

BIOLEACHING OF COPPER FROM CARAIBA MINE ORE (BRAZIL)

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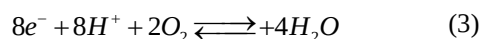
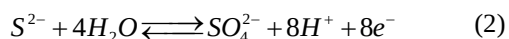
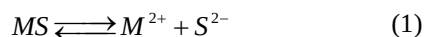
Abstract— The bioleaching of copper ore from the Caraiba Mine was assessed. A microorganism, *Acidithiobacillus ferrooxidans*, was isolated from samples collected directly in acid mining drainage in a gold mine tailings pound and used in the bioleaching of the copper sulfide ore. This ore is composed mainly of 28% of oxidized species, 43% of secondary sulfides and 24% of primary sulfide. The shaking flasks experiments with the Caraiba ore showed copper chemical leaching of about 37% and copper bioleaching of about 60% within 60 days at low temperature and native microorganism.

Keywords— Copper, Bioleaching, *Acidithiobacillus ferrooxidans*.

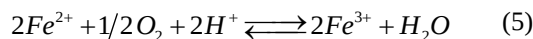
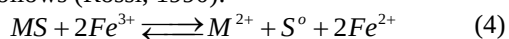
I. INTRODUCTION

The extraction of copper from low to medium-grade ores requires low-cost processing methods such as biohydrometallurgy, which have received growing attention due to economic and environmental restrictions (Giaveno *et al.*, 2003; Olson *et al.*, 2003; Watling, 2006; Pradhan *et al.*, 2008). It has been applied in a variety of low-grade base-metal ore mostly either in full-scale operation or demonstration scales in various countries around the world. Though commercial success in certain minerals have been seen for years but technical challenges are considerable which is unsolved till date especially related to the bioleaching of refractory ore such as chalcopyrite. Utilization of bioleaching process for treatment of industrial and municipality waste is also taking its pace slowly.

The traditional bioleaching mechanism of metal sulfides (MS) under aerobic condition is given by (Rossi, 1990):



where Eq. 1 is the sulfide dissociation, Eq. 2 is the anodic reaction and Eq. 3 is the cathodic reaction that can be catalyzed by acidophilic microorganisms. The hypothesis of indirect bioleaching mechanism takes into account the Fe^{3+} action on metal sulfide leaching and the role of microorganism on the re-oxidation of Fe^{2+} to Fe^{3+} , as follows (Rossi, 1990):



The most important bacteria in bioleaching of low and medium-grade copper ores are iron- and sulfur-oxidizing *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum* spp. Bioleaching of copper sulfides has been applied successfully for the extraction of copper from secondary sulfide minerals in a number of operations (Olson *et al.*, 2003). However, the bioleaching of the refractory primary copper sulfide, chalcopyrite, has just been reported in lab experiments or under pilot tests (Pradhan *et al.*, 2008).

Caraiba ore is typically composed of silicates and oxides (hypersthene, plagioclase and magnetite), copper sulfide (chalcopyrite and bornite) and has a total copper concentration of about 0.9%. The actual process uses grinding, classification and flotation, which produces a concentrate of about 34% copper. In this plant, copper recovery is between 75 and 85%. The concentrate is sent to a smelter in Camaçari (Brazil) to produce electrolytic copper.

The direct leaching of the Caraiba Mine concentrate (with a Cu content of about 22%) using acidic $FeCl_3$ solutions at moderate temperature (25 to 106°C) was performed by Cassa and Monhemius (1976). The results indicated high levels of copper extraction (above 95%) in 60 minutes.

Bioleaching studies were performed using the ore and the concentrate from the main Caraiba deposit and the low-grade ore of the Surubim deposit. The low grade ore of the Caraiba mine (with a Cu content of about 0.39%) was leached in tanks and columns using *Acidithiobacillus ferrooxidans* isolated from the same ore. The results of agitated leaching indicated low levels of copper extraction (below 50% in 100 days) and the results of the column leaching indicated very low levels of copper extraction (below 10% in 100 days) (de Souza, 1980; Martins and El-Naggar, 1982; de Andrade and de França, 1984). Bioleaching of the ore from the Caraiba mine was studied by Urenha and Alli (1990). They used an ore sample collected at the grinding circuit entrance. The Cu content was 1.12 %. Using column leaching of 1.5 kg of ore inoculated with *Acidithiobacillus ferrooxidans* after 105 days about 21% of the copper was solubilized. Leaching without inoculation produced a copper extraction of about 10%. The ore from the Surubim deposit (with a Cu content of about 1.59%) was leached in tanks and columns using *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxi-*

dans isolated for the same ore. The results of agitated leaching indicated high copper extraction (below 89% in 100 days), the results of the column leaching indicated moderated copper extraction (below 57% in 100 days) and the results of large column leaching (0.25 x 2 m) indicated low copper extraction (below 23% in 563 days). The H₂SO₄ consumption was high (about 81 kg/t). In agitated leaching, the Cu extraction without the bacteria inoculation was 56% (Marques, 1988; 1990). For this ore using a culture of *Acidithiobacillus ferrooxidans*, Novo and Garcia Jr. (1990) found 70% Cu extraction in shake flasks and about 17% in column leaching. The bioleaching of the concentrate of the Caraiba mine was studied by Sobral *et al.* (2005, 2011), Lima *et al.* (2009) and de Oliveira *et al.* (2011). The bioleaching of the Caraiba mine flotation concentrate was studied with the use of *Acidithiobacillus ferrooxidans*. The high chalcopyrite content in this sample (about 70% of the copper sulfide) made it difficult to extract copper using only the above-mentioned microorganism (below 20% in shaking flasks experiments). However, using the GEOCOATth process and a consortium of mesophilic and thermophilic microorganisms, a copper extraction of nearly 89% was reached within 75 days in column experiments.

In this study, the ability of a native bioleaching microorganism, *Acidithiobacillus ferrooxidans*, to extract copper from the ore from the Caraiba Mine mainly composed of a mixture of copper sulfides is described. The *Acidithiobacillus ferrooxidans* was isolated from acid mine drainage from a gold mine in the Jacobina region of N.E. Brazil.

II. MATERIALS AND METHODS

The ore that feeds the plant flotation in the Caraiba Mine was provided by the company for this test. Five liters of the slurry was collected at the grinding circuit exit and the flotation circuit entrance on March 28, 2013. It was filtered and dried at a low temperature to avoid oxidation. The ore is about 95% finer than 212 μ m and 55% finer than 74 μ m.

Bacterial leaching experiments of a sulfide ore containing chalcopyrite were performed in shake flasks on bench scale using *Acidithiobacillus ferrooxidans* strains isolated from a gold mine tailings pound. According to the DNA Microarray characterization, the bacterial community sample were *Acidithiobacillus* spp., *Acidithiobacillus ferrooxidans*, *Acidiphilium* spp., and *Leptospirillum* type II (represented by the species *Leptospirillum ferriphilum*).

Acidithiobacillus ferrooxidans was isolated after enrichment by T&K medium and subsequent purification on solid selective T&K-agarose medium. Bacterial growth was monitored indirectly by measuring residual Fe²⁺ in the medium by titration with potassium dichromate, by visual inspection (color change light green to reddish-brown), and by increases in the Redox potential (Eh). During the enrichment, the culture reached a stationary phase within two days after the inoculum. In solid medium isolated colonies were obtained on the

10th to 15th day of incubation. Molecular analysis by qPCR confirmed that *Acidithiobacillus ferrooxidans* was the isolated species. *Acidithiobacillus ferrooxidans* alone was used in the test to evaluate the oxidative capacity of the ore in this study.

To standardize the test inoculum used in the bioleaching experiments, the density of *Acidithiobacillus ferrooxidans* was determined using the technique of plate count performed in triplicate. A solid T&K-agarose medium and an aqueous solution (distilled water acidified to pH equal to 1.8 with concentrated sulfuric acid) with 0.5% Tween 80 were prepared.

The leaching experiment was performed in 250 mL Erlenmeyer flasks containing 37.5 g of ore and 150 mL of leaching solution (sulfuric acid solution at pH equal to 2.0) per vial (percentage of solids equal to 20%) at constant stirring 130 RPM and 30°C for 60 days. In the shaking-flask experiments, bioleaching parameters (pH, redox potential, copper extraction, ferrous- and ferric-iron concentration) were controlled regularly.

To assess the response of the ore in the presence and absence of bacteria for each leaching solution, the following steps were carried out in duplicate: (a) a flask without bacteria with the addition of formaldehyde (5% v/v) to sterilize the ore (chemical control); (b) a inoculated flask with 10% v/v of *Acidithiobacillus ferrooxidans* with 10⁶ CFU/mL (with the isolated bacteria and possible bacteria native to the ore); and (c) a flask without the inoculum and without formaldehyde, (only the bacteria native to the ore may be present).

Every 20 days, tests were performed to check the absence of *Acidithiobacillus ferrooxidans* in the flasks that were not inoculated with the isolated strain and its presence in the flasks where it was added. The tests were conducted by withdrawing 1 mL from each flask, and inoculating the medium with 20 mL of the freshly prepared T&K medium, and incubated at 130 RPM and 30°C.

To obtain information about the acid consumption of the sample, the potential for acid generation and yield of metal extraction were investigated during testing. The pH and the amount of Fe²⁺ were monitored at intervals of 48 hours. The concentration of copper in the solid and its content in the leach liquor were monitored weekly.

To measure the pH, the electrode was sterilized by immersion in formaldehyde solution 5% v/v for 30 minutes. To prevent contamination of the samples, measurements were always initiated by the control (with formaldehyde) followed by the flask containing only the ore and subsequently the flask with the inoculum of *Acidithiobacillus ferrooxidans*.

When necessary, the ore flasks were supplemented with sterile concentrated sulfuric acid until the system reached a pH range between 1.5 and 2.0. The volume of acid used for this pH adjustment was recorded to calculate the acid consumption in relation to the mass of ore.

To determine the copper content, aliquots of 10 mL of the pulp was taken at a regular interval of 7 seven

days, after homogenization of the system. The sample was filtered (pore 25 mM) and washed with deionized water until a neutral pH was reached. The solids retained on the membrane were dried and analyzed by X-ray fluorescence (XRF) with the Thermo Scientific Niton XL3 500, while the filtered liquid was analyzed by flame atomic absorption spectrometry (Spectran AA 55B-Varian) in order to obtain data regarding the extraction of copper. All the glassware and other materials used in atomic absorption had previously been sterilized by immersion in 3% neutral detergent (Extran®, Merck) for 24 hours, followed by immersion in 20% nitric acid overnight, and then washed with pure water Type I. The reagent blank of the reagents was performed together with the samples. For copper, the target of the reference material value is 16.8 mg/L, ranging between 15.8 and 17.8 mg/L. When necessary, the samples were diluted in 0.2% nitric acid so that they could be at the limits of detection.

Ferrous iron (Fe^{2+}) was determined by volumetric titration with potassium dichromate. The concentration of Fe^{2+} was determined by titration the residual Fe^{2+} with a standard solution of 0.1 N potassium dichromate. The pH and Eh (redox potential) measurements were made using a combined glass electrode and a platinum electrode (Ag/AgCl) respectively.

In this study, an experimental diagnostic leaching procedure was developed to evaluate the different mineral phases containing copper. The sequence used for the destruction of the ore is dependent upon the mineralogy of the sample. In this study, HCl, HNO_3 and cyanide treatments were used for the breakdown of minerals. The sequential diagnostic leaching procedure is: i) HCl leaching 24h, 1M, 25°C (accounts for solubilize copper oxidized species), ii) Cyanidation, 48h, $[\text{CN}^-] = 500 \text{ mg/L}$, pH=12, 25°C, iii) Cyanidation, 24h, $[\text{CN}^-] = 1500 \text{ mg/L}$, pH=12, 30°C, iv) Cyanidation, 24h, $[\text{CN}^-] = 10000 \text{ mg/L}$, pH=12, 45°C (account for copper secondary sulfides), and v) HNO_3 leaching, 65%, 48 hs (accounts for copper primary sulfides). The residual copper is located in silicates and other insoluble minerals.

III. RESULTS AND DISCUSSIONS

Figure 1 presents the diffraction pattern for the Caraiba copper ore and copper flotation concentrate. The ore is mainly composed of silicates (albite, muscovite, chlorite and quartz) and the copper sulfides are mainly bornite and chalcopyrite. Figure 2 shows a SEM image obtained for a sample of the ore used in the experiments. The figure showed the presence of sulfides of copper without Fe, which may suggest a significant amount of covellite (CuS) or chalcocite (Cu_2S), in addition to the expected presence of chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4). This indicates that some copper will be extracted in acidic solution in the absence of bacteria.

The diagnostic leaching is summarized in Table 1. It is notable that about 28% of the copper is solubilized in HCl indicating the presence of oxidized species. The secondary copper sulfides (including chalcocite, covellite and bornite) account for about 43% and the primary

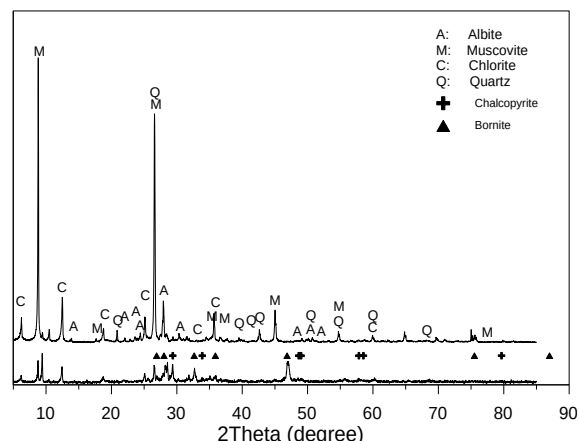


Figure 1. X-ray diffraction pattern for the Caraiba copper ore and copper flotation concentrate (bottom curve).

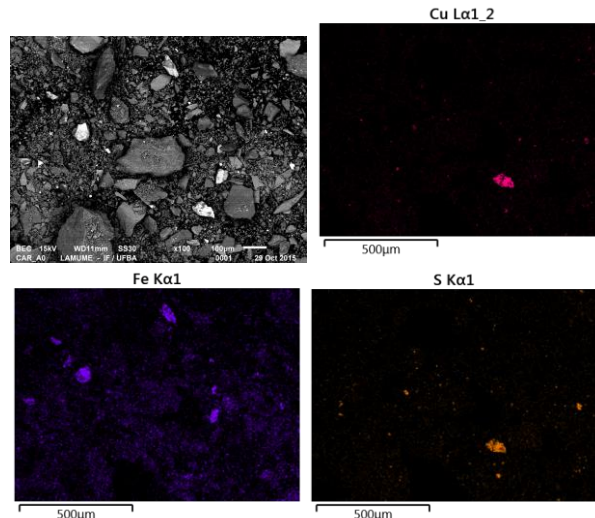


Figure 2. SEM image of the Caraiba ore.

Table 1: Diagnostic leaching of the copper ore

Leaching:	Cu (%)	Fe (%)	Partition (%)	Cu Species
Ore	0.927	9.6	-	
(i) HCl	0.666	8.9	28.2	Oxidized
(ii) NaCN	0.515	8.8	16.2	Secondary
(iii) NaCN	0.306	8.6	22.6	Secondary
(iv) NaCN	0.263	8.5	4.6	Secondary
(v) HNO_3	0.043	8.0	23.8	Primary
			4.4	Occluded

sulfide (chalcopyrite) account for about 24%. The bottom curve in Figure 1 is the flotation concentrate diffractogram that has a copper content of about 34%. In the present case, the bornite content of the ore is higher than the chalcopyrite content.

The initial pH in the process was 2.0 as this is the optimum pH value for the growth of *Acidithiobacillus ferrooxidans*. Constant monitoring of the rise in pH was carried out, which otherwise would cause the precipitation of iron salts and would maintain the optimum growth of microorganisms. The adjustment of the correct pH value is a necessary condition for the growth of the leaching bacteria and is decisive for the solubilization of the metal. Changes in pH with time in the bi-

oleaching experiments are present in Fig. 3. The curve of pH corresponds to the initial verification of this parameter (before setting the optimal range of 1.5 to 2.0). These data allow us to identify the action of microorganisms in relation to the production and consumption of acid by the system. In the early days of the experiment, the pH increased significantly, to greater than 7.0 in the experiments without the inoculum and it was about 4.0 in vials containing the isolated. This increase in pH was due to the large consumption of this solution for the oxidation leaching of the mineral acid. However, the pH in the system with the bacteria increased to a lesser extent as these microorganisms produced part of the acid used, as discussed above, by oxidation of the elemental sulfur formed by the dissolution of chalcopyrite (Watling, 2006). In the system with no microorganisms, the pH values also increased due to the slow but progressive oxidation of ferrous ions and acid dissolution of chalcopyrite, with the consumption of sulfuric acid (Watling, 2006). Therefore, under these conditions, it was also necessary to maintain the pH. From the 30th day of leaching, a greater tendency to stabilization of the pH in both flasks with and without the inoculum was seen. This was due to the decrease in the consumption of acid by the system relative to the beginning of the process and thus this reduces the extraction kinetics of copper. Table 2 shows the Redox potential during bioleaching tests at 9 and 58 days; one notes that the solution potential is enhanced from about 360 to 460 mV in the medium with bacteria, indicating the oxidant action of the microorganisms.

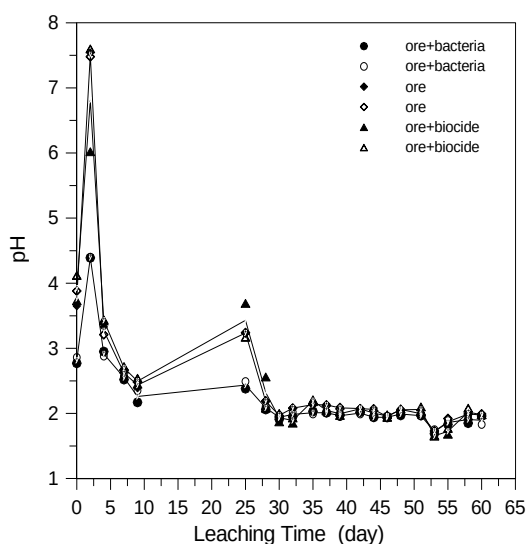


Figure 3. pH time evolution during bioleaching tests.

Table 2. Redox potential during bioleaching tests (mV).

	9 days	58 days
Ore	258.8	368.3
	255.8	366.9
Ore + Biocide	256.1	357.3
	208.6	356.1
Ore + Bacteria	459.4	403.0
	470.4	513.3

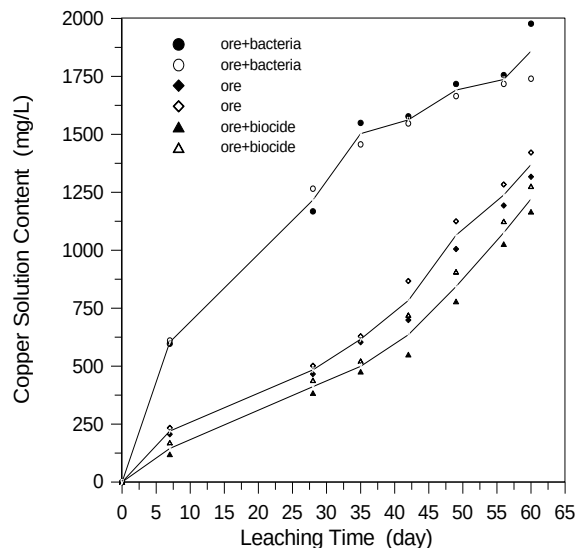


Figure 4. Solution copper on bioleaching.

As can be seen in Fig. 4, in the first week of the experiment, the copper content of the leach liquor in the flasks with the inoculum of the isolate was three times higher when compared to the other treatments without bacteria and this ratio was maintained during the first 30 days of testing. After this period, a decrease in the kinetics of recovery in the inoculated flask was observed. For the flasks without bacterial inoculum sterilized with formaldehyde or containing only the ore and leaching solution, little difference was observed between them. The vials where formaldehyde was not added show a slightly larger recovery of copper than the vials without this bactericidal agent, probably due to possible oxidation action of bacteria present in the ore itself, not *Acidithiobacillus ferrooxidans* (because in the bacterial viability test, both vials were negative for the presence of *Acidithiobacillus ferrooxidans*). One may conclude that the biomass of these bacteria present in the ore could have been too small to allow an effective response in the extraction of copper, or the possible microorganisms present were not efficient at the temperature used in the test. In the flasks with formaldehyde these possible "native" to the ore bacteria were killed by the use of this chemical, which would have led to a lower solubilization.

Table 3 shows the amounts of copper in the solid, obtained by X-ray fluorescence before and after the bioleaching experiment, and the final recovery of the metal. After 60 days of experiment, 58 and 60% of copper in the vials containing the *Acidithiobacillus ferrooxidans* was obtained whereas in flasks without the inoculum 31 and 35% (with formaldehyde) and 37 and 44% (without formaldehyde) were obtained.

Table 3: Copper ore content before and after the 60 days of experiment.

Systems Test	Copper content				Recovery (%)	
	Initial	# 1	# 2	# 1	# 2	
Ore	0.85	0.53	0.47	37	44	
Ore+ biocide	0.85	0.55	0.58	35	31	
Ore+bacteria	0.85	0.36	0.34	58	60	

In addition to the greater recovery of copper using bacteria, it was necessary to add less acid (1.8 mL) compared to the flasks without inoculum (2.5 mL). This lower consumption of acid in the inoculated flask was because the acid used by the system in the reaction of oxidation of sulfides in this flask was produced by the bacterium *Acidithiobacillus ferrooxidans* added.

The test was conducted without addition of nutrients, the ore itself was used to provide the energy needs of the bacteria. This was because the industrial plants avoid this to prevent precipitation of solids, which may affect the bioleaching process. According to the results, the ore in this case provided the necessary nutrients for the growth of the bacteria studied, and thus the success in the solubilizing of copper.

IV. CONCLUSIONS

The most abundant mineral in the Caraiba ore used in the experiments was bornite. The copper chemical and bio-leaching processes were evident when using *Acidithiobacillus ferrooxidans* strain. The stirred flasks containing microorganisms demonstrated better recovery of copper, 58 to 60%. The extraction in sterilized flasks was 31 and 35 %. The adjustment and maintenance of the pH during bacterial leaching was of paramount importance for the efficient recovery of copper because it allowed the growth of acidophilic bacteria used and prevented the formation of solid precipitate, which would hinder the ore leaching process because of the formation of a layer that prevents contact with the ore leaching solution.

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REFERENCES

- Cassa, J.C.S. and A.J. Monhemius, "Lixiviação química de um concentrado de sulfetos de cobre do minério de Caraíba," 4º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Brazil, **1**, 132-145 (1976).
- de Andrade, T.R. and F.P. de França, "Lixiviação bacteriana de cobre de baixo teor em escala de bancada", *Tecnologia Mineral*, **33**, Centro de Tecnologia Mineral (CETEM, Brazil) (1984).
- de Oliveira, D.M., L.G.S. Sobral, C.E.G. de Souza and G.H. Peixoto, "Copper extraction from primary ore using *Acidithiobacillus* ssp and *Leptospirillum ferrooxidans*," 19th International Biohydrometallurgy Symposium, Changsha, **1**, 727-730 (2011).
- de Souza, V.P., "Lixiviação bacteriana de sulfeto de cobre de baixo teor-Caraiba," *Anais do 7º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia*, Brazil, 1-26 (1980).
- Giaveno, M.A., T.L. Lavallo and E. Donati, "Use of bioreactors in the leaching of an oxidized copper ore," *Lat. Am. Appl. Res.*, **33**, 13-18 (2003).
- Lima, R.B., C.E.G. de Souza, D.M. de Oliveira, J.P.S. Junior, P.A. da Silva Medeiros and L.G.S. Sobral, "Lixiviação bio-assistida de concentrado de flotação de sulfetos de cobre em coluna," 23º Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa, Brazil, **2**, 651-656 (2009).
- Marques, M.S., "Estudo comparativo entre duas metodologias de lixiviação bacteriana de minérios de cobre," 14º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Brazil, **2**, 851-861 (1990).
- Marques, M.S. and O. Garcia Jr, "Biohidrometalurgia-Aplicação industrial e novas perspectivas," 15º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Brazil, 721-739 (1992).
- Martins, A.H. and M.M.A. El-Naggar, "Lixiviação bacteriana de minério de cobre sulfetado de baixo teor," 9º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Brazil, 633-644 (1982).
- Novo, M.T.M. and O. Garcia Jr, "Lixiviação bacteriana de minério de cobre da mina de Surubim-Ba," 14º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Brazil, **2**, 862-878 (1990).
- Olson, G.J., J.A. Brierley and C.L. Brierley, "Bioleaching review (part B): Processing in bioleaching: applications of microbial processes by the minerals industries," *J. Applied Microbiology and Biotechnology*, **63**, 249-257 (2003).
- Pradhan, N., K.C. Nathsarma, K. Srinivasa Rao, L.B. Sukla and B.K. Mishra, "Heap bioleaching of chalcopyrite: A review," *Minerals Engineering*, **21**, 355-365 (2008).
- Rossi, G., "Biohydrometallurgy," McGraw-Hill Book (1990).
- Sobral, L.G.S., P.A.M. da Silva, S.G.F. Leite, R.B. Lima, P.G. Xavier, and D.M. de Oliveira, "Biolixiviação de concentrado de flotação de sulfetos de cobre," 21º Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa, Brazil, **2**, 181-188 (2005).
- Sobral, L.G.S., C.E.G. de Souza and D.M. de Oliveira, "Pilote scale bioleaching of copper sulphide flotation concentrate using different consortium of mesophile, moderate and extreme thermophile microorganisms," 19th International Biohydrometallurgy Symposium, Changsha, **1**, 731-735 (2011).
- Watling, H.R., "The bioleaching of sulphide minerals with emphasis on copper sulphides - A review," *Hydrometallurgy*, **84**, 81-108 (2006).
- Urenha, L.C. and R.C.P. Alli, "Biometalurgia de minério de cobre da mina Caraiba (BA)," 14º Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Brazil, **2**, 835-850 (1990).

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