

## Leaching of Chalcopyrite Concentrate in Sulphuric Acid with the Aid of Mechanical Activation and Microwave Energy

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Leaching characteristics of a chalcopyrite concentrate received from Kure Copper Mine, Turkey, were investigated in sulfuric acid solutions. The investigation included the effect of leaching temperature, mechanical activation and microwave energy treatment. The extraction of copper was 10.20 % at conventional conditions in 8 h and it increased to 19.14 % with the mechanical activation. Microwave treatment of the concentrate further increased the extraction of copper to 32.21 % at a leaching temperature of 25 °C and to 53.74 % at 75 °C. X-ray analysis revealed the surface chemical alterations of the concentrate samples after microwave irradiation.

**Key Words:** Chalcopyrite concentrate, Leaching, Sulfuric acid, Mechanical activation, Microwave.

### INTRODUCTION

Among copper bearing minerals, most research has been conducted with the chalcopyrite, since it is the most abundant and most refractory of all copper sulfides<sup>1</sup>. At present, about 80 % of the copper production is accomplished by the traditional pyrometallurgical route, *i.e.*, froth flotation-smelting-refining<sup>2-4</sup>. However, there has been a growing worldwide interest in hydrometallurgical processes for the production of copper due to restrictions on the emissions of sulfur dioxide (SO<sub>2</sub>) during smelting, a fall in demand for sulfuric acid produced as a by-product during smelting operations, difficulty to produce the desired grade of copper concentrates suitable to smelting<sup>5</sup> and high capital cost of building a new smelter<sup>6-8</sup>.

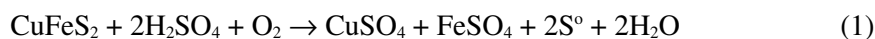
Hydrometallurgical routes of chalcopyrite have focused on direct leaching by different lixivants such as chloride/chlorine systems, sulfuric acid, nitric acid, ammoniacal solution<sup>8-12</sup>. For more than 30 years, a significant number of processes have been developed to leach copper from chalcopyrite concentrates. Although a few of the copper hydrometallurgical processes have been carried to pilot and full scale operation, such as the processes of Arbiter, the clear, the Cymet, the Sherritt-Cominco, Mintek, Outokumpu and Intec, none of these processes have become

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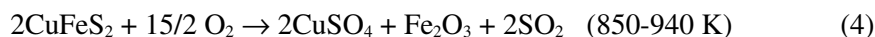
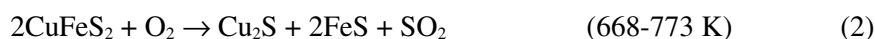
completely commercially operational, except two processes that have most recently been reported *i.e.*, (1) Hydro Copper chloride process developed by Outotec Oyj which has reached the commercial scale in Mongolia<sup>13,14</sup> and (2) a medium temperature pressure leaching process developed by the former Phelps Dodge company and has become a commercial application at the Morenci mine in Arizona<sup>7,13,15</sup>.

Sulfuric acid has been investigated for a long time for chalcopyrite ore and concentrate leaching due to its relatively low cost, environmental friendliness, fewer corrosion problems and ease of regeneration during electrowinning. However, sulfuric acid is not as effective as stronger acids like nitric acid and hydrochloric acid when used alone. In general, chalcopyrite dissolves slowly in sulfuric acid solution according to the following reaction<sup>16</sup>:



Several techniques have been used to increase the reactivity of chalcopyrite such as: organic extracting additions, sulfidizing, mechanical activation<sup>17</sup>, the use of ozone as an oxidant<sup>18</sup>, the use of promoters (silver ions, surfactants, carbon particles, iron powder or hematite), biological systems, autoclave leaching and leaching after roasting/calcination treatment<sup>8,19</sup>. Heat treatment is often used in the metallurgical industry to convert mineral sulfides into oxides or other compounds such as sulphates suitable for further treatment and recovery of metals<sup>20,21</sup>. Oxides and sulphates are readily dissolved in leach solutions, while sulfides are only dissolved slightly.

The oxidative roasting of  $\text{CuFeS}_2$  is a complex process. Depending on temperature and atmosphere,  $\text{CuFeS}_2$  may be oxidized to different products<sup>22</sup> such as  $\text{CuSO}_4$ ,  $\text{CuO} \cdot \text{CuSO}_4$ ,  $\text{CuO} \cdot \text{Cu}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . The following reactions during the heat treatment were reported<sup>2,23,24</sup>:



Direct leaching of chalcopyrite with  $\text{H}_2\text{SO}_4$  requires highly oxidizing condition. Leaching with the ferric ion,  $\text{Fe}^{3+}$ , which is the most common application, contributes a large quantity of iron to leach liquor, which interferes in separation of metal values. Thus, there is a need to examine other options such as microwave methods. The use of microwaves to improve the leaching kinetics and recovery of metals has been reported in the literature<sup>25-28</sup>.

In the present study, dissolution kinetics of a chalcopyrite concentrate in sulfuric acid solution was studied with the aid of mechanical activation and microwave energy application to increase the extraction rates.

## EXPERIMENTAL

The chalcopyrite concentrate samples used in the experiments was provided from Kure Copper Flotation Concentrator Plant, Kastamonu, Turkey (Eti Bakir A.S.). Kastamonu Kure is situated in the West Black Sea region of Turkey, which is the leading copper and pyrite ore production areas<sup>29</sup>. Mineralogical characterization of the ore was carried out by optical microscopy, scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Chalcopyrite and pyrite were the dominant minerals in the flotation concentrate sample. The sample contains fewer amounts of covellite, chalcocite, bornite, sphalerite, marcacite, pyrrhotite, linneite, bravoite and tennantite. The main gangue minerals are calcite and quartz. Chemical analysis results of the sample are presented in Table-1. The result of the XRD examination of the concentrate sample is given in Fig. 4, showing the diffractions of chalcopyrite ( $\text{CuFeS}_2$ ) and pyrite ( $\text{FeS}_2$ ), detected.

TABLE-1  
CHEMICAL ANALYSIS OF THE CHALCOPYRITE CONCENTRATE SAMPLE

Element	Content	Element	Content
Cu	16.930 (%)	Ni	0.011 (%)
Fe	37.240 (%)	S	45.380 (%)
Pb	0.029 (%)	SiO <sub>2</sub>	2.680 (%)
Zn	1.010 (%)	Ag	19.910 (g/t)
Co	0.100 (%)	Au	0.920 (g/t)

**Method:** The leaching tests were carried out at atmospheric pressure in a 1 L standard reaction vessel with a closed top and a heater-stirrer equipped with a mercury thermometer. A view of the experimental set-up is shown in Fig. 1. The stirring speed provided by a magnetic stirrer (Heidolph brand) was 400 rpm. A 50 cm long straight spiral condenser was connected to neck to enable gases to escape and to prevent evaporation losses. Sulfuric acid leaching solution (1.0 M) was prepared with analytical grade sulfuric acid (98 vol%) and distilled water. The pH of the solution was also measured during leach tests and recorded below 0.5 in all tests. The tests were carried out using 30 g of samples. In the graphs shown in this paper, all points represent a single experimental result, *i.e.*, no solution sample was taken during the leaching and all experiments were carried out separately. After each experiment, pulp was filtered and copper and iron were assayed from the leach solution using atomic absorption spectroscopy (AAS), Analytic Jena novAA 300 model device.

Mechanical activation tests were carried out in a high energy ring-and-puck grinding mill (vibrating cup mill, Unal Muhendislik, Izmir, Turkey) in dry conditions using 150 g of the received chalcopyrite concentrate samples. The concentrate samples were ground for 2, 4 and 8 min and leached in sulfuric acid solutions. Particle

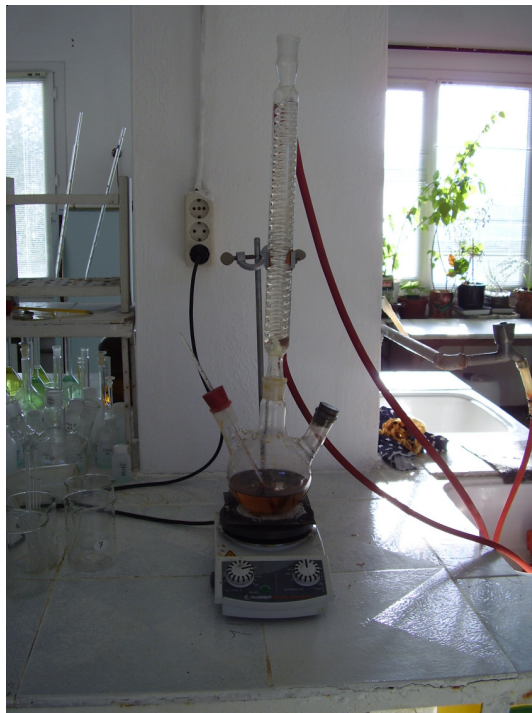


Fig. 1. Experimental set up for performing leach tests

sizes of the received and ground samples were measured as 80 % passing sizes with HORIBA/Partica LA-950V2 Particle Size Analyzer. The particle size of the received concentrate sample was 80 % passing 35  $\mu\text{m}$ .

A home type batch microwave oven with a variable power output range of 800 W and a frequency of 2.45 GHz was used. Samples of 30 g were placed on a 10 cm diameter ceramic crucible and positioned in the centre of the oven. Maximum bulk surface temperatures of the ore particles were measured using a DT-8858 Model infrared thermometer after switching off the microwave power. Microwave heating temperatures of the concentrate samples were determined at varying microwave durations of time and presented in Table-2. The microwave irradiated samples were leached in sulfuric acid solutions.

## RESULTS AND DISCUSSION

**Conventional atmospheric leaching:** The effect of temperature upon the copper recovery from the chalcopyrite concentrate sample was studied at solution temperatures of 25, 50, 75 and 95  $^{\circ}\text{C}$ . The experiments were carried out with 30 g of concentrate samples as received (80 % passing size is 35  $\mu\text{m}$ ), solid/liquid ratio of 1/10,  $\text{H}_2\text{SO}_4$  concentration of 1.0 M, a stirring speed of 400 rpm and leaching time from 30 to 1440 min. Each point on the graph represents a separate experiment.

TABLE-2  
 MAXIMUM BULK TEMPERATURES AND LEACHING RESULTS OF THE  
 CONCENTRATE SAMPLES IRRADIATED IN 1KW MICROWAVE OVEN\*

Irradiation power (W)	Irradiation time (min)	Max. bulk temperature (°C)	Cu extraction (%)	Fe extraction (%)
200	1	87	11.23	4.08
	3	109	11.39	4.19
	5	111	12.46	4.35
	10	122	12.03	4.33
	20	166	12.59	4.38
	30	174	12.77	4.50
500	1	280	17.70	8.25
	3	544	24.72	14.45
	5	555	27.03	14.73
	10	589	32.21	19.87
800	0.5	329	16.04	7.94
	1	487	20.94	10.40
	2	512	29.38	15.52
	4	603	30.88	18.25

\*(Sample weight: 30g,  $d_{80}$ : 35  $\mu\text{m}$ , S/L: 1/10,  $\text{H}_2\text{SO}_4$  concentration: 1.0 M, leaching duration: 8 h, solution temperature: 25 °C, stirring speed: 400 rpm)

The experimental results of the effect of temperature and leaching time on the copper and iron dissolution are shown in Fig. 2. As seen, the copper dissolution is very slow at the atmospheric leach conditions even at the elevated solution temperatures. About 12.71 % of copper was extracted from the chalcopyrite concentrate at a temperature of 25 °C in 24 h. Maximum copper dissolution of 18.26 % was obtained in 24 h at 75 °C. Copper dissolution dropped to 12.34 % at the temperature of 95 °C. A rise in reaction temperature was generally favourable to copper oxidative leaching but too high temperature, particularly near boiling point, affected copper leaching negatively due to decreasing oxygen dissolution in the leach slurry. As seen from the Fig. 2, copper leaching increased with the temperature up to 75 °C and dropped afterwards. Iron dissolutions were stayed constant with the leaching time at different temperatures.

**Mechanical activation:** The purpose of the mechanical activation was to increase the copper extraction by decreasing the particle size and increase its reactivity with increasing the surface area. The effect of the mechanical activation upon copper and iron recovery was studied at the solid/liquid ratio of 1/10,  $\text{H}_2\text{SO}_4$  concentration of 1.0 M, solution temperature of 25 °C, a stirring speed of 400 rpm and leaching time of 480 min.

The results are presented in Fig. 3. Particle sizes of 80 % cumulative passing values are given in the Figure at different grinding times. Each point on the plot represents a separate leach testing. Copper extraction increased slightly with the increasing grinding time from 10.82 % for the unground sample to 19.14 % after 8 min

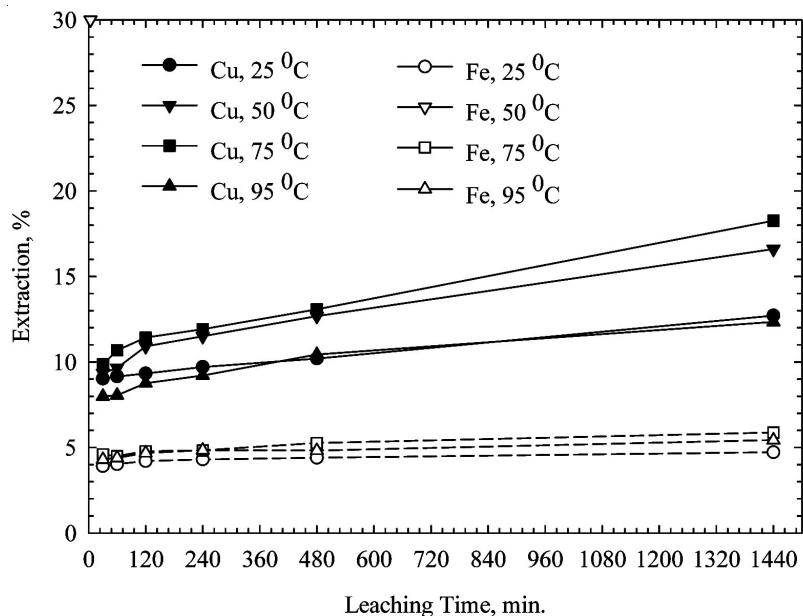


Fig. 2. Effect of temperature on leaching of copper and iron with sulfuric acid ( $d_{80}$ : 35  $\mu\text{m}$ , S/L: 1/10,  $\text{H}_2\text{SO}_4$  concentration: 1.0 M, stirring speed: 400 rpm)

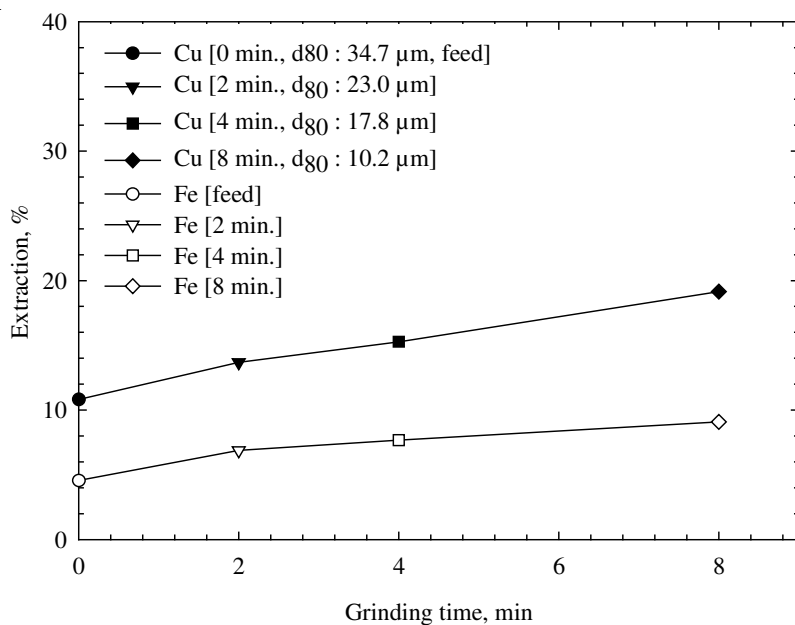


Fig. 3. Effect of mechanical activation on leaching of copper and iron with sulfuric acid (sample weight: 30 g, S/L: 1/10,  $\text{H}_2\text{SO}_4$  concentration: 1.0 M, leaching duration: 8h, solution temperature: 25 °C, stirring speed: 400 rpm)

of grinding. Iron extraction increased from 4.55 to 9.09 % after 8 min of grinding. Mechanical activation accelerated the leaching by increasing the surface area and reactivity of the concentrate. However, the increase was not substantial.

**Microwave treatment:** The effect of microwave energy application upon copper and iron recovery was studied at solid/liquid ratio of 1/10, H<sub>2</sub>SO<sub>4</sub> concentration of 1.0 M, solution temperature of 25 °C, a stirring speed of 400 rpm and leaching time of 480 min. The results are presented in Table-2 and Fig. 8. Microwave treatment of the concentrates further increased the extraction of copper to 32.21 % at a leaching temperature of 25 °C and to 53.74 % at a leaching temperature of 75 °C. At low microwave irradiation power of 200 W, copper extractions were low and stayed unchanged at about 11-12 % even at long irradiation times.

In several instances above the microwave power of 500 W, as the concentrate samples were heated, portions of the samples absorbed enough microwave energy to become incandescent. This concept is known as thermal runaway, thus, once a localized hot spot forms due to increased exposure to microwave radiation, it consumes even more energy, while the surrounding material heats only slightly. During the recording of the average bulk surface temperatures of the samples with the infrared thermometer, the hot spots, reaching the temperatures of 1200 °C, were excluded. In addition, irradiation times were shortened to 10 min at 500 W and to 4 min at 800 W as seen in Table-2, due to intense degradation of the samples.

To confirm the effect of microwave heating on the phase changes occurring during the irradiation of chalcopyrite concentrate, the samples were examined by the XRD and the results are presented in Figs. 4-7. The XRD analysis results revealed that the iron in the concentrate was partially transformed to Fe<sub>2</sub>O<sub>3</sub> (hematite) while the copper transformed to CuSO<sub>4</sub> (chalcocyanite) after the microwave power of 500 W for 10 min and 800 W for 4 min as shown in Figs. 5 and 6. At the low microwave power of 200 W, there were no surface chemical alterations or oxidation detected even at longer irradiation times (Fig. 7). Low dissolution rates of copper and iron were correlated with the low microwave power of 200 W (Table-2).

Since CuSO<sub>4</sub>, formed during microwave irradiation, is water soluble, the irradiated samples were leached in water to see whether the extraction rates of copper and iron were increased. The results indicated that the copper extraction in water was 7.97 % with the untreated samples and it increased to 11.25 % with the microwave treated samples. Similarly, iron extraction increased from 0.37 to 3.16 %.

Copper and iron extraction results obtained from the leaching of untreated and microwave treated concentrate samples were compared in Fig. 8. The samples were irradiated for 10 min at 500 W. As seen, copper extraction was 13.08 % and it increased to 53.74 % at the elevated solution temperature of 75 °C in 8 h. Again, copper leaching was affected negatively due to decreasing oxygen dissolution in the leach slurry near boiling point. Copper extraction dropped to 46.24 % at the solution temperature of 95 °C (Fig. 8).

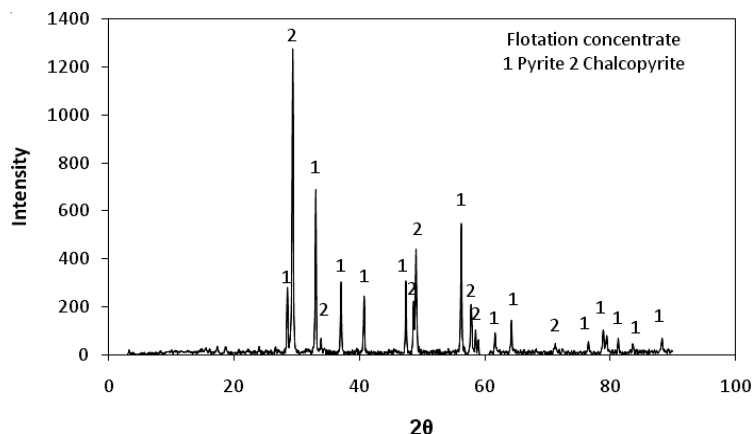


Fig. 4. X-ray diffraction pattern of chalcopyrite concentrate as received

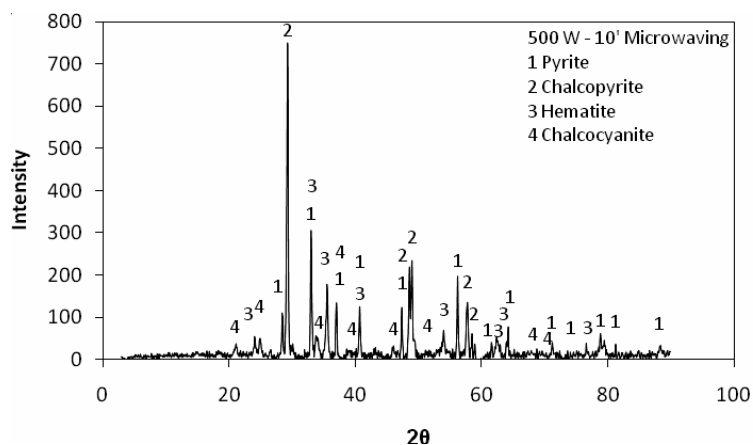


Fig. 5. X-ray diffraction pattern of chalcopyrite concentrate irradiated with microwaves at 500 W for 10 min

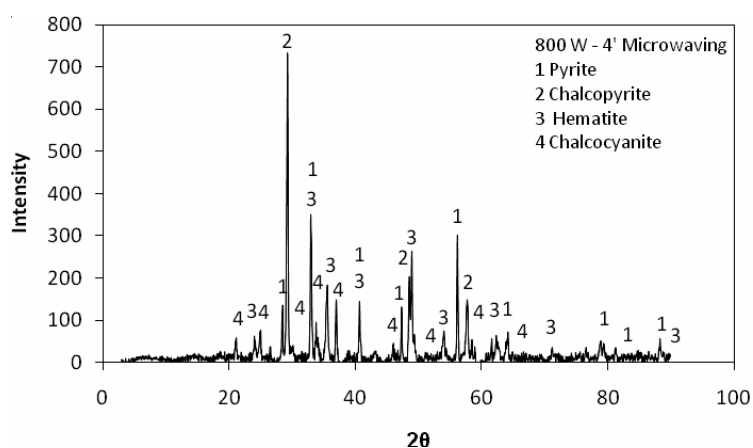


Fig. 6. X-ray diffraction pattern of chalcopyrite concentrate irradiated with microwaves at 800 W for 4 min



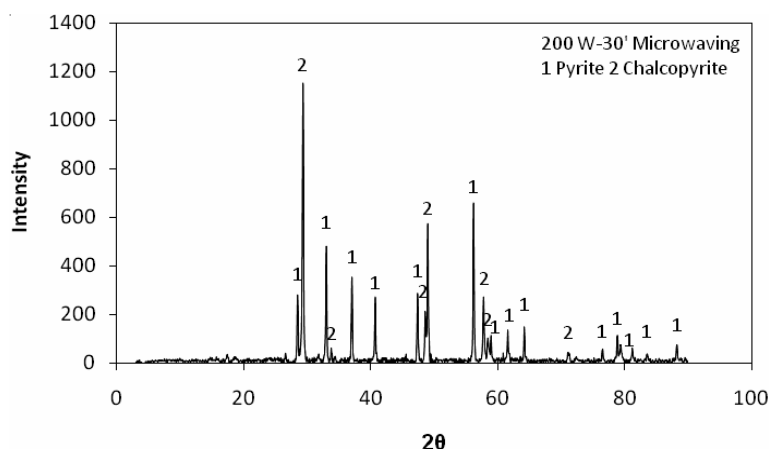


Fig. 7. X-ray diffraction pattern of chalcopyrite concentrate irradiated with microwaves at 200 W for 30 min

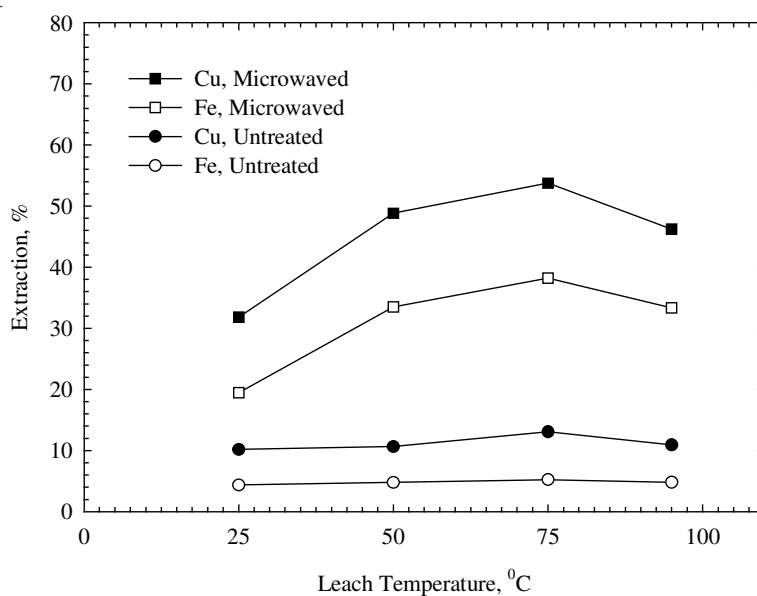


Fig. 8. Comparison of copper and iron extraction results obtained from leaching of untreated and microwave treated concentrate samples (microwave irradiation of 10 min at 500 W)

### Conclusion

In this study, the dissolution kinetics of the chalcopyrite flotation concentrate in sulfuric acid solutions have been investigated. The investigation included the effect of leaching temperature, mechanical activation and microwave energy treatment. The extraction of copper was 10.20 % at conventional leach conditions in 8 h and it increased to 19.14 % with the mechanical activation. Microwave treatment of the

concentrates further increased the extraction of copper to 32.21 % at a leaching temperature of 25 °C and to 53.74 % at 75 °C. The XRD analysis revealed that the pyritic chalcopyrite concentrate during microwave irradiation in air partially decomposed to hematite (Fe<sub>2</sub>O<sub>3</sub>) and chalcocyanite (CuSO<sub>4</sub>) which was possibly responsible for the increased copper extraction rate at higher microwave powers.

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### REFERENCES

1. C.A.C. Sequeira, D.M.F. Santos, Y. Chen and G. Anastassakis, *Hydrometallurgy*, **92**, 135 (2008).
2. S. Prasad and B.D. Pandey, *Miner. Eng.*, **11**, 763 (1998).
3. F. Habashi, *J. Min. Metall.*, **43**, 1 (2007).
4. Q. Thing-sheng, N. Guang-hua, W. Jun-feng and C. Li-feng, *T. Nonferr. Metal. Soc.* **17**, 418 (2007).
5. Y. Hua, C. Cai and Y. Cui, *Sep. Purif. Technol.*, **50**, 22 (2006).
6. Z.Y. Lu, M.I. Jeffrey and F. Lawson, *Hydrometallurgy*, **56**, 189 (2000).
7. J.O. Marsden and J.C. Wilmot, *Miner. Metall. Proc.*, **24**, 193 (2007).
8. M. Al-Harashsheh, S. Kingman and A. Al-Harashsheh, *Hydrometallurgy*, **91**, 89 (2008).
9. M. Gulfen and A.O. Aydin, *Indian J. Chem. Techn.*, **15**, 180 (2008).
10. M.M. Antonijevic and G.D. Bogdanovic, *Hydrometallurgy*, **73**, 245 (2004).
11. K.M. Subramanian and P.H. Jennie, *Can. Metall. Quart.*, **11**, 387 (1972).
12. M.E. Wadsworth, *Miner. Eng.*, **37**, 557 (1985).
13. S. Wang, *J. Metals*, 48 (2005).
14. O. Hyvarinen and M. Hamalainen, *Hydrometallurgy*, **77**, 61 (2005).
15. R.G. McDonald and D.M. Muir, *Hydrometallurgy*, **86**, 191 (2007).
16. P.A. Olubambi and J.H. Potgieter, *Miner. Process. Extr. M.*, **30**, 327 (2009).
17. M. Achimovicova, P. Balaz and J. Briancin, *Metalurgija*, **45**, 9 (2006).
18. T. Havlik and M. Ukasik, *Acta Metallur. Slov.*, **4**, 193 (2001).
19. N. Hiroyoshi, H. Miki, T. Hirajima and M. Tsunekawa, *Hydrometallurgy*, **57**, 31 (2000).
20. M. Aneesuddin, P.N. Char, M.R. Hussain and E.R. Sexena, *J. Thermal. Anal.*, **26**, 205 (1983).
21. J. Shu, V.I. Lakshmanan and J. Convey, *Can. Metall. Q.*, **38**, 215 (1999).
22. Z.D. Zivkovix, N. Mitevaska and V. Savovic, *Thermochim. Acta*, **282/283**, 212 (1996).
23. G. Bayer and H.G. Wiedemann, *Thermochim. Acta*, **198**, 303 (1992).
24. C. Sahyoun, S.W. Kingman and N.A. Rowson, *Physical Sep. Sci. Eng.*, **12**, 23 (2003).
25. T. Havlik, M. Popovicova and M. Ukasik, *Metallurgie*, **55**, 332 (2001).
26. M. Laubertova, T. Havlik and P. Galova, *Acta Metallur. Slov.*, **4**, 270 (2003).
27. M. Al-Harashsheh, S.W. Kingman, N. Hankins, C. Somerfield, S. Bradshaw and W. Louw, *Miner. Eng.*, **18**, 1259 (2005).
28. M. Al-Harashsheh and S.W. Kingman, *Hydrometallurgy*, **73**, 189 (2004).
29. A. Akcil, *Miner. Eng.*, **15**, 1193 (2002).