University of Belgrade
Technical Faculty in Bor

Chamber of Commerce
and Industry of Serbia

XV International Mineral Processing & Recycling Conference

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

Proceedings

Editors:
Jovica Sokolović
Milan Trumić

17-19 May 2023 | Belgrade SERBIA

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COLUMN LEACHING OF LOW-GRADE COPPER SULFIDE ORE WITH SULFURIC ACID

G. D. Bogdanović[1#], D. Marilović[1], B. Nikolić[2], S. J. Petrović[3]
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ABSTRACT – The paper presents the results of leaching of low-grade copper sulfide ore with average Cu content of 0.33% and an oxide content of about 7%. The experiments were carried out in sulfuric acid solution and with the addition of Fe(III) ions that had the role of oxidant. During the leaching period of 23 days, with sulfuric acid, the concentration of copper in the solution ranged from 0.05 to 0.230 g/dm^3, and iron from 0.125 to 0.350 g/dm^3. With the addition of Fe(III) ions to the process, the concentration of copper in the solution moved in the same range. These results show that a longer period is needed for the oxidation and dissolution of this raw material.

Keywords: Leaching, Copper, Sulfuric Acid, Fe(III) ions.

INTRODUCTION

Due to the low content of copper in natural deposits, today more attention is paid to the possibility of treating low-grade raw materials. Extraction of copper from such raw materials is in most cases achieved by the leaching process [1]. Percolation leaching is used for heap leaching, leaching of dump, or "in situ" leaching, i. e. it is used for leaching of raw materials that contain a low content of useful components [1,2]. For the leaching process, it is necessary to determine the chemical and mineralogical composition of the raw material.

Sulfuric acid is most often used as an agent for the leaching of copper minerals [3], and Fe(III) ions as an oxidant [4]. Copper sulfide minerals in an acidic medium is based on the following stoichiometric reactions:

Covellite:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S^0 \quad (1)$$

Chalcocite:

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S^0 \quad (2)$$

Chalcopyrite:

$$CuFeS_2 + 2Fe_2(SO_4)_3 = CuSO_4 + 5FeSO_4 + 2S^0 \quad (3)$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 = CuSO_4 + 5FeSO_4 + 2H_2SO_4 \quad (4)$$

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The dissolution of copper oxide minerals in acidic solutions is carried out mainly without the presence of oxidants, and can be represented by the following stoichiometric reactions:

Cuprite:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + 2H_2O \quad (5)$$

$$Cu_2O + \frac{1}{2}O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 2H_2O \quad (6)$$

Tenorite:

$$CuO + H_2SO_4 = CuSO_4 + H_2O \quad (7)$$

Azurite and Malachite:

$$Cu_3(OH)_2(CO_3)_2 + 3H_2SO_4 = 3CuSO_4 + 2CO_2 + 4H_2O \quad (8)$$

$$Cu_2(OH)_2CO_3 + 2H_2SO_4 = 2CuSO_4 + CO_2 + 3H_2O \quad (9)$$

The paper presents the influence of sulfuric acid and iron (III) ions as oxidant on the leaching of low-grade copper ore.

EXPERIMENTAL

Characterization of the sample

The ore sample was dried at room temperature and crushed. Particle size distribution was determined by the sieve analysis on the standard Retsch sieve series. The granulometric composition of the sample is shown in Figure 1.

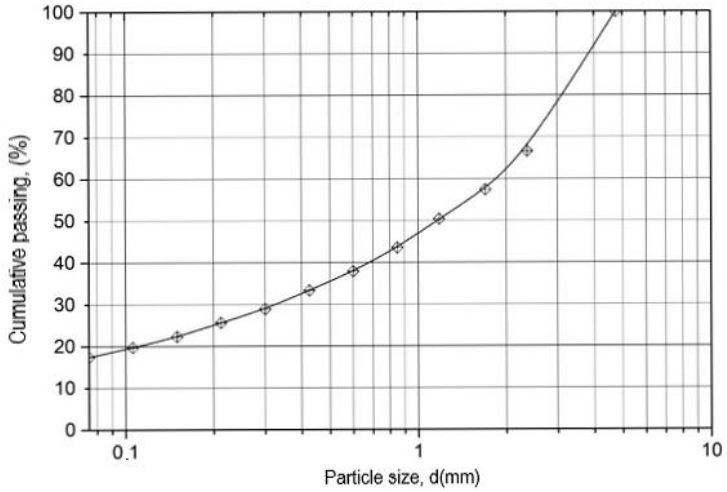

Figure 1 Particle size distribution of ore

Chemical composition of the initial sample (class -4.75 +0.00 mm) is presented in Table 1.

Table 1 Chemical composition of ore

El.	Cu_{tot}	Cu_s	S	Fe	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SiO_2	Zn	Ni	Mn
%	0.33	0.306	1.24	4.21	6.02	18.58	0.76	2.28	1.18	3.16	59.78	0.011	<0.007	0.052

Based on the obtained qualitative mineralogical analysis, the following mineral composition was determined: pyrite, chalcopyrite, covellite, cuprite, chalcocite, magnetite, rutile, goethite, galena, sphalerite and gangue minerals. The most present minerals were pyrite and chalcopyrite.

Column leaching

The leaching experiments were carried out in PVC columns, 110 mm in diameter and 1000 mm in height. In each column was added 7 kg of ore. At the top of the ore layer a layer of silica was placed for the uniform distribution of the acid solution. The leaching agent used in the experiment was 0.03 mol/dm^3 sulfuric acid solution. When the influence of oxidants was tested, the experiments were performed with the addition of 3 g/dm^3 Fe(III) ions, at a solid:liquid ratio of 1:1. The flow rate of the solution through the column during the experiment was from 8 to 10 ml/min. The ore leaching in the columns was done for 23 days. After 10 days of leaching, the flow of the leaching solution was stopped and the ore was exposed to an oxidation cycle for a period of 7 days. After the oxidation period, the sulfuric acid solution was again passed through the raw material layer in the column until the end of the leaching period.

Figure 2 Apparatus for percolation leaching

At certain time intervals, 20 cm^3 of the leaching solution was sampled. Copper and iron concentrations in the solution were analyzed by Hanna HI 83200 Atomic Adsorption Spectrophotometer and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 8300).

RESULTS AND DISCUSSION

The results in Figure 3 show that after the initial period, which corresponds to the leaching of copper oxide, the leaching rate decreases. For the sample treated only with sulfuric acid (Fig. 3a), the concentrations of Cu and Fe in the solution increased with time in the first 11 days, and the concentration of copper was 0.158 g/dm^3, and the concentration of iron was 3.037 g/dm^3. The next 7 days were followed by an oxidation period. After this period, the raw material layer in the column was re-washed with a leaching solution. The concentration of Cu in the solution after the period of oxidation slight increase and reached the value of 0.182 g/dm^3 and the concentration of iron in the solution remained the same (Fig. 3 a).

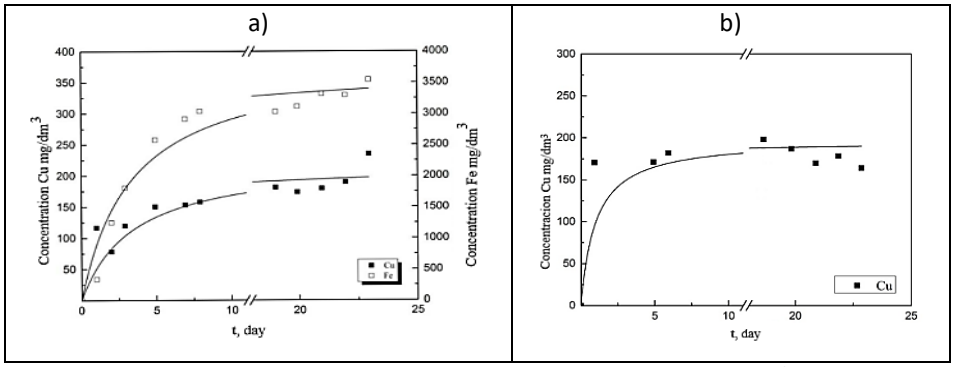

Figure 3 Concentration of Cu and Fe vs. time leaching with 0.03 mol/dm^3 H_2SO_4 solution (a) and concentration of Cu vs. time leaching with 0.03 mol/dm^3 H_2SO_4 and 3 g/dm^3 Fe(III) ions (b)

Simultaneously with the leaching of copper oxide minerals, the process of oxidation of copper sulfide minerals takes place. Since leaching is a slow process, dissolved oxygen in the leaching solution and Fe^{3+} ions, formed by leaching of iron oxide compounds and pyrite oxidation, can also act as oxidants for copper sulfides. Under real conditions, microorganisms present in the ore can oxidize Fe^{2+} to Fe^{3+} ions, which can affect the leaching rate of copper sulfide minerals. Therefore, percolation leaching of copper on a heap or on a dump can last for years, depending on the size of the heap, i.e. the dump, the copper content in it and the used copper mineral leaching agent. Oxidation of chalcopyrite (reactions 3 and 4) leads to the formation of elemental sulfur and sulfate as the final product. Elemental sulfur formed can act as a passivating layer on the surface of a mineral that leads to slow down the dissolution rate [5-9].

During the leaching of ore in the solution of 0.03 mol/dm^3 H_2SO_4 and 3 g/dm^3 Fe (III) ions, the concentration of copper in solution after 11 days was 0.187 g/dm^3 and after the oxidation period there was a small change in the concentration of copper in the solution (Fig. 3b).

Final copper extraction after 23 days in the sulfuric acid solution was 7.11%, and the extraction of oxide Cu was 97.87%. Under the tested conditions, the iron extraction value was 7.88%. Since during the column leaching a low extraction of total copper was obtained, and copper oxide minerals were not completely leached, it can be assumed

that there was a higher consumption of acid due to the occurrence of other reactions with carbonate minerals or iron minerals. As a result of these reactions, the formation of reaction products can prevent contact of the solution with the copper minerals [10,11].

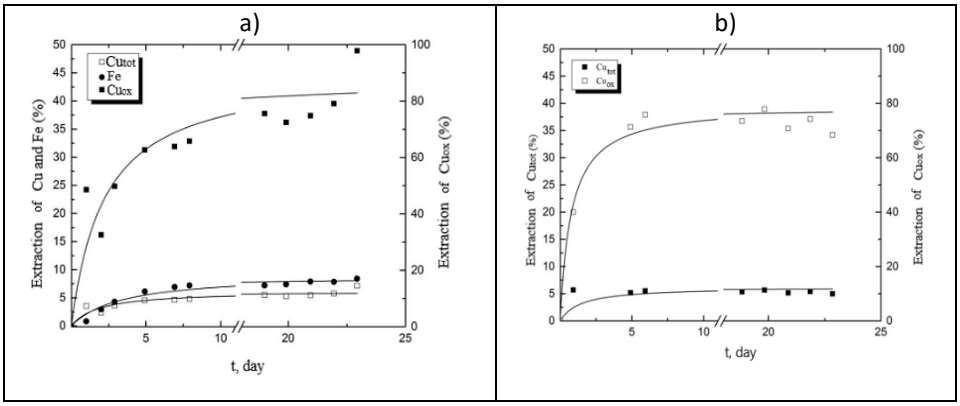

Figure 4 Extraction of Cu and Fe vs. time leaching with 0.03 mol/dm^3 H_2SO_4 solution (a) and Extraction of Cu vs. time leaching in 0.03 mol/dm^3 H_2SO_4 and 3 g/dm^3 Fe(III) ions

The final copper extraction with the addition of Fe(III) ions was about 5.6%, while the extraction of oxide copper was about 69%. It can be seen that the addition of Fe(III) ions slightly affects the leaching of copper. Considering that copper in the sample is mostly in the form of chalcopyrite, the degree of oxidation and leaching of this raw material was very low. It can be assumed that another type of processing should be used to treat such raw material.

CONCLUSION

Percolation leaching of low-grade sulfide ore in columns performed with sulfuric acid with and without oxidants, with a period of oxidation of the sample in the columns, did not give satisfactory results. The best result was obtained by leaching with 0.03 mol/dm^3 H_2SO_4 without the addition of oxidants. After 23 days of leaching in the column, the concentration of copper in the solution was 0.235 g/dm^3 and the extraction of total copper was 7.11%. Considering the content of oxide minerals in the examined raw material was 7.27%, it can be concluded that the oxidation of sulfide minerals did not succeed, even part of the oxide copper remained unleached. Analyzing the obtained results, it can be concluded that another type of processing should be used for this kind of raw material.

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