Investigation on microwave heating for direct leaching of chalcopyrite ores and concentrates

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Abstract: The use of microwave energy in materials processing is a relatively new development presenting numerous advantages because of the rapid heating feature. Microwave technology has great potential to improve the extraction efficiency of metals in terms of both a reduction in required leaching time and an increase in the recovery of valuable metals. This method is especially pertinent in view of the increased demand for environment-friendly processes. In the present study, the influence of microwave heating on the direct leaching of chalcopyrite ores and concentrates were investigated. The results of microwave leaching experiments were compared with those obtained under conventional conditions. During these processes, parameters such as leaching media, temperature, and time have been worked to determine the optimum conditions for proper copper dissolution. Experimental results show that microwave leaching is more efficient than conventional leaching. The optimum leaching conditions for microwave leaching are the solid-to-liquid ratio of 1:100 g/mL, the temperature of 140°C, the solution of 0.5 M H_2SO_4 + 0.05 M $Fe_2(SO_4)_3$, and the time of 1 h.

1. Introduction

The interest in the direct leaching of sulfidic copper ores increases because of problems such as sulfurous gas output and its control challenges, high investment cost, and high energy consumption in the pyrometallurgical extraction methods. Although direct leaching processes can easily be implemented on oxidized ores, some difficulties exist for sulfidic ores such as necessity of fine ores and strong oxidizing media requirements at atmospheric conditions.

Many studies have aimed to increase the low dissolution rate of chalcopyrite in the direct leaching method. In these studies, the leach accelerators such as silver ions, surface developers, carbon particles, iron powder, and oxygen have been added to acidic solutions. In spite of high extraction efficiency, high operating cost is an important issue [1-2].

The use of microwaves in leach processes has been investigated for improving the efficiency of metal recovery and reducing process time in connection with the growing necessity for environment-sensitive processes. Microwave heating has many advantages such as high heating rate and homogeneous heating. According to Peng and Liu's study [3], the metal recovery ratio of 28.4% was obtained after the leaching of sphalerite in ferric chloride for 30 min by conventional heating. A higher value (59.3%) was obtained when microwave heating was used.

Microwave energy is nonionized electromagnetic radiation, with frequency changes in the range of 300 MHz to 300 GHz. Microwaves give and heighten resonance of molecules and ions. Furthermore, microwave energy can be reflected, transmitted, and absorbed and leads to heat production in the absorbing material.

Microwave heating is different from conventional heat-

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ing because of its electromagnetic energy form that can penetrate deep into the sample. Although conventional heating systems heat the sample from the outside with the heat transfer mechanisms such as transport, transmission, and radiation, microwave heating has the advantage of selective and much faster heating of some phases than others in the matrix [4-5].

A big temperature difference between solid and liquid in leaching processes assists in mass transfer by means of the reaction interface. In addition, when solid particles that contain two or more phases with various heating rates are heated by microwaves, energy cracks occur; thus, the reaction interface area increases [6].

In this study, direct leaching processes of chalcopyrite ores and concentrates that have been taken from different regions of Turkey were carried out by conventional and microwave heating methods. The leaching properties of both methods were compared by copper leaching efficiency. The effect of operating parameters on the metal recovery was also investigated.

2. Experimental

Chalcopyrite ores and concentrates used in this study were from two different copper ore concentration plants in Turkey. The chemical compositions of the ores and concentrates are given in Table 1. According to X-ray diffraction (XRD) patterns, major minerals in the ores are $CuFeS_2$, FeS_2, and SiO_2.

Table 1.   Chemical composition of the ores and concentrates

Ore/concentrate	Cu / wt%	Fe / wt%	Co / wt%	Zn / wt%	Ni / wt%	Au / ppm	Ag / ppm
Ore-1	1.5-2	47-49	0.08-0.12	0.1-0.15	0.3-0.4	0-0.5	—
Concentrate-1	18-20	47-49	0.08-0.12	0.1-0.15	0.3-0.4	4-4.5	20-22
Ore-2	0.6-0.7	8	—	0.1	—	—	—
Concentrate-2	21-23	34-36	—	—	—	—	—

The ores and concentrates were crushed and ground into fines under 100 µm. Samples from these raw materials were dried at 110°C for 120 min. Firstly, dried samples were leached with sulfuric acid (H_2SO_4) at room temperature (RT) using various solid-to-liquid (S/L) ratios. H_2SO_4 concentration used in the experiments was 96% by weight. Leaching efficiencies were determined according to varying S/L, and the optimum S/L was decided to be applied to subsequent experiments. The copper leaching efficiency is the key data. The formula utilized for determining the copper leaching efficiency is as the following:

Cu leaching efficiency =

$$\frac{\text{Cu in the result solution}}{\text{Cu in the ore or concentrate}} \times 100\% \qquad (1)$$

Secondly, the optimum molarities of acid and ferric sulfate ($Fe_2(SO_4)_3$) were determined. The last step was to investigate the effects of time (1-6 h) and temperature (RT to 140°C) on the copper leaching efficiency in fixed S/L and acid molarity using both conventional and microwave leaching. Microwave leaching experiments were performed in a microwave digestion device (Berghof MWS-3). The solutions obtained after experiments were analyzed by an atomic absorption spectrometer (Perkin-Elmer Analyst 800).

Phases in the solid residues obtained after filtering the leach solutions of conventional and microwave heating processes have been identified and examined by scanning electron microscopy (SEM) and XRD analyses.

3. Results and discussion

3.1. Determination of S/L and molarity

The sample of concentrate-1 was leached in 0.1 M H_2SO_4 at RT for 120 min using S/L of 1:20, 1:50, and 1:100 g/mL in order to fix S/L for subsequent leaching experiments. The change of copper leaching efficiency with S/L is given in Fig. 1. The highest copper leaching efficiency, 5.33%, was reached at S/L of 1:100 g/mL. This S/L was fixed for following experiments.
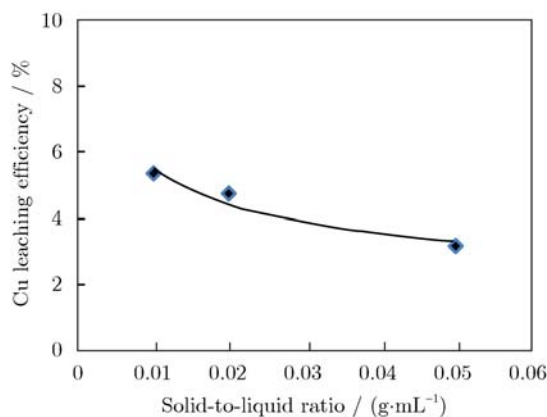

Fig. 1.   Change of copper leaching efficiency with S/L for the leaching of concentrate-1 in 0.1 M H_2SO_4 at RT for 2 h.

The optimum level of molarity was determined by leaching the sample of concentrate-1 at RT with S/L of

1:100 g/mL for 2 h in the solutions of 0.1, 0.3, 0.5, and 1 M H_2SO_4. The effect of molarity on the copper dissolution efficiency is shown in Fig. 2. The increase in efficiency takes place with an increase in molarity from 0.1 to 1. The value of 5.65% was obtained with an H_2SO_4 molarity of 0.5 M, while 5.75% was obtained with an H_2SO_4 molarity of 1 M. By reason of not much difference between two values, 0.5 M was received as the most suitable molarity of H_2SO_4.
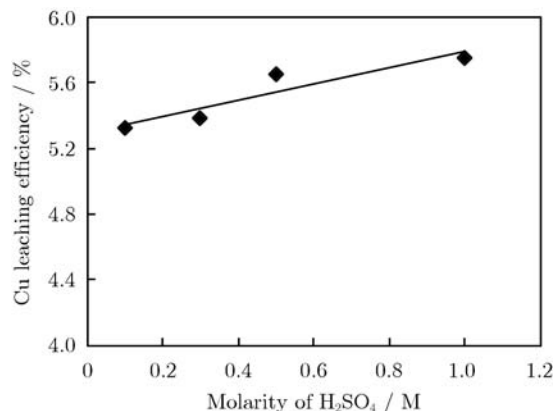

Fig. 2.   Change of copper leaching efficiency depending on the molarity of H_2SO_4 for the leaching of concentrate-1 at RT for 2 h and S/L of 1:100 g/mL.

The most appropriate molarity of $Fe_2(SO_4)_3$ for the experiments where $Fe_2(SO_4)_3$ was used as the oxidizing agent was determined by leaching concentrate-1 in 0.5 M H_2SO_4 using S/L of 1:100 g/mL at RT for 2 h with the addition of 0.05, 0.1, 0.15, and 0.2 M $Fe_2(SO_4)_3$. The results show that copper leaching efficiency decreases with increasing molarity (Fig. 3). The highest efficiency, 6.32% was obtained in the lowest molarity, 0.05 M. Therefore, the $Fe_2(SO_4)_3$ molarity worked was decided as 0.05 M.
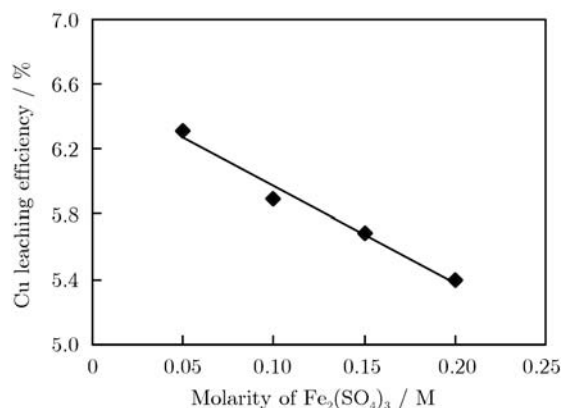

Fig. 3.   Change of copper leaching efficiency with the molarity of $Fe_2(SO_4)_3$ for the leaching of concentrate-1 in 0.5 M H_2SO_4 at RT for 2 h.

Córdoba *et al.* [7] reported that the dissolution rate

of chalcopyrite is deeply affected by the concentration of ferric ions. However, this effect appears only at low concentration. At high concentration, the effect is at the negligible level. There is not a clear effect when the ferric ion concentration exceeds of 0.01 M. Hirato *et al.* [8] found that the solubility of chalcopyrite increased when the molarity of $Fe_2(SO_4)_3$ increased from 0.001 to 0.1 M. They also denoted that the leaching efficiency decreased with increasing ferric ion concentration from 0.1 to 1 M. A similar trend is current for this study between 0.05 and 0.2 M $Fe_2(SO_4)_3$ addition as explained previous paragraphs. Findings about the reduction ratio of Fe^{2+} and Fe^{3+} on the chalcopyrite surface showed that the concentrations of Fe^{3+} and $FeHSO_4^{2+}$ increased up to 0.1 M, and after this value, $FeSO_4^+$ was formed [7-8]. Accordingly, dissolution of chalcopyrite in sulfate media depends on the existence of Fe^{3+} and $FeHSO_4^{2+}$ ions [9].

3.2. Effect of temperature

The experiments that evaluated the effect of varying temperatures on the copper leaching efficiency were carried out at 50, 60, 70, 80, 90, 100, 120, 140°C, and RT by conventional and microwave heating. In these experiments, ore-1 was dissolved in the solution of 0.5 M H_2SO_4 for 60 min. The dissolution efficiencies are given in Fig. 4. It was obtained for both methods that dissolution efficiencies increased with increasing temperature. The relatively high temperature allows higher reaction rates that result in much more amount of soluble materials. The dissolution reactions of solid materials in liquid media are endothermic reactions. Given heat input is used as dissolution energy, so higher dissolution rates are obtained. Solubility of iron was also studied in these experiments. Dissolution of iron became lower than copper and it seemed to be less sensitive to temperature.
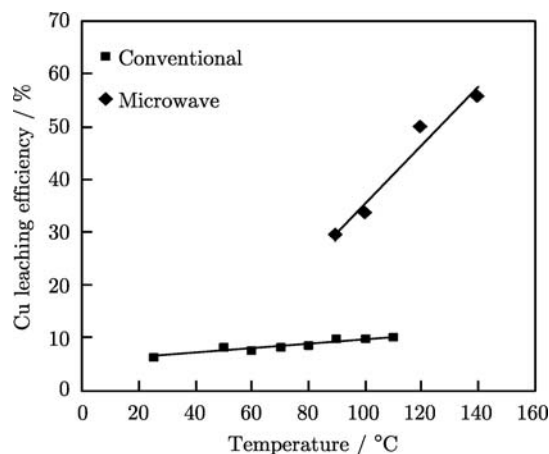

Fig. 4.   Change of copper leaching efficiency as a function of temperature for the leaching of concentrate-1 in 0.5 M H_2SO_4 for 1 h.

Higher dissolution efficiencies were obtained by microwave leaching than by conventional leaching. Elemental sulfur melts at low temperature (119°C), and molten elemental sulfur covers around the grains of chalcopyrite. This phenomenon slows down the dissolution rate [10]. However, the negative effect of the sulfur layer is reduced with microwave power.

In conventional heating, there is a temperature limitation because of the boiling point of the solution. This limitation can be overcome by working with a microwave system that includes closed pressure vessels. After the boiling point of the solution, the pressure increases in the vessel and makes a contribution to the solubility of ore/concentrate.

3.3. Effect of time

Concentrate-1 was leached in 0.5 M H_2SO_4 for 1-6 h periods at 100°C in order to reveal the effect of time on the solubility. The effect of time can be seen in Fig. 5. The efficiency values obtained by conventional leaching for Cu were 6.39% in 1 h, 7.23% in 4 h, and 7.70% in 6 h. The leaching efficiency of Fe was raised from 2.20% to 2.52% in 6 h. It may be said to have not too much effect of time on the solubility of copper for conventional and microwave leaching. The increase in dissolution of iron remained on a lower level than copper. The leaching efficiency obtained by microwave leaching was almost doubled that by conventional leaching for all dissolution periods. However, the ratio of increase remained at about 1% at the end of 6 h.
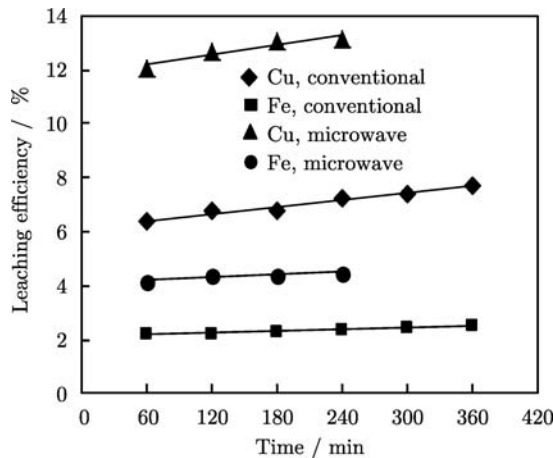

Fig. 5. Change of copper and iron leaching efficiencies as a function of time for the leaching of concentrate-1 in the solution of 0.5 M H_2SO_4 by microwave and conventional methods.

As stated in Ref. [11], this situation can be concerned about the accumulation of diffusion layers such as elemental sulfur on the mineral surface. A lower solubility of iron than copper is a result of the formation of $FeSO_4$.

3.4. Dissolution efficiencies of ores and concentrates

Dissolution efficiencies of various ores and concentrates were determined by experiments using S/L of 1:100 g/mL and 0.5 M H_2SO_4 solution at 100°C for 1, 2, and 3 h. The results obtained are shown in Fig. 6.
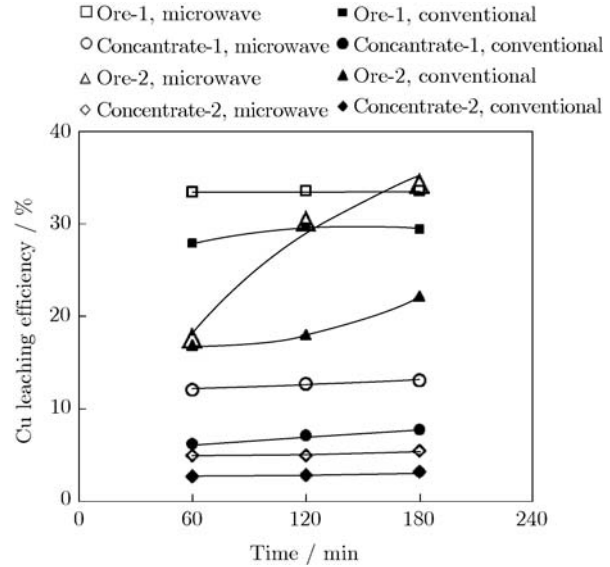

Fig. 6. Comparison of conventional and microwave leaching efficiencies of various ores and concentrates in 0.5 M H_2SO_4 solution at 100°C.

In conventional leaching, the highest copper leaching efficiency (29.40%) was obtained from ore-1 and the lowest (3.08%) from concentrate-2 at the end of 3 h leaching. Similarly, the highest leaching efficiency of copper (33.54%) was obtained from ore-1 and the lowest (5.4%) was obtained from concentrate-2 in microwave leaching. Copper solubility of the ores was higher than that of the concentrates. This situation can be explained by mineralogical differences between ores and concentrates. Ore-2 contains more gangue mineral than others. Some minerals can be reached to high temperature by microwave heating in a very short time. For example, while the temperature of chalcopyrite reaches 920°C in 1 min, the temperature of magnetite reaches 1258°C in 3 min [12-13]. Therefore, the solution containing these types of minerals would be heated and further results in an increase in solubility. In addition, when solid particles contain more than one phase that has different heating rates, cracks occur and the surface area increases. Therefore, reactions take place at a higher rate by microwave heating [14].

As seen in Fig. 6, copper dissolution efficiencies in microwave leaching are higher than conventional leaching for all samples. Also, it can be seen that microwave effect on the concentrates is higher than the ores. The copper recovery difference between conventional and microwave

leaching is about 15% for the ores and 70% for the concentrates. This may be explained by the large amount of free chalcopyrite in the concentrates. It was observed in studies on microwave heating of chalcopyrite that it was heated up very quickly and reached the temperature of 1000°C in a few minutes. A higher heating rate of chalcopyrite particles than leaching solutions results in a temperature difference between solid and liquid. Harahsheh and Kingman [6] reported that thermal currents caused by high temperature differences sweep the products of reactions from the reaction interface. This phenomenon reduces the negative influence of the elemental sulfur layer which occurs on the surface of particles and slows down the reaction during chalcopyrite leaching.

In Fig. 7, the SEM images of solid particles, i.e., insoluble residue, obtained after filtering the conventional and microwave leaching solutions of ore-1 and concentrate-1 are shown. The influence of microwave heating on the minerals can be clearly seen in Figs. 7(b) and 7(d). Some cracks and many subparticles occurred in the particles of the microwave-treated samples. The particle size is smaller than that of the conventional leaching samples. According to XRD analysis of conventional and microwave leaching residues, concentrate-1 contains chalcopyrite, pyrite, and silica.
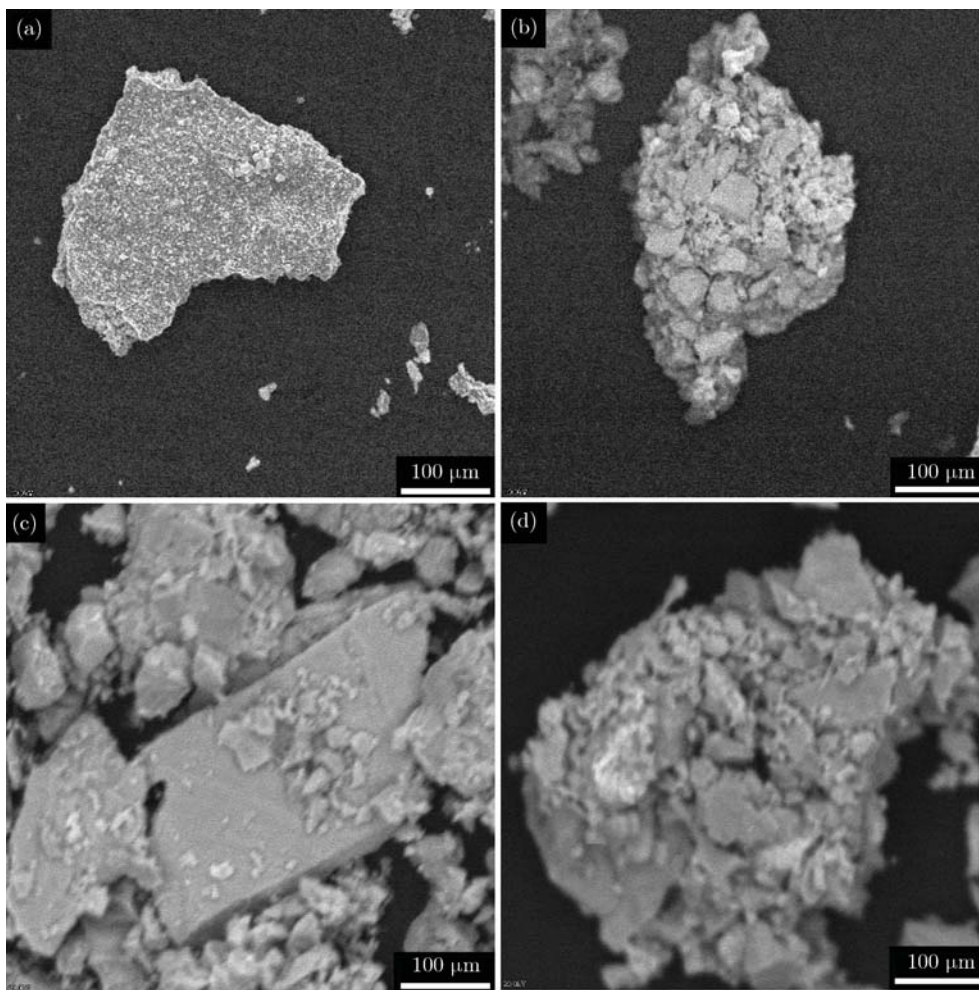

Fig. 7. SEM images of the leach residues of ore-1 and concentrate-1: (a) ore-1, conventional leaching; (b) ore-1, microwave leaching; (c) concentrate-1, conventional leaching; (d) concentrate-1, microwave leaching.

3.5. Effect of $Fe_2(SO_4)_3$ addition

Fig. 8 shows the variation of copper dissolution efficiencies with temperature as a result of the conventional leaching process of concentrate-1 in 0.5 M H_2SO_4 and 0.05 M $Fe_2(SO_4)_3$ solution for 1 h.

It is obvious that there is a significant increase in copper leaching efficiency with increasing temperature. It means that $Fe_2(SO_4)_3$ is more effective at higher temperatures. Panias and Kresteu [15] reported that the $Fe_2(SO_4)_3$ is more effective over 100°C. The copper leaching effi-

ciency of 9.92% was obtained from the leaching experiments, where only H_2SO_4 was used as a solution at 100°C in conventional leaching. When $Fe_2(SO_4)_3$ was used as an oxidative agent in the same conditions, the copper leaching efficiency was 27.47%. Similarly, $Fe_2(SO_4)_3$ addition increased the solubility of copper from 33.37% to 41.37% in the same conditions at 100°C when microwave heating was used. Since sulfide ores are difficult to dissolve in acidic environments, using $Fe_2(SO_4)_3$ as an oxidizing reagent increases the leaching efficiency.
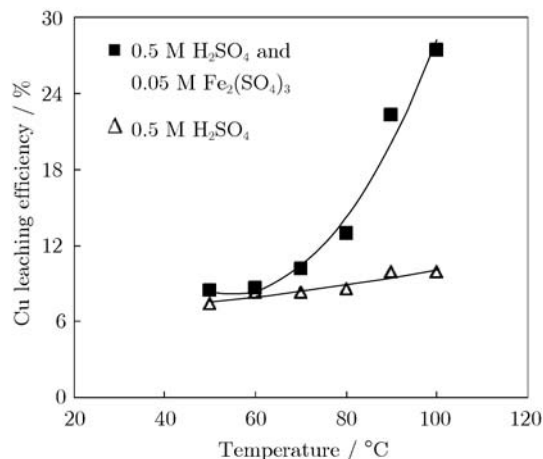

Fig. 8.   Effect of 0.05 M $Fe_2(SO_4)_3$ addition on the copper leaching efficiency.

Al-Harahsheh *et al.* [14] obtained the copper recovery ratio of 13.5% in conventional leaching and 17% in microwave leaching under the conditions of 0.5 M H_2SO_4 and 0.25 M $Fe_2(SO_4)_3$ solution, 1:250 g/mL S/L, 90°C, and 3 h.

4. Conclusions

The following general conclusions were reached as a result of conventional and microwave leaching of chalcopyrite-based ores and concentrates.

(1) Microwave leaching provides a higher leaching efficiency of copper than conventional leaching for chalcopyrite-based ores and concentrates.

(2) Increases in leaching temperature and time improve the solubility of copper in both methods.

(3) The following conditions are identified as optimum dissolution parameters for conventional leaching: S/L 1:100 g/mL, the solution of 0.5 M H_2SO_4 + 0.05 M $Fe_2(SO_4)_3$, the time of 1 h, and the temperature of 100°C. The same conditions are applicable for microwave leaching, but the optimum temperature should be 140°C.

(4) Dissolution of copper in the ores is higher than in the concentrates with both methods.

(5) Higher leaching efficiencies were obtained when a very low amount of $Fe_2(SO_4)_3$ was used as an oxidant in both conventional and microwave leaching processes.

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