BIOLEACHING OF COPPER SULPHIDE FLOTATION CONCENTRATE IN BATCH REACTION SYSTEM USING MESOPHILE AND THERMOPHILE MICROORGANISMS

BIO-LIXIVIACIÓN DE CONCENTRADO DE FLOTACIÓN DE SULFUROS DE COBRE EN SISTEMA DE REACCIÓN EN BARCADA UTILIZANDO MICROORGANISMOS MESÓFILOS Y TERMÓFILOS

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Received for review April 7th, 2011, accepted August 10th, 2011, final version August, 28th, 2011

ABSTRACT: This work aims at optimizing the use of consortiaof mesophile and thermophile microorganisms (moderate and extreme ones) in the leaching process of copper sulphidesflotation concentrate, containing approximately 30% bornite (Cu_5FeS_4) and 70% chalcopyrite ($CuFeS_2$), for extracting copper. The objective of the bioleaching tests was to evaluate the performance of those microorganisms, varying specific parameters such as: the composition of the leaching solution, the presence of an energy source (ferrous sulphate), and the inoculation of cultures. To ensure optimal conditions for the microorganisms to act, the pH, temperature, and stirring speed were controlled. Finally, from the microbial action and using agricultural fertiliser (N:P:K sources), a copper extraction of more than 85% was achieved.

KEYWORDS: Bioleaching, copper, sulphide, chalcopyrite, acidophilic microorganism.

RESUMEN: Este trabajo tiene como objetivo optimizar el uso de consorcios de microorganismos mesofílicos y termofílicos (moderados y extremos) en el proceso de lixiviación de concentrado de flotación de sulfuro de cobre, conteniendo aproximadamente 30% de bornita (Cu₅FeS₄) e 70% de calcopirita (CuFeS₂), para la extracción de cobre. El objetivo de los experimentos de la biolixiviación fue evaluar el desempeño de esos microorganismos, variando parámetros específicos como: composición de la solución lixiviante, presencia de fuentes de energía (sulfato ferroso) y la inoculación de culturas. Para asegurar las condiciones óptimas para la actuación de los microorganismos fueron controlados valores de pH, temperatura, y velocidad de agitación. Finalmente, por acción microbiana y utilización de fertilizantes agrícolas (fuente de N:P:K), la extracción de cobre alcanzada fue superior a 85%.

PALABRAS CLAVE: Biolixiviación, cobre, sulfato, calcopirita, microorganismos acidófilos

1. INTRODUCTION

The copper extraction from copper sulphides flotation concentrates follows the conventional technological process due to their specific mineralogical characteristics. Thus, the copper sulphides present in the aforementioned concentrates are directly converted into blister copper (impure metallic copper) by the flash smelting process, and further electrorefined. Although the pyrometallurgical process presents the advantage of transforming the distinct copper sulphides into metallic copper in a single step, it however has the disadvantages of generating sulphur dioxide (SO₂) along withheavy metal emissions such as cadmium, arsenic, mercury, bismuth, selenium, etc. Such a gas stream requires a specific treatment in order to avoid issuing these heavy metals into the environment.

The bioleaching treatment of sulphide concentratesis more attractive than the pyrometallurgical process as it eliminatesgas emissions. In the hydrometallurgical treatment, the copper, along with a large part of the metallic impurities, is released as soluble sulphate. The copper ions are recovered from leaching solution either by cementation or purification/concentration (solvent extraction), and followed by electrowinning.

Bioleaching consists of a natural process of sulphide dissolution, resulting from the action of a group of microorganisms that oxidizes sulphide minerals, releasing the metals in their soluble ionic species. Examples of metals which may be extracted by bioleaching are:copper, through chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄) and covellite (CuS); uranium through uraninite (UO₂) [1].

The majority of secondary copper sulphides, such as digenite, bornite, and covellite, may be successfully bioleached by mesophile microorganisms. However, chalcopyrite leaching, chalcopyrite being the main copper sulphide mineral, is still a challenge due to slow extraction kinetics [2].

In general, one of the most common solutions for he slow kinetics of the bioleaching processes is raising the temperature. However, the use of extreme thermophile microorganisms may present ssries of difficulties such as: low oxygen solubility in water; less tolerance to high concentrations of metals and catalysts, such as silver; and presenting lower resistance to the shearing of their cell membranes, than themesophile microorganisms [3–4]. However, the industry has preferred the use of moderate thermophile microorganisms, as they are more resistant to high pulp densities and high heavy metal concentrations, when compared with extreme thermophile microorganisms [5]. The use of bioleaching at high temperatures and thermophile microorganisms increases the copper extraction efficiency in comparison with those obtained by using mesophile onesat room temperature. The typical copper extraction obtained by chalcopyrite bioleaching with mesophile microorganisms is nearly 30%, while copper extraction higher than 90% may be obtained in a shorter period of time using the thermophile ones [6].

The leaching of chalcopyrite is an acid consumption reaction. Thus, as the leaching reaction goes on, a consequent increase of pH takes place, which provokes the precipitation of ferric ionssuch as jarosite. Therefore, lower pH values may result in higher copper extractionand lowerjarosite precipitation [6]. Thus, a constant monitoring and maintenance of pH values is necessary. The optimum and minimum pH values for the growth of microorganisms used in the bioleaching process are directly linked to the species used, in fact that pH 2.5(optimun) and 1.3(minimum) values for *A. ferrooxidans* and pH 1.7/ 1.0values for *L. ferrooxidans*[7].

A wide range of sulphides may be oxidized by the microorganisms found in acid rock drainage from mined areas. These microorganisms may act in an expanded temperature range (from 30 to 70 °C), acid pH range (1.8 to 2.2) and high Fe^{3+}/Fe^{2+} ions ratios [8].

The bioleaching of sulphide minerals is based on the ability of acidophilic microorganisms in oxidizing ferrous ions (reaction 1) and/ or reducing sulphur (reaction 2). The bioleaching processes may lead to significant heat generation produced by sulphide oxidation exothermal reactions. In the leaching solution, temperature values from 50 to 80 °C were observed [9, 10,11].

 $2FeSO_4 + H_2SO_4 + 1/2O_2 \xrightarrow{\text{Microorganisms}} Fe_2(SO_4)_3 + H_2O$ (1)

$$S^{0} + H_{2}O + 3/2O_{2} \xrightarrow{\text{Microorganisms}} H_{2}SO_{4}$$
(2)

What makes the bioleaching process a very interesting alternative for replacing the conventional processes is the ability of certain iron or sulphur oxidant microorganisms, such as the genders *Acidithiobacillus* and *Leptospirillum*, which grow in highly acid environments and in the presence of heavy metals. In addition, if we compare the costs of the bioleaching process with the costs of the operation of a conventional plant, it is possible a reduction of up to 50% [12].

The microorganisms used in bioleaching acquire energy through the oxidation of sulphur reduced compounds and/or ferrous ions, speeding upthe copper extraction by generating ferric ions and protons, which together form the oxidant environment for the sulphide mineral. The dissolution of sulphide can occur through the indirect mechanism (contactless), in which the ferric ion and protons in solution, attack the mineral; and the mechanism by direct contact, where the dissolution of the mineral occurs by the contact of those microorganisms with the mineral surface [13], as shown in Figure 1.

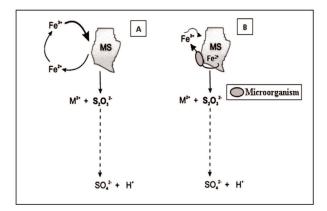


Figure 1. Bioleaching mechanisms: [A] Indirect and [B] direct contact. [*apud*14].

2. OBJECTIVE

This work aims at evaluating the use in separate of the agricultural fertiliser N:P:K (10:10:10) and P. A. chemical reagents (MKM culturemedium) in presence and absence of ferrous sulphate, extracting copper from a flotation concentrate containing chalcopyrite (CuFeS₂) and bornite (Cu₅FeS₄) during the bioleaching process.

3. EXPERIMENTAL

3.1. Flotation Concentrate

The flotation process is known as one of the methods that can separate minerals based on differences of surface properties of minerals. In this process, the minerals particles, with hydrophobic surfaces, join the air bubbles generated on the lower part of the flotation column and fluctuate to form foam on the top of the column. On the other hand, the particles with hydrophilic surfaces do not join the bubbles and sink, forming a tail [15].

The copper sulphides flotation concentrate used contains approximately 30% of bornite (Cu_5FeS_4) and 70% of chalcopyrite ($CuFeS_2$). Thus, it is perfectly possible that microorganisms obtain their sources of energy from that flotation concentrate, where, with the oxidation of chalcopyrite by oxygen in the air, the formation of ferrous sulphate (3) takes place – source of Fe²⁺; however, this ferrous sulphate is rapidly oxidized by oxygen in the presence of microorganisms, producing ferric sulphate (4), which attacks the chalcopyrite forming, still, more ferrous sulphate, repeating, thus, the oxidation cycle (5) [16]:

$$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4 \tag{3}$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{\text{Microrganisms}} 2Fe_2(SO_4)_3 + 2H_2O$$

$$\tag{4}$$

$$CuFeS_{2} + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^{o}$$
 (5)

On the other hand, the source of sulphur can be obtained through generating elemental sulphur from the indirect dissolution of chalcopyrite, where it is oxidized by microorganisms to sulphuric acid, which maintains the iron in solution (6) [16], as shown in the following:

$$S^{o} + 1.5O_{2} + H_{2}O \xrightarrow{\text{Microrganisms}} H_{2}SO_{4}$$
(6)

3.2. Microorganisms and culture medium. For accomplishing this study three microbial consortia were used:

- Mesophiles:Leptospirilum sp., Acidithiobacillus ferrooxidans e Acidithiobacillus thiooxidans;
- Moderate Thermophiles: Species not informed;
- Extreme Thermophiles: Acidianus brierleyi DSM 1651 and 6334, Acidianus infernus DSM 3191, Metallosphaera sedula ATCC 33909, Sulfolobulus metallicus DSM 6482, Sulfolobulus acidocaldarius ATCC 49426, Sulfolobulus shibatae DSM 5389.

3.2.1. Mesophile Microorganisms

The mesophile microorganisms of *Acidithiobacillus* genus were represented by species *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. This group of microorganisms operates in temperature \leq 40 °C and are the microorganisms more commonly used in bioleaching of sulphide minerals [17].

The *Acidithiobacillus ferrooxidans* strain oxidizes, besides ferrous ions, sulphur (compounds) and grows in the pH range of 1.0 to 6.0. The optimum pH, to achieve the maximum growth speed, is between 2.0 and 2.5.In relation to temperature, the microorganisms survive in a temperature interval from 2 to 40 °C, being the optimum range from 28 to 35 °C.[18].

Microorganisms of the species Acidithiobacillus thiooxidans oxidize sulphur and act in an optimum temperature range from 25 to 30 °C and optimum pH of 2.0 for its maximum growth.

The source of energy for such microorganisms can be derived from the oxidation of one or more reduced sulphur compounds, being sulphate obtained as a result of that oxidation [19].

3.2.1.1. Composition of the culture medium for mesophile microorganisms

In general, the species *A. ferrooxidans* may be grown in T& K culture medium [20] and 9K [21]. As the tests carried out use the two species together (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*), it is necessary that only one type of culture medium be used. Therefore, the microorganisms were grown in 9K culture medium, where only the source of energy is different.

Composition of 9K medium [21]: $(NH_4)_2SO_4$: 4.28 g/L, K₂HPO₄: 0.71 g/L, MgSO₄.7H₂O: 0.71 g/L, KCI: 0.14 g/L and Ca(NO₃)₂: 0.014 g/L; source of energy: FeSO₄.7H₂O: 147.4 g/L, for cultivating *A. ferrooxidans* and S^o: 1.0 g/L, for cultivating *A. thiooxidans*. Such medium is acidified with 10N H₂SO₄ up to pH 1.8 before using it.

3.2.2. Thermophile Microorganisms

A consortium acidophilic moderate thermophiles microorganisms was isolated directly from the flotation concentrate. Currently, the group of moderate thermophile microorganism includes mainly the following microorganisms: *Acidithiobacillus caldus, Leptospirillum ferriphilum, Acidimicrobium ferrooxidans Sulfobacillusthermosulfidooxidans* and *Sulfobacillus acidophilus*. They can grow by oxidizing ferrous ions, sulphur and/or sulphide minerals. The optimum growth temperature and pH ranges are from 45 to 60 °C and from 1.3 to2.5, respectively [22].

The majority of extreme thermophile microorganisms is classified as *Archaea* and survive in temperatures higher than 60°C. Almost always, have a fragile cell wall, which prevents them to survive in stirred systems, in the presence of solid, due to the consequent shear effect that occurs on their cell wall, limiting their industrial application [23]. In addition to these aggravating factors, other factors contribute to make things even worth for using such microorganisms, such as reducing the solubility of oxygen in the leaching solution and the low resistance to high concentrations of metals (high ionic strength) and catalysts as silver [5]. In the growth of extreme thermophile microorganisms, the following strains were used: *Acidianus brierleyi*, *Acidianus infermus*, *Metallosphaera sedula*, *Sulfolobulus metallicus*, *Sulfolobulus acidocaldarius*, *Sulfolobulus shibatae*. The optimum temperature for growing those microorganisms is 68 °C.

3.2.2.1. Composition of culture medium for thermophile microorganisms

The MKM culture medium, Modified Kelly Medium, [24], which contains mineral salts and iron (from the flotation concentrate, which contains around 70% of chalcopyrite (CuFeS₂) and 30% of bornite (Cu₅FeS₄)) as a source of energy, it is commonly used for the cultivating moderate and extreme thermophiles microorganisms.

The composition of MKM culture medium: $(NH_4)_2SO_4$: 0.4g/L, MgSO₄.7H₂O: 0.4g/L, K₂HPO₄: 0.04g/L, energy source: FeSO₄.7H₂O: 10g/L, S^o: 5g/L, Chalcopyrite (CuFeS₂): 10g/L, Pyrite (FeS₂):5g/L and yeast extract: 0.2 g/L (only in thermophile microorganisms cultivation). The pH of the culture medium was adjusted to 1.7 using concentrated sulphuric acid. The inoculation of microorganisms in the culture medium was accomplished in a 10% v/v ratio [25].

3.3. Bioleaching tests using mesophiles, moderate and extreme thermophile microorganisms

The mesophile microorganisms begin the bioleaching process. Subsequently, the moderate thermophiles are used, and, finally, followed by the extreme thermophile, according to the experimental conditions listed in the Table 1 as follows:

Table 1 – Experimental conditions used in the stirred flask			
bioleachingwith 1% of pulp density (w/v).			

Step	Microbial Consortium	Temp.(°C)	Time (days)
1	Mesophiles	30	40
2	Moderate Thermophiles	50	20
3	Extreme Thermophiles	70	10

The tests were carried out in Erlenmeyer flask of 250 mL capacity. In each flask 1.5 g of copper concentrate and 150 mL of leaching solution were added.

In each new stage, the flotation concentrate was filtered

and reused, maintaining the solid/liquid ratio in 1%.

The tests for evaluating the performance of the microorganisms were accomplished varying the following parameters:

- Salty solution (commercial agricultural fertilizer N:P:K -10:10:10 – in tap water/ chemicals in deionised water);
- Culture medium composition in relation to energy source (with/ without Fe²⁺);
- Presence of microbial inoculum.

Being the pH adjusted, periodically, in the range of 1.5 to 1.8 and the stirring speed maintained at 150 rpm. The temperature, in each test, was kept constant in accordance with the microorganisms used. The tests were carried out in duplicate.

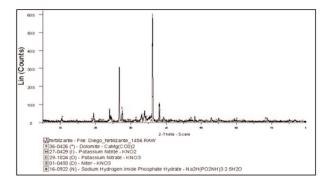


Figure 2.X-ray difratograms of fertilizer sample

4. RESULTS AND DISCUSSIONS

4.1. Analysis of the microorganisms activity

4.1.1. Considering the redox potential (Eh) and pH:

The redox potential is related with the ferric/ferrous ions ratio by the Nernst equation:

$$E = E_{Fe^{2+},Fe^{3+}}^{0} + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$
(1)

Ferrous ions, from the chalcopyrite dissolution and the culture medium-bearing ferrous sulphate, are oxidized by microorganisms to ferric ions through the following equations:

$$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4 \tag{7}$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{Microrganisms} 2Fe_2(SO_4)_3 + 2H_2O$$
(8)

Thus, it is realized that the ferric/ferrous ions concentrations ratio is increasing, which canbe observed by monitoring the redox potential.that increases during the leaching process.

Figure 3, shows that the lowest values of redox potential are observed in the control tests curves, without ferrous sulphate and without microbial inoculum, for both fertiliser and for chemicals. However, the peak values correspond to the tests where inoculation was done.

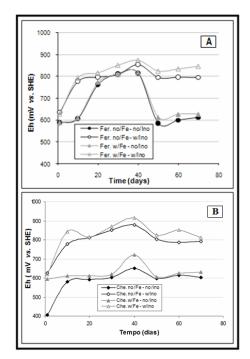


Figure 3. Redox potential readings (mean values), in mV *vs.* SHE, in the bioleaching tests using agriculture fertilizer (A) and chemicals (B).

Among the tests with inoculum, the effect of adding ferrous sulphate to the culture medium could be analyzed. As the Fe^{2+} concentration increases due to the sulphide oxidation, more ferric ions are produced and, therefore, the Eh values are higher. When the curve goes down, as observed on Figure 3, is due to the onset of another test, when a new culture is used.

Therefore, through the redox potential analysis, it is possible to infer the importance of the microorganisms

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regarding to ferrous ions oxidation.

In the bioleaching tests, all microorganisms used are acidophilus. Therefore, to keep the pH in the right range was of utmost importance for that extractive process to take place.

The pH values in the plots of Figure 4, below, correspond to the measurement of it before adjusting it in the optimum range of 1.5 to 1.8 for evaluating the microorganisms' activity. This is due to the oxidation of elemental sulphur, formed during the chalcopyrite dissolution, to sulphuric acid by the microorganisms, increasing the acid content of the leaching solution,

according to the following reactions:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0$$
 (9)

$$S^{0} + 1,5O_{2} + H_{2}O \xrightarrow{\text{Microrganisms}} H_{2}(SO_{4})$$
(10)

In the tests containing microbial inoculum and ferrous sulphate lower pH values were observed, due to a higher Fe^{3+} concentration (oxidation product), by shifting the reaction (9) toward generating elemental sulphur, producing consequently sulphuric acid (10) as the oxidative process goes on [26].

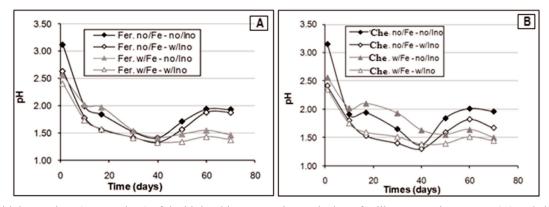


Figure 4.Initial pH values (mean values) of the bioleaching tests using agriculture fertilizer as nutrient source (A) and chemicals (B)

4.1.2. Considering the Ferrous and ferric concentrations:

Figure 5, below, highlights the leaching process, using agriculture fertiliser in tap water, ferrous sulphate and microbial inoculum.

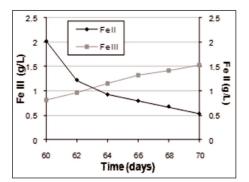


Figure 5. Measurement of $Fe^{2+} e Fe^{3+}$ ions concentrations, in g/L, in the leachate produced during the bioleaching process using extreme thermophile microorganisms.

following the ferrous and ferric ions concentrations during the use of extreme thermophile microorganisms, it is possible to conclude that the Fe²⁺ concentration decreases, as the Fe³⁺ concentration increases. This is due to the oxidation of ferrous ions by the microorganisms present in the bulk, according toequation (8). Such oxidation is shown in Figure 3, where it is possible to observe an increase in redox potential (819 mV *vs.* SHE to 840 mV *vs.* SHE) during the aforementioned test, using agriculture fertilizer, with ferrous sulphate and microbial inoculums. This increase in the ferric ions concentration is important for extracting copper, according to reaction (9), with consequent shifting of equilibrium toward Cu²⁺ generation.

4.1.3. Considering the copper extraction:

According to the results of redox potential, pH and ferric and ferrous ions concentrations, the test where agricultural fertiliser was used as NPK source, presented better copper extraction - 86%.

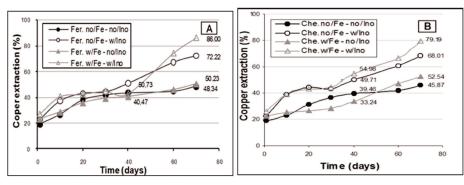


Figure 6. Copper extraction (mean values) during the bioleaching process using agriculture fertiliser as source of nutrients (A) and chemicals (B).

This result is corroborated by the diffatogram shown in Figure 7 B, where it is observed a marked reduction in the chalcopyrite peak, when compared with the diffatogram of Figure 7 A.

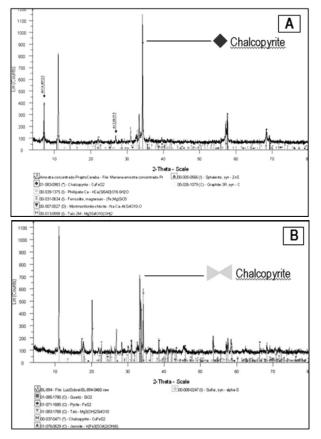


Figure 7.Difratograms referring to semi-quantitative analysis of the mineral species comprising the flotation concentrate before the bioleaching test (A) and after that process (B), using agriculture fertiliser as source of nutrients.

5. CONCLUSIONS

The performance of the reaction system using both chemical reagent and agriculture fertilizer as sources of nutrients for the microbial inoculum, in the bioleaching process, increased the copper extraction to 11% and 14%, respectively.

However, the commercial agriculture fertiliser presented better performance in copper extraction, which was of 86%, in comparison to 79% forchemical reagent. This is an indication of the possibility of using such fertilizer in a culture medium, waving for being used in an industrial scale bioleaching process.

The addition of the ferrous sulphate, either using agriculture fertiliser or chemicals, in theexperiments, increased the ratio of copper extraction. In this context, the result suggested that the ferrous ions were available for microbial oxidation as an alternative source of energy in the process.

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