Physicochem. Probl. Miner. Process. 50(2), 2014, 657−666

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received December 5, 2013; reviewed; accepted February 17, 2014

LEACHING OF CHALCOPYRITE CONCENTRATE IN HYDROGEN PEROXIDE SOLUTION

Tevfik AGACAYAK[*], **Ali ARAS**[*], **Salih AYDOGAN**[*], **Murat ERDEMOGLU**[**]

[*] Selcuk University, Mining Engineering Department, 42075 Konya, Turkey, tevfik@selcuk.edu.tr
[**] Inonu University, Mining Engineering Department, 44280 Malatya, Turkey

Abstract: The leaching conditions of chalcopyrite ($CuFeS_2$) concentrate in a hydrogen peroxide medium were investigated by studying the effects of its leaching parameters, such as stirring speed, temperature, hydrogen peroxide concentration and the particle size of the concentrate on Cu extraction. It was found that stirring speed has no effect on the leaching. Copper extraction from chalcopyrite is directly proportional to hydrogen peroxide concentration, but the extraction decreases at temperatures above 60°C. The maximum copper extraction was obtained with the following conditions without stirring: 240 min of leaching time, 3.0 M hydrogen peroxide concentration, 40°C leaching temperature and 53-75 μm particle size fraction.

Keywords: *chalcopyrite, dissolution, hydrogen peroxide, leaching, extraction*

Introduction

Chalcopyrite ($CuFeS_2$) is the most important commercial copper sulphide mineral and is the principal source of commercially produced copper. It is generally associated with other sulphide minerals such as galena (PbS), sphalerite (ZnS) and pyrite (FeS_2). In conventional technology Cu is recovered from $CuFeS_2$ concentrates by crushing, beneficiation concentration, roasting and smelting techniques, followed by electrorefining and electrowinning operations (Habashi, 1978). Approximately 80-85% of the total world copper production is carried out through pyrometallurgical processes that produce SO_2 gas (Antonijević et al., 2004). Hydrometallurgical methods were developed opposed to the classic pyrometallurgical routes due to stringent regulations on SO_2 emission (Habashi, 1999; Antonijević et al., 2004). Although SO_2 gas is used in the production of sulphuric acid, it causes storage and transportation problems.

Chalcopyrite is the most abundant copper mineral and the most refractory and difficult to leach (Plumlee, 1999; Vanhanen, 1999). For that reason, numerous

http://dx.doi.org/10.5277/ppmp140219

leaching studies have been performed by many researchers using various oxidants in acidic media, such as cupric ion (Liddicoat and Dreisinger, 2007; Al-Harahsheh et al., 2008; Yevenes et al., 2010; Skrobian et al., 2005; Lundstrom et al., 2005; Tchoumou and Roynette, 2007), ferric ion (Al-Harahsheh et al., 2008; Akcil and Ciftci, 2002; Dutrizac, 1990; Hirato et al., 1987; Yoo et al., 2010; Cordoba et al., 2008; Nazari and Asselin, 2009), dichromate ion (Antonijevic et al., 1994; Aydogan et al., 2006; Altundogan et al., 2004), nitrate ion (Sokic et al., 2009), hydrogen peroxide (Balaz and Briancin, 1990; Antonijevic et al., 2004; Mahajan et al., 2007; Turan and Altundogan, 2013), hypochlorite (Ikiz et al., 2006) and oxygen (Padilla et al., 2007; Puvvada and Murthy, 2000). Among these agents, hydrogen peroxide is a strong and environmentally safe oxidizing agent. It is reported that hydrogen peroxide produces no reaction products apart from water during the oxidation of sulphide minerals (Antonijevic et al., 2004). Oxidative dissolution of chalcopyrite in hydrogen peroxide solutions can be summarised as follows (Dold, 2005):

$$2CuFeS_2 + 17/2O_2 + 5H_2O \leftrightarrow 2Cu^{2+} + 2Fe(OH)_3 + 4SO_4^{2-} + 4H^+ . \tag{1}$$

The reactions that take place in Cu extraction from chalcopyrite concentrate are (Habashi, 1999):

$$2CuFeS_2 \leftrightarrow 2Cu^{2+} + 2Fe^{2+} + 4S^{2-} \tag{2}$$

$$H_2O_2 \leftrightarrow H_2O + 1/2O_2 \tag{3}$$

$$2Fe^{2+} + 1/2O_2 + 5H_2O \leftrightarrow 2Fe(OH)_3 + 4H^+ \tag{4}$$

$$4S^{2-} + 8O_2 \leftrightarrow 4SO_4^{2-} . \tag{5}$$

Elemental sulphur is stable in an acid medium, but it oxidizes slowly in water at high temperatures (above 150°C) with oxygen pressure to form sulphuric acid (Habashi, 1999):

$$S + 3/2O_2 + H_2O \leftrightarrow H_2SO_4. \tag{6}$$

The present paper, aims to investigate the effects of leaching parameters such as stirring speed, temperature, hydrogen peroxide concentration and particle size, on the dissolution of chalcopyrite in an oxidative medium (only with hydrogen peroxide solution). Copper ions were extracted selectively from chalcopyrite concentrate at atmospheric pressure and lower temperature with a high recovery. Generally, chalcopyrite leaching studies were carried out using a combination of different media. Mahajan et al. (2007) and Antonijevic et al. (2004) obtained copper extraction in a mixture of H_2O_2–H_2SO_4–ethylene glycol and a H_2SO_4–H_2O_2 medium, respectively.

Material and methods

Material

Samples of the chalcopyrite concentrate were taken from the Menka Flotation Plant (Sivas, Turkey), where the $CuFeS_2$–PbS–ZnS complex ore is enriched. The particle size of the concentrate was –212 μm. The concentrate was wet sieved to obtain 212×106, 106×75 and 75×53 particle size fractions. The chemical analysis of each size fraction is given in Table 1.

Table 1. Chemical analysis of chalcopyrite concentrate (wt.%)

Particle size (μm)	Cu (%)	Fe (%)	Zn (%)	Pb (%)	S (%)	Others (%)
212×106	23.52	23.17	1.01	1.13	27.27	23.9
106×75	26.91	26.56	1.46	1.70	31.48	11.89
75×53	24.90	25.16	2.42	3.08	30.57	13.87

Experimental procedure

A Pyrex beaker of 1 dm^3 was used as a leaching reactor placed in a temperature-controlled water bath and closed with a rubber cover. Stirring was carried out by a Heidolph RZR 2021 model mechanic stirrer equipped with a Teflon-covered propeller. A 2 g/dm^3 chalcopyrite sample with a fraction size of 75×53 μm was used for all experiments. Then, the stirring speed was raised to 600 rpm, the temperature was varied in the range of 30–70 °C, the hydrogen peroxide concentration was in the range of 0.5–3.0 M and the particle size range was 212×106, 106×75 and 75×53 μm. The amount of Cu in the leaching solution was determined using a GBC SensAA model flame atomic absorption spectrometer (AAS). For this purpose, 1 cm^3 of leaching solution was withdrawn from the reactor at various time intervals and diluted with water to 100 cm^3 in a volumetric flask. Distilled water and reagent grade chemicals were used for all required solutions.

Results

Effect of stirring speed

The effect of stirring speed on the dissolution of chalcopyrite was investigated at different stirring speeds that ranged from 0 to 600 rpm in a 2.0 M H_2O_2 solution at 50 °C (Fig. 1). It can be seen from Fig. 1 that the Cu extraction was independent of the stirring speed. Thus, all subsequent experiments were carried out without stirring except for homogenizing the solution prior to the sampling for the Cu analysis.

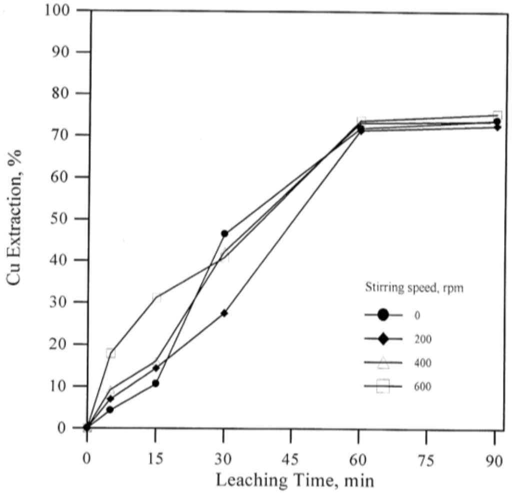

Fig. 1. Effect of stirring speed on chalcopyrite dissolution.
Conditions: 2.0 M H_2O_2, 50°C, 2 g/dm^3 (75×53 µm) chalcopyrite concentrate

Effect of temperature

The experiments were carried out in the 30–70°C temperature range in the solutions containing 2.0 M H_2O_2 (Fig. 2). It can be seen in Fig. 2 that the Cu extraction obtained in 90 min of leaching time reached above 80% at 40 °C. However, in the 90–240 min leaching time interval, Cu extraction reached almost stable values. In addition, it decreased with increasing temperature in the range of 50–70 °C compared to lower

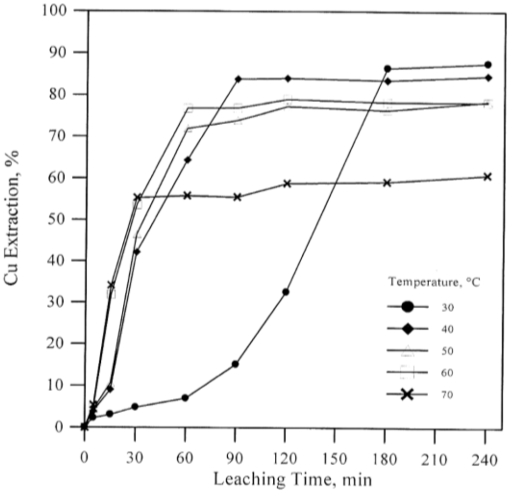

Fig. 2. Effect of temperature on chalcopyrite dissolution.
Conditions: 2.0 M H_2O_2, 2 g/dm^3 (75×53 µm) chalcopyrite concentrate, no stirring

temperatures. These findings suggest that the decomposition of hydrogen peroxide happens more readily at higher temperatures (Antonijevic et al., 1997; Mahajan et al., 2007). Antonijevic et al. (1997) reported that the accelerated decomposition of hydrogen peroxide was above 60 °C.

Effect of H_2O_2 concentration

The experiments were carried out in solutions containing various H_2O_2 concentrations at 40°C. The results are given in Fig. 3. Cu extraction increased with increasing H_2O_2 concentration within a 240 min leaching time. However, in the 90-240 min leaching time interval, Cu extraction almost reached stable values for the solutions containing 2.0 and 3.0 M H_2O_2. In addition, the Cu extraction rate decreased for the solutions containing 0.5 and 1.0 M H_2O_2.

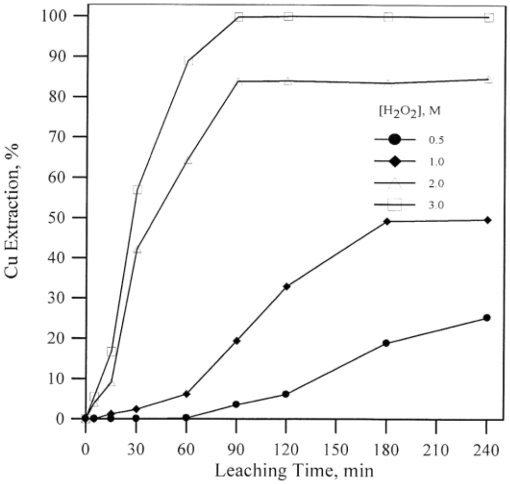

Fig. 3. Effect of H_2O_2 concentration on chalcopyrite dissolution.
Conditions: 40 °C, 2 g/dm^3 (75×53 μm) chalcopyrite concentrate, no stirring

Effect of particle size

The experiments were carried out using three different particle size fractions in the solutions containing 3.0 M H_2O_2 at 40°C. The results are given in Fig. 4. Cu extraction increased with decreasing particle size because of the increase in surface area at unit weight.

Discussion

According to the XRD analysis (Fig. 5), the chalcopyrite concentrate used in the leaching experiments contained mainly chalcopyrite and pyrite. After leaching, the

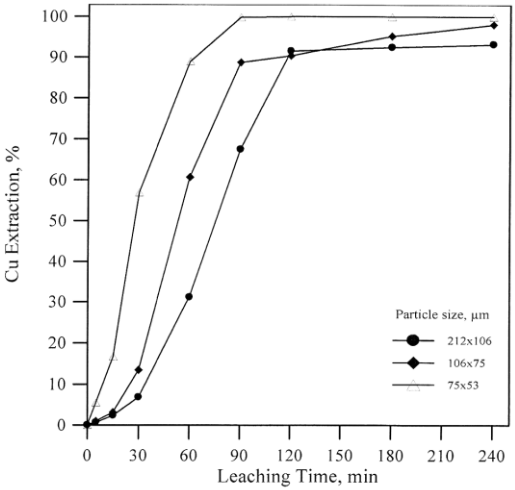

Fig. 4. Effect of particle size on chalcopyrite dissolution.
Conditions: 3.0 M H_2O_2, 40 °C, 2 g/dm^3 (75×53 µm) chalcopyrite concentrate, no stirring

major mineral determined in the residue was chalcopyrite. Pyrite was almost absent. In addition, no elemental sulphur was detected, at least in its crystal form. In addition, elemental sulphur production was not observed during the leaching experiments. However, amorphous iron compounds were observed with an optical microscope (Fig. 6). In the leaching solutions, approximately 5% Fe extraction was achieved. Therefore, it was concluded that rather than the iron existing in the chalcopyrite, the iron in the pyrite is extracted. In order to confirm this, pyrite leaching experiments were performed under conditions identical to those of the chalcopyrite leaching experiment, and this phenomenon was supported by the XRD results (Fig. 7).

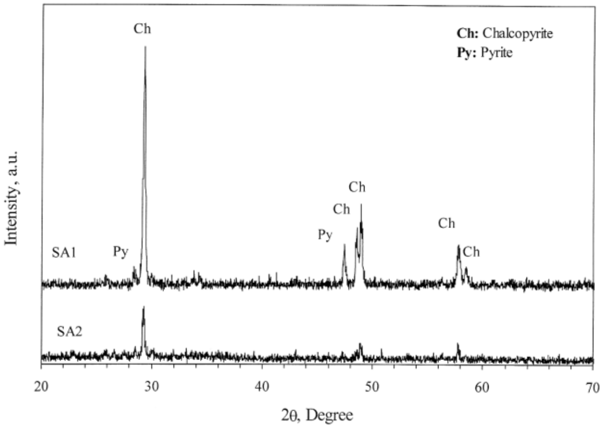

Fig. 5. XRD patterns for the chalcopyrite concentrate (SA1)
and the residue obtained after the leaching (SA2)

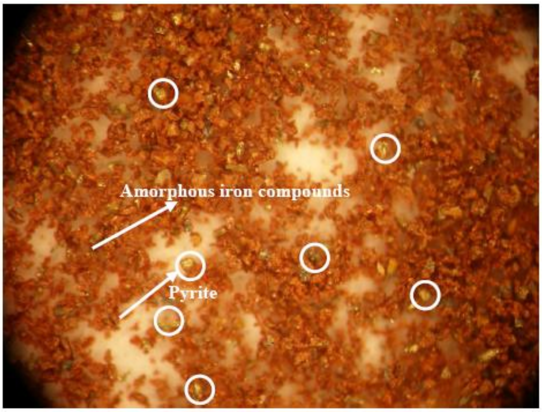

Fig. 6. Microscopic photograph of chalcopyrite concentrate after hydrogen peroxide leaching
Conditions: 3.0 M H_2O_2, 40°C, 2 g/cm^3 (75x53 μm) chalcopyrite concentrate, no stirring

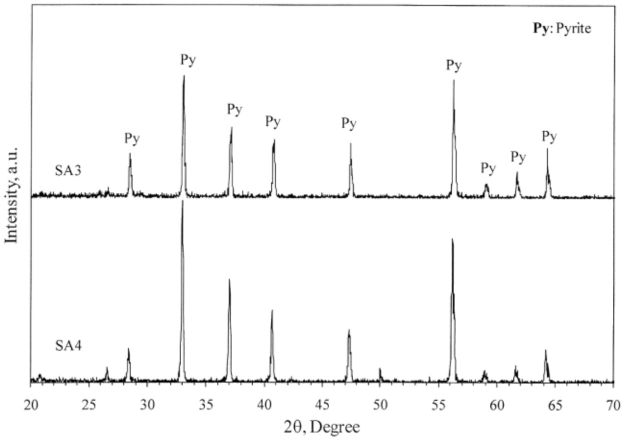

Fig. 7. XRD patterns for a pyrite concentrate before (SA3) and after (SA4) the leaching

During the leaching, a clear pH decrease was observed (Fig. 8) from the beginning of the experiment. Hence, it was concluded that the reaction produces acid in the solution. The dissolution of pyrite in hydrogen peroxide occurred in the reaction as follows:

$$FeS_2 + 7.5H_2O_2 \leftrightarrow Fe^{3+} + 2SO_4^{2-} + H^+ + 7H_2O. \tag{7}$$

The potential-pH diagram for sulphur is given in Fig. 9 (Habashi, 1999). Figure 9 shows that sulphate ions occurred in the oxidizing conditions achieved in this study. Besides, by adding $BaCl_2$ to the centrifuged leach solution, it was proved that sulphate ions existed in the leach solution, and white barium sulphate precipitate was observed.

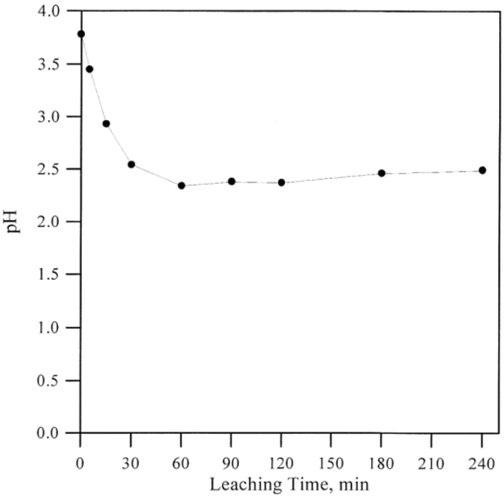

Fig. 8. Variation of pH with leaching time. Conditions: 3.0 M H_2O_2, 40°C, 2 g/dm^3 (75×53 μm) chalcopyrite concentrate, no stirring

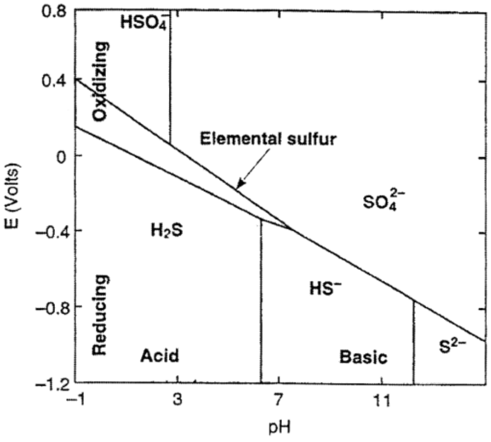

Fig. 9. Potential-pH diagram for sulphur (Habashi, 1999)

Conclusions

In this study, the extraction of Cu from chalcopyrite concentrate in hydrogen peroxide solutions was studied. It was determined that the dissolution process was independent of the stirring. In general, the Cu extraction rate increased with increasing temperatures during the early times of the leaching period. However, it decreased prolonged periods of times, due to the decomposition of hydrogen peroxide at higher temperatures. Cu extraction increased with increasing H_2O_2 concentration in the 240 min leaching time. However, in the 90–240 min leaching time interval, it reached stable values for the solutions containing 2.0 and 3.0 M H_2O_2, respectively. Cu extraction increased with decreasing particle size because of the increase in surface area at unit weight. Optimum leaching conditions of chalcopyrite concentrate in H_2O_2 solution were found as: H_2O_2 concentration: 3.0 M, leaching temperature: 40 °C, stirring speed: 0 rpm; particle size: 75×53 μm. Under these conditions, copper recovery may be as high as 99%. In the studied conditions, it was determined that Cu extraction from chalcopyrite concentrate is possible and iron ions dissolved from chalcopyrite and precipitated. In addition, the pyrite mineral that was present in the concentrate dissolved; thus, the XRD analyses supported these results.

References

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.

AL-HARAHSHEH M., KINGMAN S., AL-HARAHSHEH A., 2008. *Ferric chloride leaching of chalcopyrite: Synergetic effect of $CuCl_2$*. Hydrometallurgy 91, 89–97.

ALTUNDOGAN H.S., BOYRAZLI M., TUMEN F., 2004. *A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate*. Minerals Engineering 17, 465–467.

ANTONIJEVIC M.M., JANKOVIC Z.D., DIMITRIJEVIC M.D., 1994. *Investigation of the kinetics of chalcopyrite oxidation by potassium dichromate*. Hydrometallurgy 35, 187–201.

ANTONIJEVIC M.M., DIMITRIJEVIC M., JANKOVIC Z., 1997. *Leaching of pyrite with hydrogen peroxide in sulfuric acid*. Hydrometallurgy 46, 71–83.

ANTONIJEVIC M.M., JANKOVIC Z.D., DIMITRIJEVIC M.D., 2004. *Kinetics of chalcopyrite dissolution by hydrogen peroxide in sulphuric acid*. Hydrometallurgy 7, 329–334.

AYDOGAN S., UCAR G., CANBAZOGLU M., 2006. *Dissolution kinetics of chalcopyrite in acidic potassium dichromate solution*. Hydrometallurgy 81, 45–51.

BALAZ P., BRIANCIN J., 1990. *Leaching and properties of mechanically activated chalcopyrite.* Fizykochemiczne problemy mineralurgii 22, 193–200.

CORDOBA E.M., MUNOZ J.A., BLAZQUEZ M.L., GONZALEZ F., BALLESTER A., 2008. *Leaching of chalcopyrite with ferric ion. Part I: General aspects*. Hydrometallurgy 93, 81–87.

DOLD B., 2005. Basic *Concepts of Environmental Geochemistry of Sulfide Mine-Waste*. XXIV Curso Latinoamericano de Metalogenia UNESCO–SEG, Lima, Peru.

DUTRIZAC J.E., 1990. *Elemental sulfur formation during the ferric chloride leaching of chalcopyrite*. Hydrometallurgy 23, 153–176.

HABASHI F. 1978. *Chalcopyrite, its Chemistry and Metallurgy*, McGraw-Hill, New York.

HABASHI F., 1999. *A Textbook of Hydrometallurgy*. Métallurgie Extractive Québec, second edition, 750 p. Canada.

HIRATO T., MAJIMA H., AWAKURA Y., 1987. *The leaching of chalcopyrite with ferric sulphate*. Metall. Trans. B 18B, 489–496.

IKIZ D., GULFEN M., AYDIN A.O., 2006. *Dissolution kinetics of primary chalcopyrite ore in hypochlorite solution*. Minerals Engineering 19, 972–974.

LIDDICOAT J., DREISINGER D., 2007. *Chloride leaching of chalcopyrite*. Hydrometallurgy 89, 323–331.

LUNDSTROM M., AROMAA J., FORSEN O., HYVARINEN O., BARKER M.H., 2005. *Leaching of chalcopyrite in cupric chloride solution*. Hydrometallurgy 77, 89–95.

MAHAJAN V., MISRA M., ZHONG K., FUERSTENAU M.C., 2007. *Enhanced leaching of copper from chalcopyrite in hydrogen peroxide–glycol system*. Minerals Engineering 20, 670–674.

NAZARI G., ASSELIN E., 2009. *Morphology of chalcopyrite leaching in acidic ferric sulfate media*. Hydrometallurgy 96, 183–188.

PADILLA R., VEGA D., RUIZ M.C., 2007. *Pressure leaching of sulfidized chalcopyrite in sulfuric acid–oxygen media*. Hydrometallurgy 86, 80–88.

PLUMLEE G.S., 1999. The *environmental geology of mineral deposits*. In: Plumlee, G. S. and Logsdon, M.J. (Eds.) Reviews in Economic Geology, The environmental geochemistry of ore deposits. Part A: Processes, Techniques, and Health Issues, v. 6A, 71–116.

PUVVADA G.V.K., MURTH, D.S.R., 2000. *Selective precious metals leaching from a chalcopyrite concentrate using chloride/hypochlorite media*. Hydrometallurgy 58, 185–191.

SKROBIAN M., HAVLIK T., UKASIK M., 2005. *Effect of NaCl concentration and particle size on chalcopyrite leaching in cupric chloride solution*. Hydrometallurgy 77, 109–114.

SOKIC M.D., MARKOVIC B., ZIVKOVIC D., 2009. *Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid*. Hydrometallurgy 95, 273–279.

TCHOUMOU M., ROYNETTE M., 2007. *Leaching of complex sulphide concentrate in acidic cupric chloride solutions*. Trans. Nonferrous Met. Soc. China 17, 423–428.

TURAN M.D., ALTUNDOGAN H.S., 2013. *Leaching of chalcopyrite concentrate with hydrogen peroxide and sulfuric acid in an autoclave system*. Metallurgical and Materials Transactions 44B, 809–819.

VANHANEN M.R., 1999. *Finnish expert report on best available techniques in copper production and by-production of precious metals*. The Finnish Environment, Finland.

YEVENES L.V., MIKI H., NICOL M., 2010. *The dissolution of chalcopyrite in chloride solutions: Part 2: Effect of various parameters on the rate*. Hydrometallurgy 103, 80–85.

YOO K., KIM S., LEE J., ITO, M., TSUNEKAWA M., HIROYOSHI N., 2010. *Effect of chloride ions on leaching rate of chalcopyrite*. Minerals Engineering 23, 471–477.