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VALORIZATION OF COPPER FROM LOW-GRADE ORE BY LEACHING: INFLUENCE OF SULPHURIC ACID CONCENTRATION

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ABSTRACT – This paper presents an investigation of low-grade copper ore leaching using sulphuric acid where dissolved oxygen and iron(III) ions play a role of oxidant**.** The influence of initial acid concentration on copper and iron extraction was examined. The copper concentration in the leach solution ranged from 0.78 to 1.25 g/dm^3, whereas the iron concentration ranged from 1.89 -2.32 g/dm^3. It was found that the metal extraction increases with increasing acid concentration. The total copper extraction of 38% was attained with 0.5 M H_2SO_4 after 180 min of reaction.

Keywords: Acid Leaching, Copper, Low-Grade Ores.

INTRODUCTION

Hydrometallurgical processes are very often used for extraction of metals from ores (especially for oxide and polymetallic ores), industrial process residues, production scrap, and urban waste [1-4]. These methods use water as a solvent and were originally developed for the extraction of copper and gold, as well as for the extraction of uranium from low-grade ores [5].

Processing of mineral raw materials by hydrometallurgical processes is conducted by the following processes: grinding, chemical or biological leaching; separation of the residue; purification of the leach solution by solvent extraction or ion exchange; and metal recovery by precipitation or electrolysis. Currently, about 25% of the copper worldwide is produced by means of leaching in combination with the solvent extraction and electrolysis. Heap, dump and “in situ" leaching are technologies preferred for the processing of low-grade ores containing copper oxides or secondary copper sulfides [2].

Copper oxide minerals readily leach in any acidic solutions and the sulphuric acid has the greatest industrial application. In the case of leaching secondary copper sulfide minerals, such as chalcocite and covellite, oxidation is necessary (iron (III) ions, oxygen, etc.) and an important role in this is played by bioleaching, with the help of bacteria. The bacteria oxidize Fe (II) ions to Fe (III) ions, which improves the copper extraction rate [1]. Oxidative leaching of secondary copper sulfide minerals in an acidic medium is based on the stoichiometric reactions (1-4) and copper oxide minerals according to the stoichiometric reactions (5 -7) [2]:

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Chalcocite

$$Cu_2S + 1/2O_2 + H_2SO_4 \rightarrow CuS + CuSO_4 + H_2O \quad (1)$$

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow CuS + CuSO_4 + 2FeSO_4 \quad (2)$$

Covellite

$$CuS + 2O_2 \rightarrow CuSO_4 \quad (3)$$

$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S \quad (4)$$

Malachite

$$Cu_2(OH)_2CO_3 + 2H_2SO_4 \rightarrow 2CuSO_4 + 3H_2O + CO_2 \quad (5)$$

Azurite

$$Cu_3(OH)_2(CO_3)_2 + 3H_2SO_4 \rightarrow 3CuSO_4 + 4H_2O + 2CO_2 \quad (6)$$

Cuprite

$$Cu_2O + 1/2O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 2H_2O \quad (7)$$

The aim of this paper is to investigate the leaching of low - grade sulfide ore using sulphuric acid in order to obtain enriched solutions that would be suitable for the use of solvent extraction or ion exchange techniques for further treatment.

EXPERIMENTAL

A sample of low-grade copper ore was used for this study. Particle size distribution in a sample of ore was determined by the sieve analysis on the standard Tyler sieve series as shown in Table 1.

Table 1 Particle size distributions of ore

Particle size (mm)	Percent (%)	D (%)
+2.36	9.89	100
-2.36 +1.7	5.65	90.11
-1.7 +1.18	6.01	84.46
-1.18 +0.85	3.12	78.45
-0.85 +0.6	7.36	75.33
-0.6 +0.425	5.75	67.97
-0.425 +0.3	6.38	62.22
-0.3 +0.212	6.53	55.84
-0.212 +0.15	4.69	49.31
-0.15 +0.106	5.1	44.62
-0.106 +0.075	4.71	39.52
-0.075 +0.00	34.81	34.81
	100	

The chemical composition of the sample is presented in Table 2. It can be concluded that the sample represents a low-grade ore with a high content of copper oxide minerals (30%). It was estimated that, by the use of mineralogical and X-ray analysis, the most present copper minerals were chalcocite and chalcopyrite. Malachite, cuprite and azurite were found from copper oxide minerals. The most abundant sulphide mineral was pyrite.

Table 2 Chemical composition of ore

Component	Cu_{-total}	$Cu_{-sulfide}$	Cu_{-oxide}	S	Fe	Fe_2O_3	C_aO	M_gO
(%)	0.33	0.23	0.098	2.12	2.35	3.36	0.33	0.83
Component	SiO_2	K_2O	Al_2O_3	Na_2O	Zn	Ni	Mn	
(%)	63.18	3.07	21.58	0.24	0.009	<0.007	0.019	

The experiments were conducted in a 400 mL glass reactor with a magnetic stirrer. At the room temperature, 50 g sample was added to 50 ml leaching solution of desired concentrations and stirring was started. After different time period from 5 to 180 minutes, the suspension was filtered and the filtrate was analyzed by Optical emission spectrometers with inductively coupled plasma using the instrument PerkinElmer Optima 8300 (PerkinElmer, USA). The experiments were monitored as a function of time and acid concentrations. All solutions used were prepared using analytical grade chemicals and distilled water.

RESULTS AND DISCUSSION

The effect of acid concentrations (0.01 M, 0.03 M, 0.1 M, 0,5 M, 1 M H_2SO_4) on the copper and iron dissolution was investigated at solid /liquid ratio 1:1 and stirring speed of 400 rpm. The results are shown in Figures 1-3. During the experiments, the change of the pH and electrode potential of leach solutions was monitored over time as shown in Figures 4 and 5.

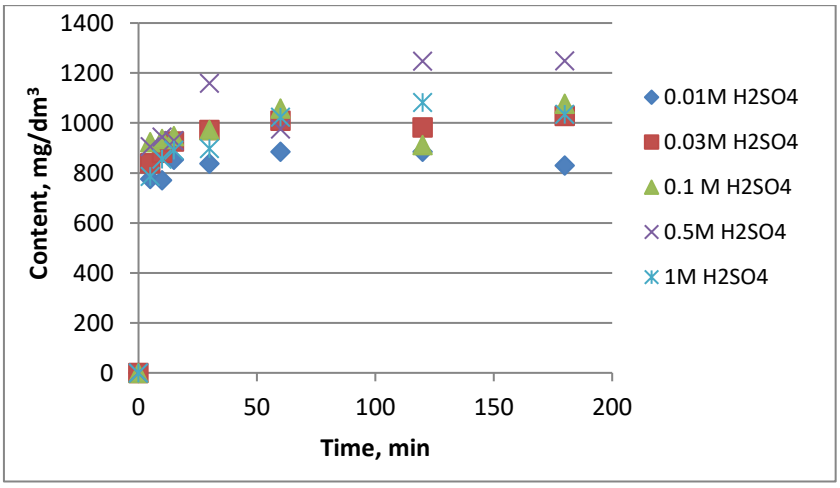

Figure 1 Effect of the sulphuric acid concentration on copper content in the leachate vs. time

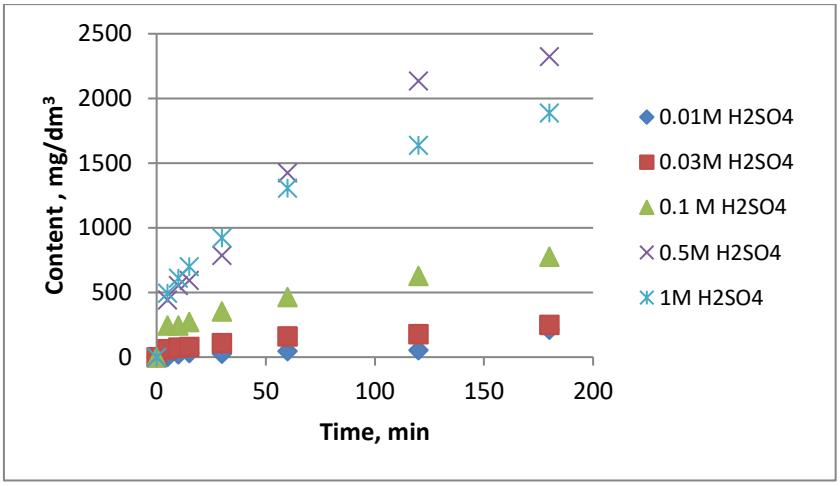

Figure 2 Effect of the sulphuric acid concentration on iron content in the leachate vs. time

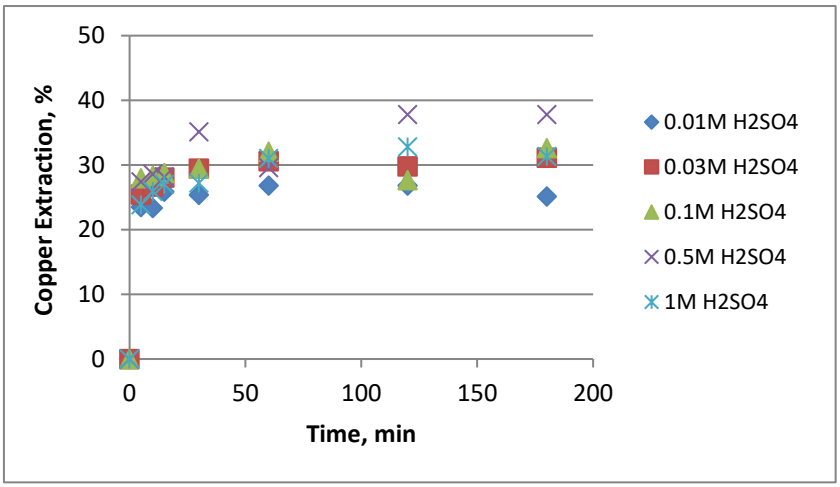

Figure 3 Effect of sulphuric acid concentration on copper extraction

The presented results (Figures 1 and 2) show that the copper and iron ions concentration increase with time. Also, the metal extraction increases with an increase in the acid concentration. Concentration of copper (II) in solutions, after 180 minutes of leaching, is in the range of 0.78 g/dm^3 (0.01 M H_2SO_4) to 1.25 g/dm^3 (0.5 M H_2SO_4). The results (Figure 2) showed that iron concentration increased slightly with increasing acid concentration from 0.01 to 0.1 M H_2SO_4. Higher acid concentration (0.5-1 M) had a significant effect on the reaction rate and final iron concentration was in the range of 1.89-2.32 g/ dm^3.

Final copper extractions in the 0.01 M H_2SO_4 and 0.5 M H_2SO_4 solution were 24% and 38%, respectively. At lower sulphuric acid concentration (0.01 M H_2SO_4), the lowest copper extraction value was found, which was the result of the lack of leaching agents.

The highest copper extraction rate (30 min leaching) at all tested acid concentrations indicated a high solubility of copper oxide minerals. Simultaneously with leaching of oxide minerals, a process of oxidation of sulfide copper minerals takes place due to the presence of Fe (III) ions and atmospheric oxygen in the solution. The sulfide mineral oxidation rate depends on the oxygen concentration, temperature, particle size, type of sulfide minerals, pH of the solution, Eh solution, presence of indigenous species of bacteria, etc.

Change in the potential and pH value of leach solutions with time is shown in Figures 4 and 5. It can be seen in Figure 4 that the potential is in a range of 255 to 367 mV which indicates that Fe (II) is dominant in the obtained solutions regarding Fe (III) ion. Due to this, oxidation processes of sulfide minerals are slower, resulting in low copper extractions in the solution.

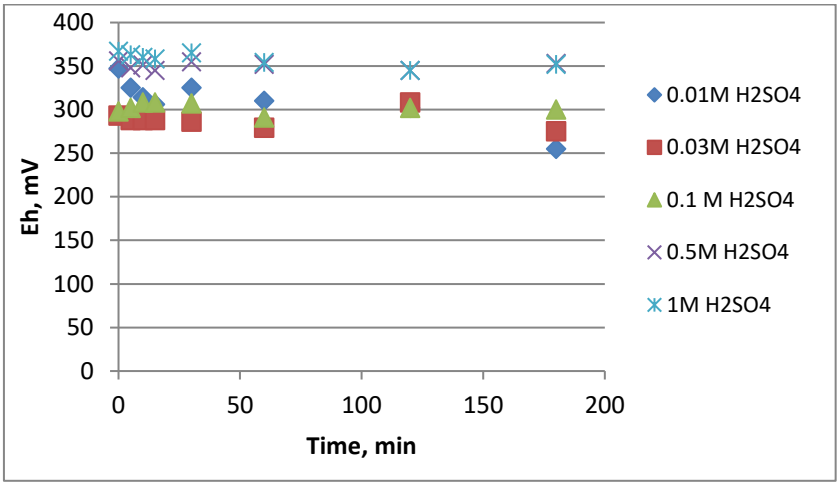

Figure 4 The change of the Eh of the leaching solution vs. time

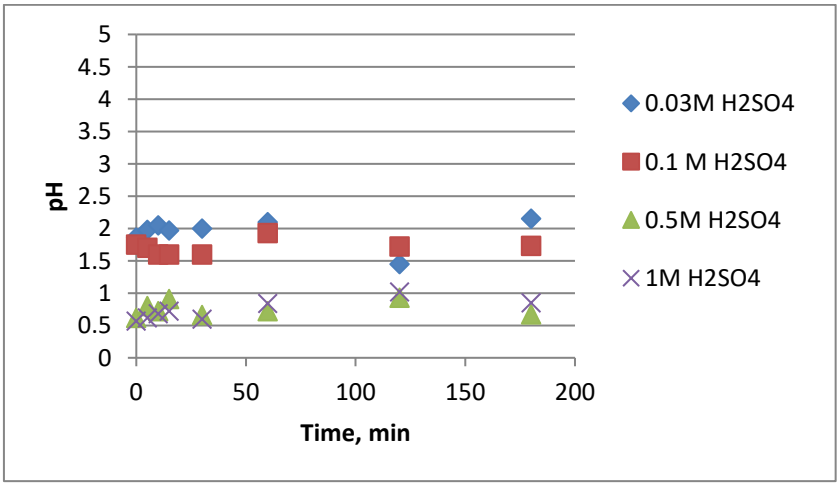

Figure 5 The change of the pH of the leaching solution vs. time

Figure 5 shows that the pH value increases in the initial period of the leaching process (up to 10 minutes), after which it remains constant throughout all experiments. During the leaching process, sulphuric acid is consumed due to reactions with copper minerals, but also due to reactions with iron oxide minerals and by other gangue minerals in the ore (carbonates and siliceous minerals). However, the oxidative reaction rate of iron sulfide minerals (e.g. pyrite) is responsible for the generation of acid, which contributes to the overall reduction of sulphuric acid consumption [6, 7].

CONCLUSION

It was found out that the majority of present copper and iron oxide minerals are dissolved during ore leaching by the use of sulphuric acid solutions, which was shown a significant concentration of copper and iron ions in obtained solutions. With increased leaching time and sulphuric acid concentration, copper and iron content in the solution increases, as well as extraction rate of these metals. At higher acid concentrations, copper sulfide minerals are more easily oxidized by oxygen and iron (III) present in leaching solutions. The total copper extraction was in the range of 24% to 38% and quite high concentration of copper ions was achieved (0.78 to 1.25 g/dm^3), suitable for further processing in the course of copper production.

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