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Comparison of Microwave-Assisted and Conventional Leaching for Extraction of Copper from Chalcopyrite Concentrate

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Abstract**—**Chalcopyrite ($CuFeS_2$) is the most common primary mineral used for the commercial production of copper. The low dissolution efficiency of chalcopyrite in sulfate media has prevented an efficient industrial leaching of this mineral in sulfate media. Ferric ions, bacteria, oxygen and other oxidants have been used as oxidizing agents in the leaching of chalcopyrite in sulfate and chloride media under atmospheric or pressure leaching conditions. Two leaching methods were studied to evaluate chalcopyrite ($CuFeS_2$) dissolution in acid media. First, the conventional oxidative acid leaching method was carried out using sulfuric acid (H_2SO_4) and potassium dichromate ($K_2Cr_2O_7$) as oxidant at atmospheric pressure. Second, microwave-assisted acid leaching was performed using the microwave accelerated reaction system (MARS) for same reaction media. Parameters affecting the copper extraction such as leaching time, leaching temperature, concentration of H_2SO_4 and concentration of $K_2Cr_2O_7$ were investigated. The results of conventional acid leaching experiments were compared to the microwave leaching method. It was found that the copper extraction obtained under high temperature and high concentrations of oxidant with microwave leaching is higher than those obtained conventionally. 81% copper extraction was obtained by the conventional oxidative acid leaching method in 180 min, with the concentration of 0.3 mol/L $K_2Cr_2O_7$ in 0.5M H_2SO_4 at 50 ºC, while 93.5% copper extraction was obtained in 60 min with microwave leaching method under same conditions.

Keywords**—**Extraction, copper, microwave-assisted leaching, chalcopyrite, potassium dichromate**.**

I. Introduction

COPPER can be extracted from chalcopyrite by conventional hydrometallurgical or pyrometallurgical process [1], [2]. Production of copper by hydrometallurgical methods has more attention due to the some significant advantages of the process such as the possibility of application on complex and low grade ores, less energy consuming and little environmental impact [2]. Therefore, several technologies have been developed to leach copper from chalcopyrite concentrates. However, there are still few commercial scale operations for copper production from chalcopyrite concentrates due to various technical and economic issues [3]-[5]. Chalcopyrite leaching in acidic solutions is known to be very slow by the reason of formation of insoluble non-porous layer that prevents further mineral dissolution. The slow dissolution kinetics of chalcopyrite is main challenge for leaching operation [6], [7]. For this reason, there is much interest in developing new alternative leaching techniques to improve copper extraction from chalcopyrite concentrates or ores in the presence of some additives [8].

The use of microwave in leach processes is one of the most promising technique for improving metal extraction and reducing process time in connection with the increasing necessity for environmentally sensitive processes [9]-[11]. Microwave heating in leaching process offers following advantages when compared conventional heating [12].

- rapid heating;
- controllable heating;
- homogenous heating;
- selective heating;
- quick start-up and stopping;
- higher level of safety and automation.

Microwave heating is a kind of electro-heat process such as induction, radio frequency, direct resistance, and infrared heating, that utilize specific parts of electromagnetic energy [13]. Microwave energy is non-ionized electromagnetic radiation which has frequencies changing in the range of between 300 MHz to 300 GHz [14].

Several research studies in the use of microwave energy to enhance copper recovery from chalcopyrite have been conducted recently [15] and consequently reported that there is a serious disagreement with respect to the influence of microwaves on hydrometallurgical systems and the reason behind the higher recovery of the metal during microwave leaching compared to that of conventional leaching has not yet to be explained clearly. [13]. The aim of this study is to compare the oxidative leaching process of chalcopyrite concentrate by microwave-assisted leaching and conventional leaching. Sulfuric acid and potassium dichromate were used as leaching media and oxidizing agent respectively. Parameters affecting leaching process such as sulfuric acid concentration, leaching temperature and oxidizing agent have been examined.

II. Experimental Procedure

Chalcopyrite concentrate that was obtained from copper ore plants (Eti Copper Inc.) in Turkey was used in the experiments as raw material. Prior to the leaching, the samples of concentrates were sieved into size fraction <100 micron. The chemical analyses of samples were determined by atomic absorption spectrometry (AAS, Perkin-Elmer Analyst, 800)

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and given in Table I.

TABLE I
CHEMICAL ANALYSIS OF CHALCOPYRITE CONCENTRATE

	Cu	Fe	Co	Zn	Ni	Au(ppm)	
(%)	24	48	0.10	0.13	0.35	4.25	21

The conventional acid leaching experiments were carried out in a shaking water bath (GFL, 1083) which was set at the desired temperature. H_2SO_4 solutions at required concentrations were mixed with various concentrations of $K_2Cr_2O_7$ as oxidant in 250 ml beakers. The beakers were placed in the shaking water bath. The temperature of the solutions was measured using a thermometer. When the temperature reached at adjusted value, the samples of chalcopyrite were added into the solution with the constant pulp density of 10 g/L. The pulp in the beaker was stirred for 180 min. Samples of solution were withdrawn from the beakers at every 30 minutes periodicity.

Microwave-assisted leaching experiments were carried out in a Microwave Accelerated Reaction Systems device (MARS -Xpress.) A volume of 50 ml with 0.5 mol/L H_2SO_4 solutions mixed with selected concentrations of $K_2Cr_2O_7$ in PTFE vessels with same pulp density with conventional method. The pulp in the vessels were heated to adjusted temperature for 5 min and leached with microwave energy for 30 and 60 min. After leaching procedure was completed the vessels were cooled to the room temperature for 5 minutes.

Samples taken from both conventional and microwave-assisted leaching experiments were filtrated to separate solid residues from solutions. Finally, separated solutions were analysed by AAS in order to determine the copper extraction efficiency.

III. RESULTS AND DISCUSSION

A. Effect of Sulfuric Acid Concentration

The effect of sulphuric acid concentration on chalcopyrite dissolution (Fig. 1) shows increasing copper extraction with increasing sulphuric acid concentration from 0.1M to 0.5M

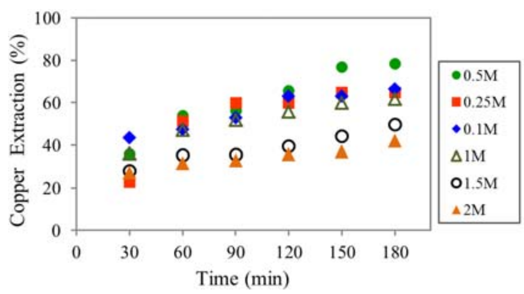


Fig. 1 Effect of H_2SO_4 concentration on copper extraction ($K_2Cr_2O_7$: 0.15 mol/L; temperature: 50°C)

However, above the H_2SO_4 concentration of 0.5M, the chalcopyrite extraction decreases with increasing acid concentration. The copper extracted after 150 min at 50°C with 2M and 0.5M H_2SO_4 in the presence of 0.15 mol/L $K_2Cr_2O_7$ was 37% and 76%, respectively. However, earlier it was reported that the dissolution of copper after 150 min at 50°C with 0.5M H_2SO_4 and 0.1mol/L $K_2Cr_2O_7$ was about 56% [7].

B. Effect of Temperature

Fig. 2 shows that temperature has positive effect on the oxidative leaching of chalcopyrite concentrate in the presence of 0.15 mol/L $K_2Cr_2O_7$.

The leaching efficiency of copper increased significantly with increasing the reaction temperature of chalcopyrite dissolution from room temperature to 50°C and reached about 78% after 180 min. At the temperatures of 50°C and 70°C; there are no significant differences between the efficiencies of copper extractions from 30 to 150 min leaching time. However, at the end of the 180 min, it was increased from 78% to 88.74% when temperature raised from 50°C to 70°C.

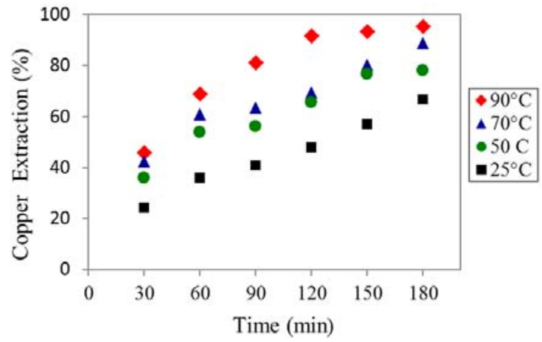


Fig. 2 Effect of temperature on copper extraction ($K_2Cr_2O_7$:0.15M; H_2SO_4:0.5M)

The achieved highest extraction efficiency of Cu was 95.41% at 90°C after 180 min. In order to investigate the other leaching parameters, 50°C was chosen for the leaching temperature.

C. Effect of Potassium Dichromate Concentration

The effect of $K_2Cr_2O_7$ concentration (0.01-0.4 mol/L) on the copper extraction from chalcopyrite using 0.5M H2SO4 is given in Fig. 3 and it is indicated that the concentration of dichromate influenced the dissolution of chalcopyrite positively. The copper extraction increased from 14.33% to 86% after 180 min when the concentration of $K_2Cr_2O_7$ was increased from 0.01 mol/L to 0.4 mol/L.

The achieved highest extraction efficiency of Cu was 95.41% at 90°C after 180 min. In order to investigate the other leaching parameters, 50°C was chosen for the leaching temperature.

D. Microwave Leaching

The microwave leaching of chalcopyrite has also been investigated as complementary method to conventional oxidative sulphuric acid leaching. The extractions of copper obtained as a result of microwave leaching in 0.5M H_2SO_4 using 0.03 mol/L and 0.5 mol/L $K_2Cr_2O_7$ at 50°C and 90°C are presented in Fig. 4.

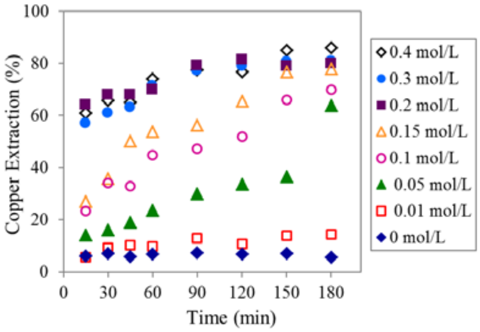
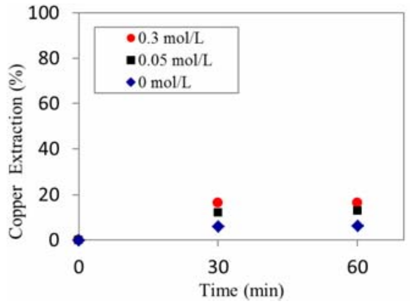
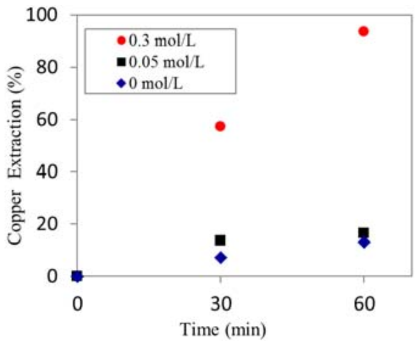


Fig. 3 Effect of potassium dichromate concentration (mol/L) on copper extraction (H_2SO_4: 0.5M; temperature: 50°C)



(a)



(b)

Fig. 4 Copper extractions of microwave leaching in 0.5M H_2SO_4, without oxidant and in the presence of 0.05 mol/L and 0.3mol/L $K_2Cr_2O_7$ at a) 50°C and b) 90°C

When the temperature was 50°C, the extraction of copper was only 6.33%, 13.07% and 16.48% after 60 min, without oxidant and in the presence of 0.03 mol/L and 0.5 mol/L $K_2Cr_2O_7$, respectively. This may be attributed that the dissolution reactions (with or without oxidant) are not proceed completely in limited microwave leaching duration of chalcopyrite. However, microwave digestion devices are not suitable for prolonged dissolution times.

It can also be seen from Fig. 4 (b) that when the temperature increased to 90°C, the extraction of copper has only a little difference between in the lack of oxidant (13.16%) and with the addition of 0.03 mol/L $K_2Cr_2O_7$ (16.45%) for 60 min reaction time. But, when the concentration of $K_2Cr_2O_7$ increased to 0.5 mol/L, the extraction of copper is up to 93.52% for same reaction time. Therefore, it is reasonable that microwave heating has remarkable positive effect on the copper extraction on high temperatures and high oxidant conditions.

IV. Conclusion

In this study, leaching of chalcopyrite concentrate in sulfuric acid was carried out using $K_2Cr_2O_7$ as oxidant under both conventional acid and microwave-assisted acid leaching conditions for hydrometallurgical copper extraction. The following conclusions can be drawn from the present study:

1. $K_2Cr_2O_7$ is an effective reagent for both the conventional and microwave oxidative acid leaching of chalcopyrite concentrate to extract copper in H_2SO_4.
2. Although the microwave leaching process did not show competent copper extraction under the lower concentrations of $K_2Cr_2O_7$ and lower temperature, it effectively increased the extraction of copper and reduce the maximum copper extraction time under relatively higher conditions compared to conventional leaching.
3. 81% of copper were leached with addition of 0.3 mol/L $K_2Cr_2O_7$ to 0.5M H_2SO_4 solution at 50ºC after 180 min leaching time in conventional acid method whilst, more than 93% copper were extracted under same conditions after 60 minutes in microwave leaching.

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