching in the Computerized Column Unit**

The bioleaching tests were accomplished in 60 cm high column with 12.7 cm of diameter. This test was divided in 3 (three) steps: 1$^{st}$) bioleaching using mesophile consortium; 2$^{nd}$) bioleaching using moderate thermophile consortium; 3$^{rd}$) bioleaching using extreme thermophile consortium. At the end of each step, the leachate recirculation was stopped so as to add other microbial consortium (10$^6$ cells per gram of flotation concentrate). The microorganisms were added directly in the column through a spraying vessel.
The temperature of the column, the redox potential and pH of the leaching solution were constantly monitored by the automated system through combined electrode and, whenever necessary, 10N H$_2$SO$_4$ was added.

The bioleaching test was begun accomplishing the coating of the support rock (marginal ore) (Geo-coating®) with flotation concentrate, using acidified water at pH=1.5. The inoculation of the system was accomplished after 24 hours of the coating operation. That inoculation proceeded adding the microbial mesophile bacteria inoculum to the top of the column, using a spraying system. The bioleaching process started from percolating the MKM culture medium in concentration of 20% (0.2x - teams), containing 10 g/L of Fe$_2$(SO$_4$)$_3$, at an irrigation rate in the 15 to 20 L/h.m$^2$ range.

The temperature was kept at 30°C for 20 days, up to the stabilization of the redox potential and copper extraction. After that step, the top of the column was inoculated with thermophile moderate microorganisms and the leaching solution tank temperature increased to 50°C.

After the stabilization of the redox potential, the addition of extreme thermophile microbial inoculum to the top of the column was accomplished and the leaching solution tank temperature increased to 70°C.

The flotation concentrate was bioleached with mesophile, moderate and extreme thermophile microorganisms for 20, 13 and 27 days, respectively. The remaining humidity of the solid material after the leaching process was about 10%.

**Bio-leaching Tests Monitoring the Process Parameters**

The process parameters such as pH, being constantly adjusted for the range of 1.8 to 2.2, redox potential were monitored, and Fe$^{2+}$ and Fe$^{3+}$ ionic species concentrations and copper extraction were frequently evaluated. The leaching tests were kept under stirring at 150 rpm, at 30°C for 62 days.

**RESULTS AND DISCUSSION**

**Flotation Concentrate**

According to the chemical analysis, the copper content of the flotation concentrate was 37.3%, and the particle size analysis of that concentrate has shown nearly 60% of the concentrate particles are equal or less than 325 mesh, what turns that concentrate more reactive favouring the bio-leaching process.

**Counting of microorganisms**

In the inoculum of mesophile microorganisms it was obtained a counting of 1.2x10$^8$ cells/cm$^3$ of *A. ferrooxidans* and 6.6x10$^7$ cells/cm$^3$ of *A. thiooxidans*; in the consortia of moderate and extreme thermophile microorganisms it was counted 8x10$^7$ cells/cm$^3$ and 3.7x10$^7$ cells/cm$^3$, respectively. In agreement with Olson *et al.* (2006), 10$^6$ cells/g of flotation concentrate were used.
Bio-leaching Tests Monitoring the Process Parameters

Redox Potential

Although the bio-oxidative process has been continuously monitored, by measuring the pH, redox potential and electrolytically determining, every now and again, the copper concentration, it was observed that the reaction system began to indicate the end of the bio-oxidative process of the aforementioned sulphide minerals, as the redox potential was no longer increasing, the pH was automatically kept in a safe range for the acidophilic microorganism to survive and the copper concentration in the PLS, indicative of the continuity of the bio-oxidative process, already presented a stability. At that moment, it was, then, the test was finished and the following experimental procedure was adopted:

- The PLS irrigation system was stopped;
- The complete Drainage of the PLS wetting the column content;
- Removal of the remaining residue on the support rock surface;
- Exhaustive washing of the residue with diluted sulphuric acid solution (pH 2) followed by a hot water washing operation and subsequent drying at 40°C for 48 hours.
- After drying, the residue was disaggregated, homogenized, and a representative sample was taken for x-rays diffraction and copper content analysis.

After drying, the residue was milled, homogenized, and the representative sample was taken goes x-ray diffraction and copper content analysis.

The graph of Figure 2 shows that the redox potential increased significantly when the moderate thermophile microorganisms began to work, as the temperature of the reaction system increased to 50°C, reaching values higher than 850 mV vs. SHE.

![Figure 2 Redox potential reading in mV vs. SHE.](image-url)
**Fe^{2+} and Fe^{3+} ionic species concentrations**

It is known that the ferric ion is a powerful leaching agent of metallic sulphides. The Figure 3 shows that after 20 days of leaching process, the ferrous ions concentration start to decrease and the ferric ions concentration increased, consequently, which was corroborated with an increase in the redox potential for the same period, as observed in Figure 2.

![Monitoring of Fe^{2+} and Fe^{3+} concentrations, in g/L, in the leaching liquor from the bio-leaching process](image)

**Copper extraction**

In the first 5 days of test, a copper extraction of about 27% can be observed. Such extraction happens due to the presence of copper soluble salts present in the flotation concentrate. During the whole leaching test, the copper concentration was growing; however, with a decrease of the copper extraction rate after 30 days of leaching. This decrease is related to the presence of chalcopyrite, a highly refractory mineral. At the end of the test, after 60 days of leaching, a copper extraction nearly 80% was reached. The copper extraction reached in this study is not enough to consider the end of the bioleaching process but an indication of the necessity to extend the leaching time so as to enhance the copper extraction and make the remaining precious metals-bearing residue easier to be treated.
CONCLUSIONS

The use of a microbial consortium in a column biolching process was quite effective regarding the digestion of refractory sulphides, where a copper extraction near to 80% was reached within 60 days of test.

The ferrous and ferric ions concentrations, during the test, are directly related with the redox potential values, as it was possible to observe that in the moment that the Fe$^{3+}$ concentration tended to an increase, reaching concentration higher than 5 g/L, the redox potential also increased, providing a higher leaching rate.

According to the results reached so far, one can foreseen the application of such technology for extracting copper, nickel, gold etc., from their ores or flotation concentrates.

ACKNOWLEDGEMENTS

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REFERENCES


