



PERGAMON

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Minerals Engineering 15 (2002) 1193–1197

MINERALS
ENGINEERING

This article is also available online at:
www.elsevier.com/locate/mineng

Technical Note

A preliminary research on acid pressure leaching of pyritic copper ore in Kure Copper Mine, Turkey

A. Akcil *

Department of Mining Engineering, Mineral Processing Division, Suleyman Demirel University, Isparta, TR 32260, Turkey

Received 13 August 2002; accepted 21 October 2002

Abstract

The combination of roasting and pressure leaching is an alternative process that offers advantages over conventional processes because of the shorter leaching time and higher metal recovery. The copper and iron sulphide minerals examined in this study were chalcopyrite (CuFeS_2) and pyrite (FeS_2). The best results obtained were with a pre-treatment by roasting followed by acid pressure leaching in an autoclave system. The extraction of copper achieved was over 85%. Copper dissolution in this system is affected by particle size, leaching time and oxygen pressure. This paper presents the preliminary research on acid leaching of pyritic copper ore in an autoclave system under laboratory conditions.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Pressure leaching; Sulphide ores; Roasting; Hydrometallurgy

1. Introduction

In the literature, oxide and sulphide copper ores mainly are known as azurite, malachite, tenorite, chrysocolla, brochantite, enargite, chalcopyrite, chalcocite, covellite, bornite. Amongst the copper sulphide minerals, chalcocite, Cu_2S , is the easiest to dissolve and chalcopyrite, CuFeS_2 , the most abundant copper mineral, is the most refractory and difficult to leach (Vanhanen, 1999).

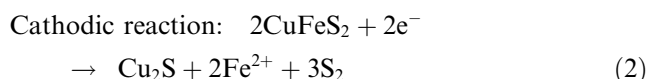
Leaching of copper sulphides like chalcopyrite by strong and weak acidic medium has been investigated by many researchers (Akcil and Ciftci, 2002; Arbiter and McNulty, 1999; Berezowsky et al., 1991; Filippou et al., 1997; Forward and Veltman, 1959; Habashi, 1999a; Harvey and Yen, 1998; Hiroyoshi et al., 2002; Kawulka et al., 1978; Perek and Arslan, 2002; Rao and Ray, 1999; Subramanian and Jenninc, 1972; Swinkels and Berezowsky, 1978; Xu et al., 2000). The research focused on chalcopyrite concentrates and its slags with dissolution by various leachants including sulphuric acid, ammonia, hydrochloric acid, cyanide and acetic acid.

The present work reports on a study carried out on Turkish pyritic copper ores. The process under investi-

gation allows for the treatment of these “dirty” sulphide ores with high metal impurities levels through a combination of roasting and pressure leaching.

2. A brief review of the process

Chalcopyrite is the most difficult of the copper sulphides to treat by hydrometallurgical routes. The anodic dissolution of chalcopyrite leads to the formation of a metal-deficient copper-rich polysulphide layer, which passivates the electrode surface (Elsherief, 2002). Chalcopyrite is very stable in dilute acid at room temperature. When chalcopyrite is attacked it leaves behind a phase rich in copper sulphide, with the iron going into solution according to the scheme (Habashi, 1999b):



The sulphide ion liberated forms H_2S with the H^+ ions in solutions:

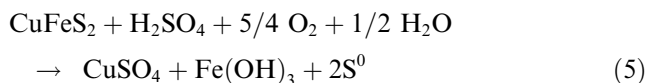


The overall reaction is



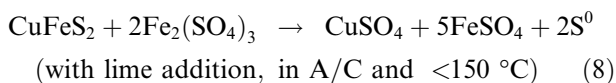
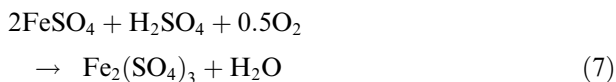
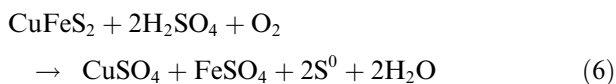
* Tel.: +90-246-2111240; fax: +90-246-2370434.

E-mail address: ata@mmf.sdu.edu.tr (A. Akcil).



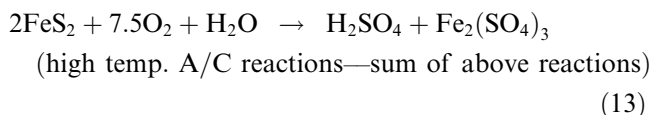
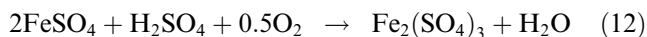
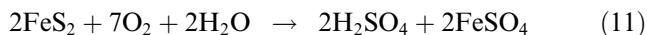
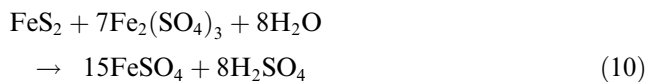
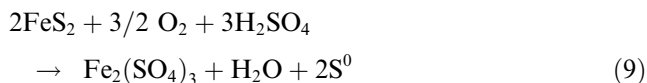
The selective leaching mechanisms for various minerals in sulphuric acid and ferric sulphate media are presented below:

- Chalcopyrite (CuFeS_2) in leaching medium



- Pyrite (FeS_2) in leaching medium

Pyrite is resistive to sulphate solutions at temperatures below 150°C as a result of the protective sulphur layer formed during oxidation and its electrochemical properties. The oxidation of pyrite produces ferrous sulphate, which further reacts with sulphuric acid and oxygen to produce ferric sulphate in this medium.



3. Experimental

3.1. Materials

For the leaching tests, samples were provided from Kure Copper Mine, Turkey (Eti Bakır A.S.). Kure is situated in the West Black Sea region of Turkey, which is one of the leading copper and pyrite ore production areas.

There are three types of reserves at Kure Copper Mine (Table 1). Representative samples were taken over a period of one month from the ore stock and mixed.

In the Kure Copper Mine (concentrator plant)

- Plant input (run of mine): 1.73–1.93% Cu and 36–38% S, approx. 930.000 ton/year,

Table 1

Reserve share of run-of-mine in Kure Copper Mine (2001)

Ore type	Reserve (%)
Massive rich	20
Massive pyritic	15
Pyritic copper	65

Table 2

Chemical analyses of feed samples (run-of-mine)

Sample code	Grade (%)		
	Cu	Fe	S
RMC1	4.1	36.4	44.1
RMC2	4.5	37.6	44.3
RMC3	3.9	36.9	43.5

- Plant output (concentrates): 15–17% Cu and 46–48% S, approx. 90.000 ton Cu and approx. 460.000 ton S.

In the Kure deposits, minerals of the main ore are pyrite and chalcopyrite. In addition, quartz, carbonate, clay minerals as gangue and some important rare minerals are found (Akçil, 2000).

Tests were conducted on massive ore. After a crushing and grinding step, a sample of 120 kg of $-106 \mu\text{m}$ (100%) from massive ore stock was used in pre-roasting and leaching tests. Three types of feed samples were used for these tests (Table 2).

3.2. Equipment

The tests were carried in a laboratory equipped with facilities for carrying out hydrometallurgical operations such as roasting and autoclave leaching processes. The composition of all solutions and samples were determined from the laboratory tests using A.A.S (Perkin-Elmer). In the roasting test, a laboratory Muffle furnace was employed. Autoclave tests were done in a 2 litre corrosion resistant reactor, which could be heated to a maximum of 400°C and could maintain a maximum stirring rate of 1600 rpm. The reactor was equipped with a cross-shaped four-blade impeller for agitation. Slurry samples were taken and analysed at regular intervals during leaching. The tests were performed in duplicate and the mean values were reported. During each test, a sample of pulp was taken with a pump-valve as a sampling outlet. All the chemicals employed were analytical grade (Merck). Fig. 1 shows the test work flowsheet.

4. Results and discussion

4.1. Pre-roasting and determination of optimum conditions

Prepared samples were pre-roasted in a laboratory Muffle furnace at $640 \pm 15^\circ\text{C}$ for 60–65 min. After pre-

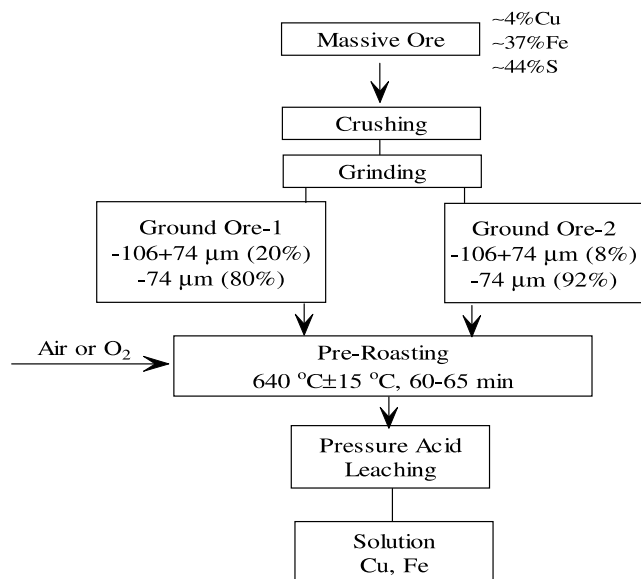
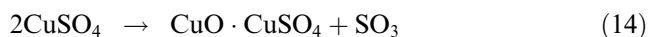


Fig. 1. Schematic of laboratory process.

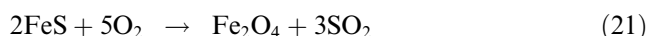
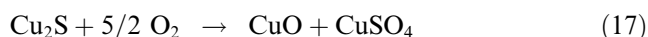
roasting, samples were leached by acid medium in a laboratory autoclave. During the acid leaching tests, several variables were examined (Table 3).

In most cases, oxidative leaching is achieved in presence of an oxidising agent such as gaseous oxygen, or a lixiviant such as Fe^{3+} . Pressure leaching in an autoclave is a capital-intensive process, and therefore unsuitable for small or low grade operations. On the other hand, leaching with Fe^{3+} contributes a large quantity of iron to leach liquor, which interferes in separation of metal values.

Pre-roasting as carried out in this test provides an alternative to partially oxidise the sulphides. If the sulphate sample is decomposed in the presence of a substance or substances which fix the oxygen pressure, the total pressure is no longer subject to error from thermal segregation, and the range of total pressure may be conveniently adjusted by appropriate choice of the oxygen controlling couple. Decomposition of copper sulphates thermally was represented by Kellogg (1964):



It may be pointed out that Bandyopadhyay et al. (2000), Razouk (1965) and Leung (1975) have suggested the following mechanism for the oxidation of chalcopryrite at various different temperatures:



Increase in the temperatures of the oxidation of pure cupric sulphide with O_2 produced a higher amount of copper oxide. Roasting of cupric sulphide with steam at temperatures 300 and 500 °C produced cuprous oxide (Cu_2O) as the major phase, whereas Fe_3O_4 was the main product from FeS . Copper sulphate formation was negligible in the roasting of 1:1 mixture of $\text{CuS}:\text{FeS}$ with steam in the temperature range 300 to 500 °C. Thermodynamically, the formation of CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ is feasible of lower temperatures, whereas their oxides are more stable at higher temperatures and lower partial pressures of SO_2 and O_2 . The roasting of CuS and FeS with a steam–oxygen mixture at 500 °C may proceed (Prasad and Pandey, 1999).

4.2. Pressure acid leaching

4.2.1. Effect of particle size and leaching time

In leaching with oxygen pressure, three types of massive ore samples (RMC1, RMC2, RMC3) were used and two different particle sizes (G.O.-1 and G.O.-2) were tested. Constant parameters were S/L: 20%, P_{O_2} : 5 atm, agitation speed: 170 rpm and sulphuric acid concentration: 0.6 M.

After pre-roasting of G.O.-1 and G.O.-2, pressure leaching of samples was carried out at similar conditions. The concentrations of metals (Cu and Fe) for the two different particle sizes are shown in Figs. 2 and 3.

The finer particle size ($-106 + 74 \mu\text{m}$ (8%), $-74 \mu\text{m}$ (92%)) was found to be more suitable for high extraction of copper although a small amount of iron oxide was also found to be formed at this leaching condition, Fig. 3. For this particle size, practically all of the sulphide phases are liberated and copper recovery reaches 85%. For coarser particle test, Fig. 2, G.O.-1, the recovery of copper was slightly lower and the iron dissolution was increased. According to Fig. 2, the maximum copper dissolution was found to be 81% after 120 min. In Fig. 3, maximum copper dissolution was found to be 88%.

Table 3
Variable and constant conditions of pressure acid leaching

Parameter	
Ground ore-1	$-106 + 74 \mu\text{m}$ (20%) $-74 \mu\text{m}$ (80%)
Ground ore-2	$-106 + 74 \mu\text{m}$ (8%) $-74 \mu\text{m}$ (92%)
Time	60–180 min
Pressure	5–35 atm (± 0.2 atm)
Temperature	80 °C (± 3 °C)
Agitation speed	170 rpm (± 10 rpm)
Solid/liquid	20%
pH	1.2–2.5

All samples were pre-roasted at 640 ± 15 °C.

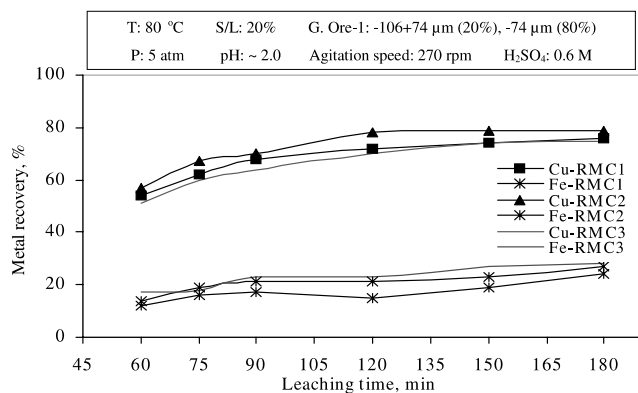


Fig. 2. Effect of leaching time on ground ore-1.

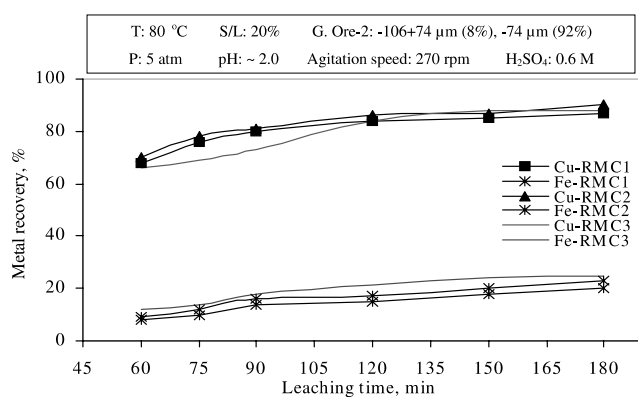


Fig. 3. Effect of leaching time on ground ore-2.

4.2.2. Effect of oxygen pressure

To determine the optimum oxygen pressure, the tests were conducted holding other parameters constant (particle size, temperature, leaching time, agitation speed and pH).

Fig. 4 shows the effect of different oxygen pressures (5, 10, 15, 20, 25, 30, 35 atm) at a leach time of 120 min at a temperature of 80 °C using a S/L of 20%. It is apparent from this figure copper extraction increases with

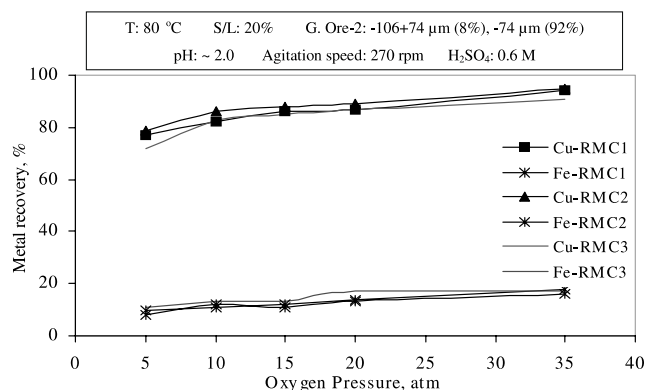


Fig. 4. Effect of oxygen pressure on autoclave leaching.

increasing oxygen pressure while iron extraction remained relatively unaffected. The process variables (particle size, leaching time and oxygen pressure) were tested to optimize recovery of copper while minimizing iron extraction. A further test to investigate oxygen pressure in conjunction with acidic solutions on its ability to selectively extract Cu was also performed on sulphide ore. All further tests employed 15 atm oxygen pressure.

5. Conclusions

In this laboratory study, the copper sulphide, chalcocite, was selectively dissolved by sulphuric acid (H₂SO₄) under oxygen pressure after pre-treatment by roasting. Sulphidic copper ores (RMC1, RMC2, RMC3) were pre-roasted with air/oxygen at 640 \pm 15 °C. This was followed by pressure leaching the roasted samples with an oxygen pressure of 15 atm, at temperature of 80 °C and a S/L of 20%. The results indicate that finer particle sizes aid the roasting and autoclave processes, for obvious reasons, and increased oxygen pressure enhances copper extraction in the pressure leaching stage while not impacting the iron extraction. Copper extractions of 85% were achieved while iron extraction was kept low at 18%. The ability to treat low-grade copper sulphide ores is extremely important. A process that can handle the impurities and be cost effective will aid the development of these deposits. The pre-treatment of these ores using roasting followed by a low temperature autoclave leach has proven effective as a treatment option.

Acknowledgements

The author would like to specially thank Dr. T.J. Harvey, USA, for his invaluable comments on an earlier version of this paper. The author would also like to thank two referees for providing critical comments in revising the manuscript.

References

- Akcil, A., 2000. Pre-researches of Kure historical copper slags prior to solution. In: ALTA 2000 (Copper-6), Adelaide, Australia, October 2–3, 2000, pp. 1–9.
- Akcil, A., Ciftci, H., 2002. A study of the selective leaching of complex sulphides from the Eastern Black Sea Region, Turkey. *Minerals Engineering* 15 (6), 457–459.
- Arbiter, N., McNulty, T., 1999. Ammonia leaching of copper sulphide concentrates. In: Young, S.K., Dreisinger, D.B., Hackl, R.P., Dixon, D.G. (Eds.), *Hydrometallurgy of Copper*, pp. 197–212.
- Bandyopadhyay, D., Singru, R.M., Biswas, A.K., 2000. Study of the roasting of chalcocite minerals by ⁵⁷Fe Mössbauer spectroscopy. *Minerals Engineering* 13 (8–9), 973–978.

- Berezowsky, R.M.G.S., Collins, M.J., Kerfoot, D.G.E., Torres, N., 1991. The commercial status of pressure leaching technology. *JOM* 43 (2), 9–15.
- Elsherief, A.E., 2002. The influence of cathodic reduction, Fe^{2+} and Cu^{2+} ions on the electrochemical dissolution of chalcopyrite in acidic solution. *Minerals Engineering* 15, 215–223.
- Filippou, D., Konduru, R., Demopoulos, G.P., 1997. A kinetic study on the acid pressure leaching of pyrrhotite. *Hydrometallurgy* 47, 1–18.
- Forward, F.A., Veltman, H., 1959. A process for direct leaching zinc sulphide concentrates with sulphuric acid and oxygen under pressure. *J. Metals* 11 (2), 836–840.
- Habashi, F., 1999a. *A Textbook of Hydrometallurgy*, second ed. Métallurgie Extractive Québec, Québec, Canada.
- Habashi, F., 1999b. *Kinetics of Metallurgical Processes*, second ed. Métallurgie Extractive Québec, Québec, Canada.
- Harvey, T.J., Yen, W.T., 1998. The influence of chalcopyrite, galena and pyrite on the selective extraction of zinc from base metal sulphide concentrates. *Minerals Engineering* 11 (1), 1–21.
- Hiroyoshi, N., Arai, M., Miki, H., Tsunekawa, M., Hirajima, T., 2002. A new reaction model for the catalytic effect of silver ions on chalcopyrite leaching in sulfuric acid solutions. *Hydrometallurgy* 63 (3), 257–267.
- Kawulka, P., Kirby, C.R., Bolton, G.L., 1978. The S.C. copper process. Part II: Pilot plant operation. *CIM Bulletin*, 122–130.
- Kellogg, H.H., 1964. A critical review of sulfation equilibria. *Transactions of the Metallurgical Society of AIME* 230, 1622–1634.
- Leung, L.S., 1975. The overall kinetics of roasting of chalcopyrite. *Metallurgical Transactions* 6B, 341–343.
- Prasad, S., Pandey, B.D., 1999. Sulphation roasting studies on synthetic copper–iron sulphides with steam and oxygen. *Canadian Metallurgical Quarterly* 38 (4), 237–247.
- Perek, K.T., Arslan, F., 2002. Pressure leaching of Kure massive rich copper ore. In: 11th International Metallurgy and Material Congress, Istanbul, Turkey, June 5–9, 2002.
- Rao, K.S., Ray, H.S., 1999. Thermal analysis studies on multimetal sulphides: characterisation, roasting and leaching. *Transactions of the Indian Institute of Metals* 52 (4), 171–196.
- Razouk, R.I., 1965. The roasting of copper sulphides. II. Natural copper sulphides. *Journal of Applied Chemistry (London)* 15, 191.
- Subramanian, K.M., Jenninc, P.H., 1972. Review of the hydrometallurgy of chalcopyrite concentrates. *Canadian Metallurgical Quarterly* 11 (2), 387–399.
- Swinkels, G.M., Berezowsky, R.M.G.S., 1978. The SC copper process. Part I: The process. *CIM Bulletin*, 105–121.
- Vanhanen, M.R., 1999. Finish expert report on best available techniques in copper production and by-production of precious metals. The Finnish Environment Institute, Finland, 71.
- Xu, C.H., Newell, R., Quast, K., Ellis, K., 2000. Ammonia leaching: an alternate route for copper recovery. In: *Minprex 2000: International Congress on Mineral Processing and Extractive Metallurgy*. Australasian Institute of Mining and Metallurgy Publications Series, vol. 5, pp. 241–248.