BIO_FP08 - BIOLEACHING OF A CHALCOPYRITE CONCENTRATE WITH MESOPHILE AND THERMOPHILE MICROORGANISMS: A PILOT SCALE APPROACH.

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ABSTRACT

This technical contribution aimed at extracting copper from a flotation concentrate comprising copper sulphides such as chalcopyrite (CuFeS₂), at a content of nearly 70%, and bornite (Cu₅FeS₄) as 30%, amounting a copper content of 28.8%. The pilot column was loaded with around 1 ton of a mix of a support rock coated with flotation concentrate in a ratio of 9:1, respectively (890kg of support rock to 96.2 kg of flotation concentrate). The support rock used was a copper primary ore in particle size ranging from 6mm to 1.25mm. The coating operation was done pouring the flotation concentrate slurry, with 70% of solids, on top of the support rock on a rotating mixer. The aqueous phase of the slurry was a mix of sulphuric acid solution, at a pH 1.5, with the mesophile, moderate and extreme thermophile microorganisms at 10⁶ cells per gram of flotation concentrate. During the leaching process a period of 7 days were used to make the mesophile microorganisms from acting at 30°C, where the copper concentration in solution started levelling out. At that time the temperature was raised gradually up to 50°C, where the moderate thermophile microorganisms reach their optimum temperature, remaining there for 14 days levelling out the copper concentration as such. Finally, the temperature was raised up to 66°C, which is the extreme thermophile temperature, remaining at that value for 83 days. Therefore, the copper extraction reached, considering the contribution of the three consortium used, was of 90.6%, which was really high bearing in mind the considerable chalcopyrite content of that concentrate. We are expecting to enhance such extraction with optimization of the experimental parameters.

Keywords: Bioleaching, flotation concentrate, autotrophic microorganisms and copper sulphide
1. INTRODUCTION

1.1 Bioleaching

The dissolution of sulphide minerals occur naturally in the mining area, and for a long time was considered as a purely chemical phenomenon, due to oxidant chemical reactions mediated by water and atmospheric oxygen [1] and, in a bioleaching system three types of mechanisms may occur: direct contact mechanism, indirect contact mechanism and indirect mechanism [2].

In the direct contact mechanism the interaction of cells with the sulphide mineral surface takes place, followed by an enzymatic attack to the mineral components capable of being oxidized such as Fe\(^{2+}\) ions. In this mechanism, the micro-organism extracts electrons directly from the mineral, which after passing by subsequent biochemical reactions are transferred to oxygen (final electrons acceptor). The mechanism of direct contact can be described by Equation 1.

\[
2CuFeS_2 + 8.5O_2 + H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + H_2O
\]

The discovery of an extracellular polymeric substance, of microbial origin, has helped to elucidate the microorganism interaction mechanisms with a mineral substrate (Figure 1B). Studies showed that the excretion of exopolymeric material is important for the microbial adhesion, and the subsequent mineral dissolution, as the iron being attached to the polymeric material gives positive charge to the cell [3]. Thus, an electrostatic attraction is established between the microbial cell and the negatively charged surface of some minerals [4]. The interaction between microorganism/mineral mediated by EPS is called as the indirect contact mechanism [2, 5].

In another mechanism, called indirect one, the mineral is chemically oxidized by ferric ion (Fe\(^{3+}\)) in solution [2, 5].

\[
CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^6
\]

During the chemical oxidation of the mineral, the ferric ion is reduced to the ferrous ion (Fe\(^{2+}\)). The function of the microorganism, in this case, is to oxidize the ferrous ion back to ferric ion; thus, regenerating that oxidizing agent (Equation 3). In addition, as the elemental sulphur is generated (Equation 2) it is
important the oxidative action of microorganisms (Equation 4), so as to prevent the deposition of elemental sulphur on the mineral, forming a barrier to the diffusion of the oxidising agent up to the mineral surface, which could prevent the oxidation reaction of the mineral constituents.

\[ 2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \]  
\[ S^0 + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \]  

1.2 GEOCOAT™ process

The GEOCOAT™ process, developed by GeoBiotics, LLC, involves the coating of a support rock by fine particles (i.e., flotation concentrate). The objective is to use the advantages of heap leaching, which involves low capital and operational costs [6]. Figure 1 shows an outline representing the constitution of the heap.

![Figure 1. An outline on the heap is raised. Arrows indicate the distribution of liquor and the aeration.](image)

The process can be applied to the bio-oxidation of gold-bearing refractory sulphide ores and bioleaching of ores bearing copper, nickel, cobalt, zinc sulphide minerals, and the poly-metallic as such.

To perform the coating of the support rock, the mass of flotation concentrate reaches up to 10% of the total mass of material used to raise the heap [7].
2. EXPERIMENTAL

2.1 Mineral Sample

In this study it was used a flotation concentrate sample bearing 30% of copper. This concentrate was produced from the processing of an underground mining ore, and it is composed of 30% of bornite (Cu$_5$FeS$_4$) and 70% of chalcopyrite (CuFeS$_2$).

In this study a sample of copper flotation concentrate was used, which was produced from processing an underground mine ore. This concentrate was carefully homogenized and a representative sample was taken and properly analysed and further technologically characterized.

A primary ore sample was used as support rock for being coated, as in the Geocoat process. In this case, the copper primary ore was sent to a jaw crusher and further dry classified in Keason sieves in particle size range between +3mm and -6mm.

2.2 Characterization Techniques

The X-Ray diffraction (XRD) was the technique used for identifying the mineral species present in the flotation concentrate. The diffractogram was generated in an equipment Bruker-D4 Endeavor, under the following operational conditions: radiation Co K$\alpha$ (35 kV/40 mA); goniometer speed of 0.02 $\degree$ 2$\theta$ in step with counting time of 1 second per step and collected from 4 to 80) $\degree$ 2$\theta$. The qualitative spectra interpretations were done by comparison with standards contained in the database PDF02 (ICDD, 2006) in Bruker Diffrac Plussoftware.

The x-ray fluorescence (XRF) was the technique used for multi-element analysis. The X-Ray fluorescence spectrometer was generated in equipment Bruker-AXS model S4-Explorer equipped with a Rh tube. For a quantitative analysis of the sample the spectrum generated from it was evaluated by the software Spectra plus v. 1.6 in standerless method mode.

The copper content in the concentrate and primary ore under study were evaluated after acid digesting a sample of them, and the metal in solution dosed by atomic absorption spectrometry (AAS).
2.3. **Microorganisms and Culture Medium**

Three consortia of iron and/or sulphur oxidising microorganisms were used: mesophiles (cultivated at 30°C), moderate thermophiles (cultivated at 50°C) and extreme thermophiles (cultivated at 68°C). While assembling the reaction system, $10^6$ cells per gram of flotation concentrate were inoculated.

The cultivation were made using MKM culture medium (Modified Kelly Medium), which has the following composition: Basic salts Solution ($\text{NH}_4\text{SO}_4$: 0.8 g/L, $\text{K}_2\text{HPO}_4$: 0.08 g/L, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$): 0.8 g/L. The pH was adjusted to 1.8 was done with 5M $\text{H}_2\text{SO}_4$ solution; energy Source: 25 g/L of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, 2.5 g/L of $\text{S}^0$, 5 g/L of pulverized pyrite and 10 g/L of chalcopyrite concentrate. For the cultivation of thermophile consortia an additional 0.2 g/L of yeast extract was added.

2.4 **Bioleaching Test**

The experiment was accomplished on a pilot scale, in a 4 meters high and 0.45 meters in diameter column made of glass fibber. This column was loaded with the mineral sample previously prepared in the GEOCOAT™ way where a primary copper ore sample was used as support rock being coated with the flotation concentrate. In the bioleaching test 890 kg of support rock and 96.2 kg of flotation concentrate were used, and such test was run for 83 days. Figure 2 shows schematically, the reaction system used in the experiment.

![Figure 2. Reaction system used in the column bioleaching process.](image-url)
The mineral bed was continually irrigated with a diluted solution of MKM culture medium and microorganisms. This irrigation was carried out through a spray that formed a mist cone at the top of the column at a flow rate of 24.5 L. m⁻².h⁻¹.

2.5 Analytical methods

The concentrations of iron ionic species in solution were analyzed by spectrophotometry. This method is based on the complexation reaction of ferrous ion (Fe²⁺) by orthophenanthroline (FenH⁺) with formation of an orange complex (Fe(Fen)₃²⁺) (Oliveira, 2009). The copper concentration in solution was determined by atomic absorption spectrometry in equipment Varian Spectra 50B.

The pH and redox potential measurements were carried out, directly, in the reaction system using the ANALION UM2000 equipment with a combined glass and platinum electrodes (against Ag /AgCl), respectively.

Cell counts were accomplished using a Coleman optical microscope coupled to the N200 phase contrast, with the aid of the Thoma chamber [8, 9]. Samples were diluted to allow for a total count between 150 and 300 cells in a volume of 1 mm³ corresponding to the 16 quarters of central chamber.

3. RESULTS AND DISCUSSION

According to the results in Table 1, it has been found that about 60% of the particles in the flotation concentrate are with a particle size equal or less than 325 mesh. With such particle size range the concentrate becomes more favourable to the oxidative attack, due to its high specific surface area.

<table>
<thead>
<tr>
<th>Range in diameter (# - mesh)</th>
<th>Particle size (mm)</th>
<th>Weight fraction retained (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.106</td>
<td>10.7</td>
</tr>
<tr>
<td>200</td>
<td>0.074</td>
<td>23.0</td>
</tr>
<tr>
<td>325</td>
<td>0.043</td>
<td>27.0</td>
</tr>
<tr>
<td>&gt; 325</td>
<td>&lt; 0.043</td>
<td>38.7</td>
</tr>
</tbody>
</table>
Figure 3, as follows, shows the diffractogram corresponding to the semi-quantitative analysis of mineralogical species present in the flotation concentrate under study.

In accordance with the diffractogram of Figure 2, it was found that the mineralogical constituents were bornite (Cu₅FeS₄), chalcopyrite (CuFeS₂) as major constituent (70.0 %) and quite refractory to oxidative processes.

![Diffractogram](image)

**Figure 3.** Diffractogram corresponding to semi-quantitative analysis of the flotation concentrate mineralogical species.

The copper contents in the flotation concentrate and primary ore under study were 28.81 % and 1.02 %, respectively, as the result of analysing the solution, after acid digestion of the samples, by atomic absorption spectrometry (AAS).

The X-ray fluorescence analysis shows the metals present in the flotation concentrate, represented in Table 2, in the form of metal oxides.

The semi-quantitative analysis results (X-rays diffraction and fluorescence) of the metals taking part of the mineralogical species in the flotation concentrate can be seen in Table 2, in the form of their oxides. It contains high copper content, element of interest in this study, which is confirmed by the high sulphur and iron contents, elements associated with the copper sulphides present (chalcopyrite and bornite).
Table 2. X-ray fluorescence analysis of the flotation concentrate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>% (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>1.57</td>
</tr>
<tr>
<td>CaO</td>
<td>0.90</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.07</td>
</tr>
<tr>
<td>CuO</td>
<td>28.80</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>19.65</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.13</td>
</tr>
<tr>
<td>MgO</td>
<td>5.40</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
</tr>
<tr>
<td>NiO</td>
<td>0.28</td>
</tr>
<tr>
<td>SeO₂</td>
<td>0.03</td>
</tr>
<tr>
<td>SiO₂</td>
<td>12.20</td>
</tr>
<tr>
<td>SO₃</td>
<td>26.47</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.13</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
</tr>
</tbody>
</table>

After 83 days of test it was possible to extract 90.60 % of copper (Figure 4). It is observed that the extraction was increasing, and the copper was available since the first day. This immediate availability of copper is due, in the first place, to the digestion of bornite (Cu₅FeS₄), as this kind of mineral is more prone of being oxidised by ferric ions in acid medium (at pH lower than 2).

![Copper extraction in the bioleaching tests.](image)

Figure 4. Copper extraction in the bioleaching tests.

Figure 5 shows the curves of temperature of the reaction system, considering the room temperature, average temperature inside the column and the column heating ramp, and still the curve of irrigation flow rate of leaching
solution at the top of the column. As can be seen the bioleaching column heating ramp covers, throughout the test, the range of optimum temperature of the three microbial consortia used: mesophiles (30°C), moderate thermophilies (50°C) and extremes thermophiles (68°C).

![Figure 5. Temperature and irrigation profile of the bioleaching column.](image)

Figure 5, below, shows the redox potential and pH changes over bioleaching time. As can be observed, the redox potential is already high, in the first place, at the beginning of the operation due to the availability and oxidative action of ferric sulphate from the bornite dissolution (Equations 5 and 6).

\[
\begin{align*}
Cu_2FeS_4 + 2H_2SO_4 + 9O_2 & \rightarrow 5CuSO_4 + FeSO_4 + 2H_2O \\
2FeSO_4 + H_2SO_4 + 0.5O_2 & \rightarrow Fe_2(SO_4)_3 + H_2O
\end{align*}
\]

The action of microorganisms determined the maintenance of potential in high values (above 600 mV vs. SHE)(Figure 6), which is a reference to the oxidation rates of iron ionic species, as it represents the tendency of the solution to be oxidized or reduced, i.e., their ability to capture or release electrons. Simultaneously it occurs the solubilization of the metal of interest, as well as the iron.
To avoid raising the pH of the reaction system, which could jeopardize the effectiveness of the bioleaching process, it was carried out the monitoring and the addition of 5M H₂SO₄ solution for keeping the pH values lower than 1.5. At the end of 83\textsuperscript{th} day of experiment, the sulphuric acid consumption was evaluated as being 102 kg.t\textsuperscript{−1}.

4. CONCLUSION

After 83 days of bioleaching process, along the lines of the GEOCOAT\textsuperscript{TM} process, it was possible to extract 90.6 % of copper from the flotation concentrate;

The ramp for the heating of the bioleaching column provided, during the test, the range of optimum temperatures of three microbial consortia used, mesophiles (30°C), moderate thermophiles (50°C) and extreme thermophiles (68 °C).

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REFERENCES


