# BIOLOGICAL GENERATION OF SULPHURIC ACID FOR BIOLEACHING OF COPPER OXIDE ORES

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## ABSTRACT

In the extractive metallurgy sector sulphuric acid is used for extracting metals from different mineral species. From sulphide minerals, the metals can be extracted by using acidophilic microorganisms that need low pH for the oxidation of such species to take place releasing the metal of interest into solution for being further recovered through a particular downstream process. In the case of a weathered ore, where it is found mineral species derived from previous sulphide species weathering processes in nature, such oxides, carbonates, sulphates etc., one just needs to react these species with sulphuric acid solution. However, operations such as metal leaching often have mines and plants located in remote areas and in countries lacking the infrastructure necessary to handle the extremely dangerous concentrated sulphuric acid. Most leaching operations use aqueous solutions of such acid that contain less than 20 $g.L^{-1}$ of sulphuric acid. Therefore, this technical contribution goes a little bit further and aimed at generating sulphuric acid, biologically, mixing, in particular, a copper oxide ore with elemental sulphur, in a bench scale, in a orbital shaker, where the ground copper oxide ore and elemental sulphur were suspended in an acid solution bearing acidophilic microorganism and nutrients (MKM medium) with initial pH adjust to 1.8. During the leaching process the pH and Eh were monitored until the acid concentration reached nearly $4.17 g.L^{-1}$, which corresponds to pH 1.37, as a result of the bio-oxidation of elemental sulphur. The copper-bearing drained solution, apart from being enough concentrated in copper, to be further used in the downstream process, was enough concentrated in sulphuric acid for being detrimental to the microorganisms metabolism. Finally, it was realized that running the leaching process for four days nearly 90% of the copper was extracted.

**KEYWORDS:** bioleaching; sulphuric acid; copper oxide.

## 1. INTRODUÇÃO

In times of economical down turn and, therefore, a period of lower copper prices, it is increasingly important to improve current copper extraction processes regarding their efficiency. So far as we can tell, approximately 20% of the world copper production are reached by hydrometallurgical leaching processes, in particular by leaching oxide copper ores with sulphuric acid and subsequent downstream processing of the leachate through solvent extraction followed by the electrowinning of copper (SX-EW).
At present, heap leaching is a well-known industrial process for the treatment of minerals with oxidized species and secondary sulphides from base metals, usually supported by bacterial techniques. The latter, are now also being widely explored and tested in the treatment of primary sulphides.

Sulphuric acid is used in a wide variety of commercial settings. In mining operations, such acid is used in heap or run-of-mine stock-pile leaching of ore materials and recovery of desired metal values through SX-EW. This acid supply for use in heap leaching of copper, and other base metals can be obtained from different sources (US Patent, 2005). However, there are significant costs associated with the production, purchase, transfer and transportation of acid that is generated by any of these processes. In addition to the cost, the amount of acid required for heap leaching operations varies with time depending on the availability of feed material for raising that heap. In general, this demand has been increasing worldwide in recent years.

Conventionally, copper oxide ores have been leached in a heap using sulphuric acid solution and leachate being further sent through downstream processes for getting pure metallic copper (KORDOSKY, 2005). The Figure 1, as follows, shows the whole process for extracting copper from oxide ore.

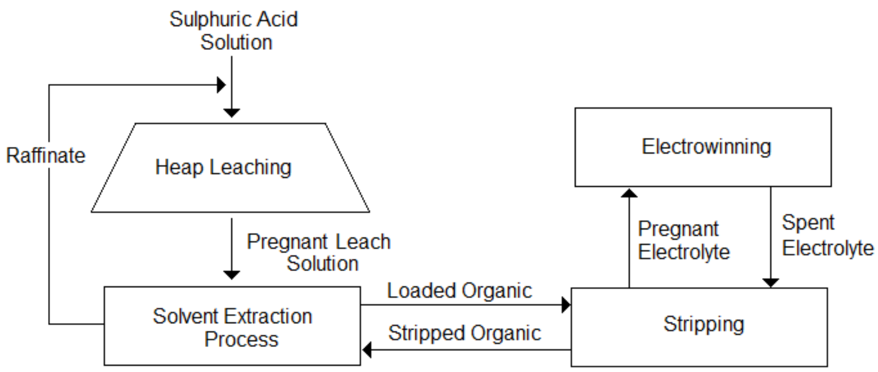


**Figure 1. Conventional leach/solvent extraction/electrowinning flow sheet.**

While various biological oxidation methodologies are known, such methodologies have uniformly been used, so far, in connection with metal recovery processing techniques. Accordingly, a method to produce low cost acid in an environmentally acceptable manner, such as through the use of biological oxidation processing, would be advantageous. In this study, the ground ore mixed with elemental sulphur powder were suspended in an acid solution bearing nutrients and mesophiles microorganisms so as to produce most of the acid enough to solubilise the copper bearing minerals.

## 2. METHOLOGY

### 2.1. Mineral Sample

In this study a copper weathered ore was used. After crushing, grinding, and homogenization procedures, a particle size varying from 0.105 and 0.149 mm was classified for being used in a simplified technological characterization and in leaching experiments. The analyzes carried out by atomic absorption spectrometry, after an appropriate acid digestion of a representative sample of the ore, revealed a copper content of 0.64% .

The copper-bearing mineral species comprising the copper ore are: Brochantite ($Cu_4(SO_4)(OH)_6$, Malachite ($Cu_2(CO_3)(OH)_2$), Yakhontovite ($Na_{2.25}K_{0.75}Mg_4Al_{4.5}Mg_{2.5}Si_{21.5}Al_{2.5}O_{60}$), Posnjakite ($Cu_4(SO_4)(OH)_6$), Woodwardite ($Cu_4.Al_2(SO_4)(OH)_{12}$), Lavendulan ($NaCaCu_5.(AsO_4)_4.Cl.5(H_2O)$, Byite ($Cu.2Pb.4(SO_4)(OH)_8$), Phosphofibrite ($KCuFe^{3+}\cdot_{15}(PO_4)_{12}.(OH)_{12}.12(H_2O)$), Tsumebite ($Pb.2Cu(PO_4)(SO_4)(OH)$), as shown in the difratogram of Figure 2.

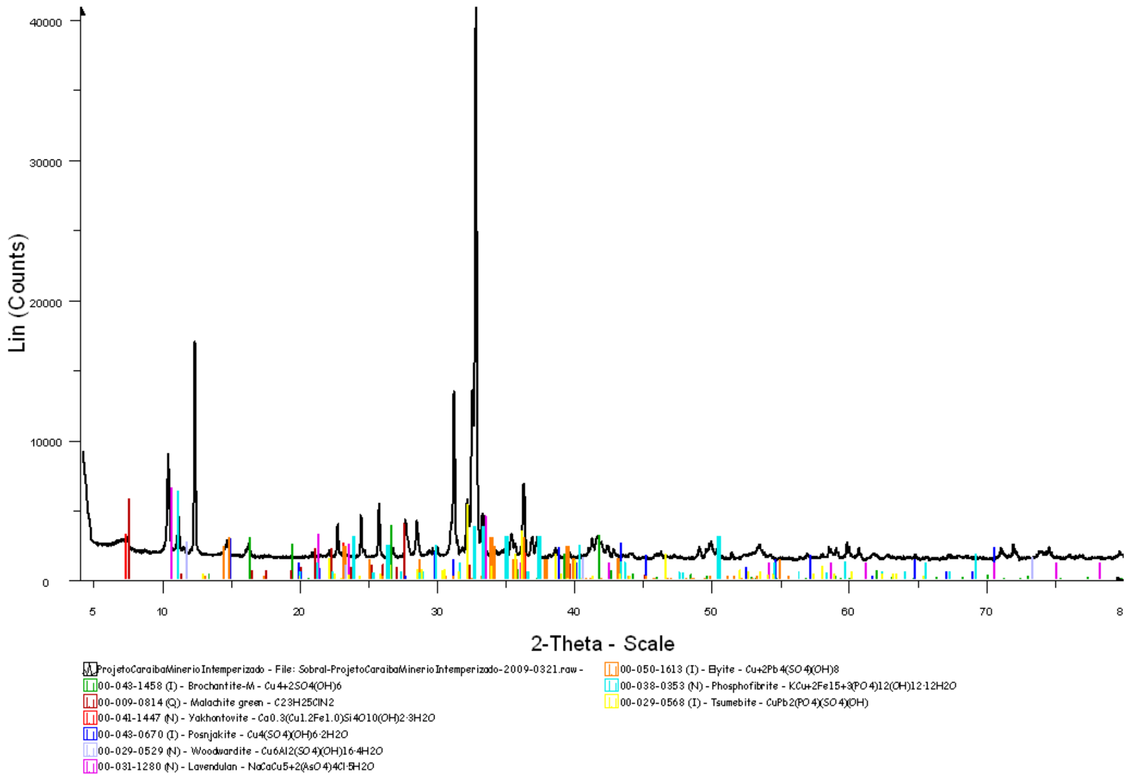


**Figure 2. Difratogram of the copper ore.**

### 2.2. Micro-organism

The bacteria *Acidithiobacillus thiooxidans* (Strain FG01) used in that study was cultivated at 30ºC, in orbital shaker at 150 rpm, using the modified 9K (GARCIA, 1991) culture medium (pH 2.8), with the following composition: $(NH_4)_2SO_4$ (1.0 $g.L^{-1}$), $MgSO_4.7H_2O$ (0.5 $g.L^{-1}$), $K_2HPO_4$ (0.5 $g.L^{-1}$), $S^{\circ}$ (10 $g.L^{-1}$)

### 2.3. Leaching experiment

The experiments were accomplished in 500 ml Erlenmeyer flasks containing 200 ml of MKM culture medium (OLIVEIRA, 2009) in a 1:5 dilution and 10 g of copper oxide ore (pulp density of 10% w/v). The culture medium had its pH adjusted to 1.5 with 5M $H_2SO_4$ solution with the following composition (Table I):

**Table I. Composition of the culture medium used in the bioleaching tests.**

| Reagent | [$g.L^{-1}$] |
|---|---|
| $(NH_4)_2SO_4$ | 0.4 |
| $MgSO_4.7H_2O$ | 0.4 |
| $K_2HPO_4$ | 0.04 |

The microbial inoculum was added at a ratio of 10% v/v and 10 $g.L^{-1}$ of elemental sulphur were also added. Simultaneously, leaching tests were accomplished without adding elemental sulphur. In this case, it was necessary to adjust the pH through the addition of sulphuric acid to maintain pH around 1.5. The Erlenmeyer flasks were incubated in an orbital shaker under at 150 rpm, at a temperature of 30° ± 1°C for 15 days. No sterilized samples were used looking for, thus, establishing conditions close to reality before industrial application. The water losses by evaporation were estimated by the mass losses and compensated by adding water before each sampling.

## 3. RESULTS AND DISCUSSION

After 4 days of process 90%, approximately, of copper extraction were reached. The copper extraction while running the leaching process adding elemental sulphur was similar to that achieved in conventional chemical leaching as can be observed in Figure 3. The experiment was carried out for fifteen days; however, it was not possible to extract the whole copper from the ore, as some of the mineral species bearing copper are not ready soluble in the acid solution used.

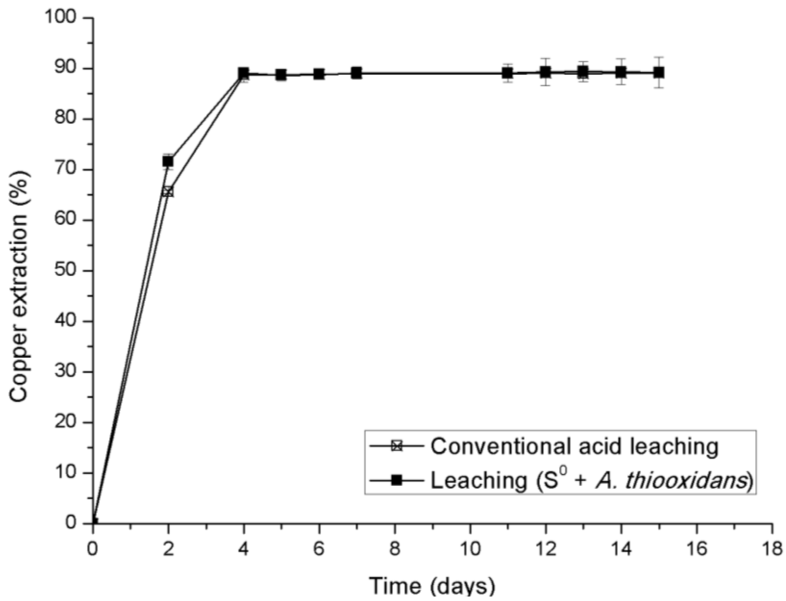


**Figure 3. Copper extraction in the leaching tests.**

The Figure 4 shows the variation of the redox potential throughout the experiments. It was realized, in the test where elemental sulphur was added, such potential values remained higher when compared to conventional acid leaching where the raise of the redox potential is just due to the available ion species in solution during the acid dissolution of minerals.

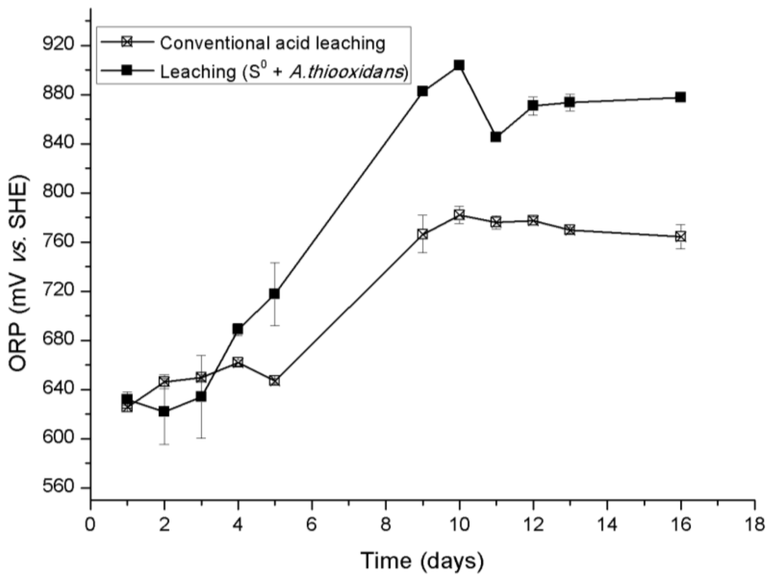


**Figure 4. Variation of redox potential in the leaching tests.**

Regarding the pH variation (Figure 5a), it was observed the same trend in both tests. The big difference between these tests is that, in the test called "Conventional acid leaching", it was necessary to add sulphuric acid for keeping the pH around 1.5. In the test where elemental sulphur was added the generation of sulphuric acid took place according to Equation 1.

$$S^0 + 1.5O_2 + H_2O \xrightarrow{A.thiooxidans} H_2SO_4 \qquad (1)$$

The oxidation of sulphur by the bacteria present in the reaction system has ensured the supply of sulphuric acid required for dissolving the mineral species bearing copper.

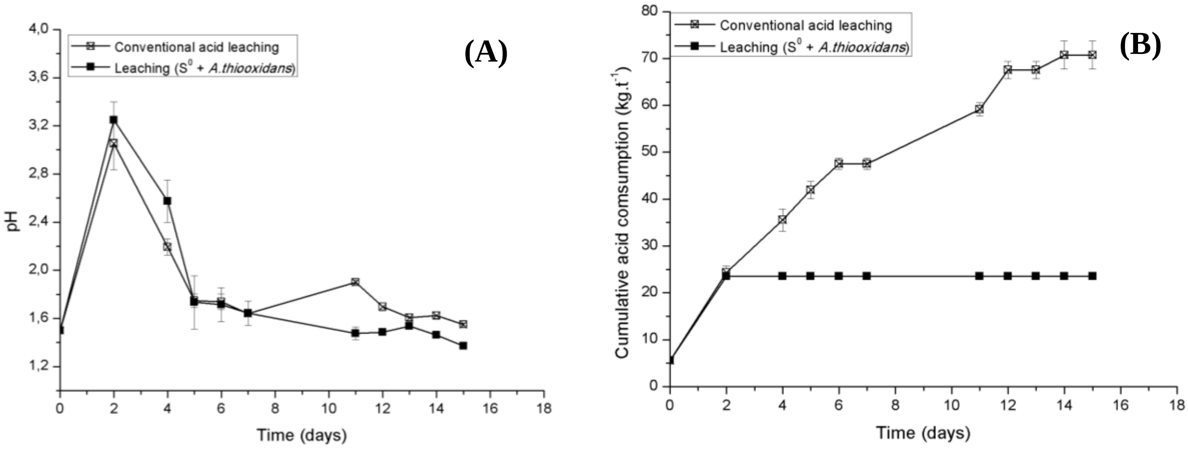


**Figure 5. pH variation (A) and acid consumption (B) in the leaching tests.**

To extract 88.71 % of copper using conventional chemical leaching it was necessary to use 35.53 kilograms of sulphuric acid per tonne of ore. In the test with *in situ* acid production nearly 90% of copper were extracted in the same period of time (4 days).

## 4. CONCLUSIONS

After running the leaching test for four days, in bench scale, it was possible to observe that:

i. Nearly 90% of the copper content in the ore were extracted by *in situ* biological generation of sulphuric acid;

ii. In the test where elemental sulphur was mixed with the copper ore, the continuous generation of sulphuric acid took place, which ensured the suitable pH and Eh for leaching most of the copper-bearing mineral species due to the action of *A. thiooxidans* in the operation conditions used;

iii. The copper extraction results wave for the possibility of leaching base metals oxide ores, scaling up such technology so as to get the right figures for raising a demonstration heap with *in situ* generation of sulphuric acid.

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