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Kinetics of chalcopyrite galvanic leaching using sulfate medium at low temperature in the Galvanox™ process

S. Salehi ^{a,*}, M. Noaparast ^b, S. Z. Shafaie ^b^a Department of Mining Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran^b School of Mining Engineering, College of Engineering, University of Tehran, Iran

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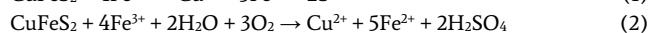
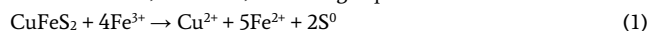
ABSTRACT

In this research, the dissolution of chalcopyrite was investigated under atmospheric pressure, with a sulfate medium at low temperatures, in 30°C to 50°C. In the galvanic interaction between chalcopyrite and pyrite, pyrite is used as a leaching catalyst. Effects of different parameters such as temperature, stirring speed, pyrite to chalcopyrite ratio, particle size, and solution potential were examined. Results showed that maximum copper recovery in low temperature was achieved after 24 hours, under the following condition: stirring speed of 800rpm, pyrite to chalcopyrite ratio of 4, solution potential of 440mV, temperature of 50°C, and particle size of -38 microns. In addition, kinetic studies indicated that chalcopyrite dissolution with pyrite followed the shrinking core model, and the reaction was controlled by the surface reaction. Activation energy (E_a) was calculated as 88 kJ/mol.

Keywords: Chalcopyrite; Galvanic leaching; Kinetic; Low temperature

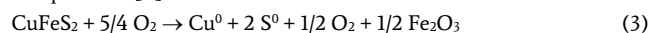
1. Introduction

Hydrometallurgical processes in extraction of copper from chalcopyrite can be categorized according to the type of the used lixiviant. These processes are grouped as sulfate, chloride, sulfate-chloride, ammonia, and nitrogen processes. Hydrometallurgical processes in extraction of copper from chalcopyrite can be categorized according to the type of the used lixiviant. These processes are grouped as sulfate, chloride, sulfate-chloride, ammonia, and nitrogen processes.



In this medium, because of the formation of passive layers on the chalcopyrite surface that results in slow and incomplete leaching, the kinetics of chalcopyrite leaching is slow [1-2]. The nature of how these passive layers are formed is still in debate. Various theories propose the formation of passive layers on the chalcopyrite surface such as sulfur layer [2], copper-rich polysulfide layer [3], and iron salt layers [4]. Recently, it has been discovered that in ferric sulfate media, the addition of pyrite reacts similar to a catalyst, and increases the copper recovery. This process is called Galvanox™ [5]. The Galvanox™ process is the atmospheric leaching of primary copper concentrates in a sulfate medium. It has been shown that in the presence of pyrite, the kinetics of

leaching accelerates significantly as a result of a strictly chemical reaction, and therefore requires no microbe. In addition, fine grinding is not required in this process. Also, since the operating temperature is low, and the chemical conditions are mild, the near-quantitative yield of elemental sulfur is observed. This decreases both oxygen consumption, and the necessity to neutralize large quantities of sulfuric acid. The operating temperature (80°C) is below the melting point of sulfur which eliminates the need for surfactants. The Galvanox™ chemistry is shown in equation 3 [6]:



The complete copper recovery in the Galvanox™ process can be achieved at a considerably higher rate than other ferric sulfate leaching processes [5]. But as chalcopyrite is a semiconductor, the dissolution of the mineral increases in the presence of pyrite. The anodic and cathodic half-cell reactions of this process in ferric sulfate would be expressed as Equations 4 and 5 [7]:

Anodic:



Cathodic:



* Corresponding author. Tel.: +98-9132835865.

E-mail address: soghrasalehi90@gmail.com (S. Salehi).

Thus, the cathodic reaction takes place on the surface of pyrite, rapidly, and increases the dissolution of chalcopyrite. The kinetic models and the activation energies of the oxidative dissolution of chalcopyrite in ferric sulfate media are reported by various authors which are given in Table 1.

In this study, the reaction kinetics of chalcopyrite in ferric sulfate media in the presence of pyrite in low-temperature is studied in order

to investigate

the leaching mechanisms of chalcopyrite. In addition, the effects of different variables such as stirring speed, temperature, particle size, pyrite to chalcopyrite (Py/Cp) ratio, and solution potential on the reaction rate were also investigated.

Table 1. Chalcopyrite leaching rate and mechanisms in sulfate medium.

T (°C)	Leach medium	Ea (kJ/mol)	Mechanism	Reference
50-97	K ₂ Cr ₂ O ₇ +H ₂ SO ₄	24	Diffusion through a porous product layer by shrinking core model	[8]
45-100	FeCl ₃ + H ₂ SO ₄	42	Diffusion	[9]
70-90	NaNO ₃ + H ₂ SO ₄	83	Mixed control model	[10]
25-50	H ₂ O ₂ + H ₂ SO ₄	60	Surface reaction control by shrinking core model	[11]
30-80	K ₂ Cr ₂ O ₇ +H ₂ SO ₄	48-54	Chemical reaction control	[12]
125-150	O ₂ +H ₂ SO ₄	93.5	Surface reaction control by shrinking core model	[13]
30-80	H ₂ O ₂ + H ₂ SO ₄	39	Surface chemical reaction control by shrinking core model	[14]
50-94	Fe ₂ SO ₄ +H ₂ SO ₄	71±12.5	Diffusion through product layer	[15]
45-100	Fe ₂ SO ₄ +H ₂ SO ₄	75	Diffusion through product layer	[16]
50-92	Fe ₂ (SO ₄) ₃ +H ₂ SO ₄	79.5	Surface reaction control by shrinking core model	[17]
55-85	Fe ₂ (SO ₄) ₃ +H ₂ SO ₄	76±10	Chemical reaction control	[18]

2. Experimental Materials and Methods

A typical copper sulfide concentrate sample was supplied by Sarcheshmeh copper flotation unit (Kerman, Iran), and was used in this study. Figure 1 shows the XRD pattern of the representative concentrate sample. X-ray diffraction (UNI- SANTIS, model: XMD300, Germany) of the sample demonstrated that chalcopyrite (CuFeS₂) was the major mineral. X-ray fluorescence (Philips, model: PW1480, Netherlands) analysis of fractions of the concentrate sample is presented in Table 2. The pyrite crystals ore samples were collected from Meydook copper mine located in Kerman province of Iran, and were crushed and ground to minus 75µm. In Table 3, the mineralogical composition of the copper concentrate, and the pyrite sample are presented using XRD analysis.

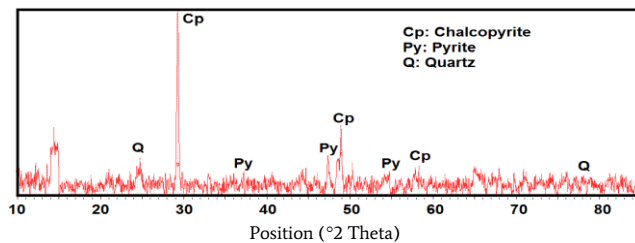


Figure 1. XRD pattern of the copper concentrate sample.

The leaching experiments were carried out in a stirring tank reactor containing 500mL suspension at 5% pulp density (w/v), total iron concentration of 0.1 M, and initial pH of 1.2 sulfuric acid with a purity of approximately 98% was used for increasing the medium acidity. After setting the pH levels, ferrous and ferric sulfate or H₂O₂ were added to set the redox potential at the desired levels. The desired temperature was obtained using an electrical heater. For determining the dissolved metal concentration, 5m pulp samples were being taken periodically from the reactor, and centrifuged for 3 minutes at 5000rpm to remove solids. The leaching system is shown in Figure 2. The solid regained after centrifugation was returned to the reactor, and the volume of the evaporated liquid was daily substituted by adding distilled water. Samples were assayed for copper content by atomic absorption spectroscopy (Varian, model 240). Distilled water was used in all of the experiments.

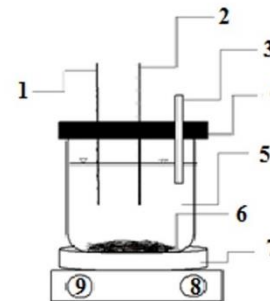


Figure 2. Schematic view of the leaching reactor 1-Thermometer, 2- Eh probe, 3-Sampling system, 4- Blind, 5- Pulp, 6- Copper concentrate and pyrite samples, 7- Magnetic impeller, 8- Temp controller, 9- Impeller controller.

Table 2. Chemical analysis of the different size fractions of the representative chalcopyrite concentrate.

Particle size (µm)	Wt (%)			
	Cu	Fe	S	Ag(ppm)
-74+53	21.47	29.95	35.78	21.2
-53+38	23.94	29.51	35.41	26.8
-38	27.21	28.58	34.51	36.6

3. Results and Discussion

3.1. Effect of Stirring Speed

Stirring speed was studied in three different levels (800, 1000, and 1200rpm). Other conditions were solution potential: 440mV, temperature: 50°C, chalcopyrite and pyrite particle size: -38µm and pyrite to chalcopyrite ratio: 2. The results of stirring speed on the dissolution of chalcopyrite are shown in Figure 3. According to the figure, excitement speed has no significant effect on the dissolution of chalcopyrite. Results indicate that chemical reactions are more effective than physical ones; thus, the dissolution reaction rate is not controlled by film diffusion [16]. Therefore, the stirring speed of 800rpm was used to run all the experiments, as turbulence at this speed would be lower than the other stirring speeds.

Table 3. Mineralogical composition of the copper concentrate and pyrite samples.

Mineral	Copper concentrate (%)			Pyrite (%)
	-75+53 (μm)	-53+38 (μm)	-38 (μm)	
Chalcopyrite	81.3	66.2	74.8	-
Pyrite	3.4	7.4	13.2	95.6
Quartz	7.6	9.7	-	2.3
Sphalerite	2.2	-	11.8	-
Oxides (total)	9.63	6.7	7.21	-
Covellite	-	-	-	2.1

3.2. Effect of Pyrite to Chalcopyrite (Py/Cp) Ratio

The effect of pyrite to chalcopyrite ratio on copper extraction in the presence of pyrite over 24 hours is given in Figure 4. It is observed that as the Py/Cp ratio increases, the copper recovery also increases. The increase of Py/Cp ratio to higher values than 4 has no significant effect on the copper recovery. Dixon and Tshilombo (2005), observed that as the amount of pyrite increased up to a certain level, further pyrite additions did not improve the leaching process [19]. This phenomenon has been confirmed by other authors [20, 6, 21-23].

3.3. Effect of Solution Potential

The copper extraction as a function of the solution potential is shown in Figure 5 at the temperature of 50°C, particle size of -38 μm , Py/Cp ratio of 4, and stirring speed of 800rpm. In the literature [19], it has been shown that increasing the solution potential from 410 to 460mV leads to an increase in the chalcopyrite leaching rates in the presence of pyrite; therefore, the solution potential has a significant effect on the copper recovery. In this study, maximum copper recovery was achieved in 440mV.

Nazari et al. (2011) have shown that increasing the solution potential set point from 425 to 470mV accelerated the chalcopyrite leaching rates in the presence of pyrite [24]. Also, Koleini et al. (2011) reported that the highest copper recoveries were obtained in redox potential around 410-440mV [19].

3.4. Effect of Temperature

The effect of temperature on copper recovery was investigated by setting temperature at various values (30, 40, and 50°C), under solution potential of 440mV, chalcopyrite and pyrite particle size of -38 μm , Py/Cp ratio of 4, and stirring speed of 800rpm. Figure 6 shows that the temperature has a significant effect on the copper recovery, and the highest recovery to be at 50°C.

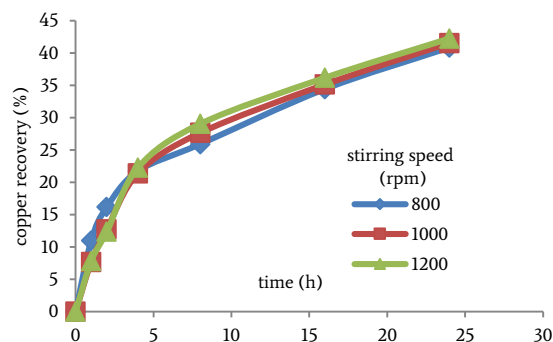
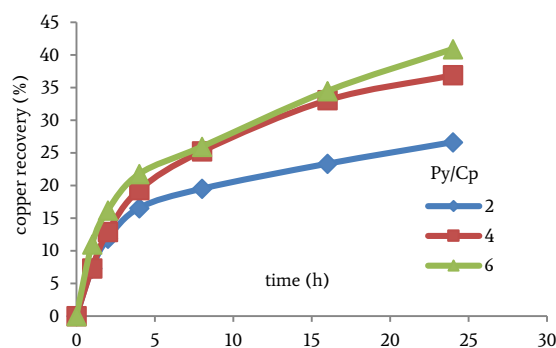
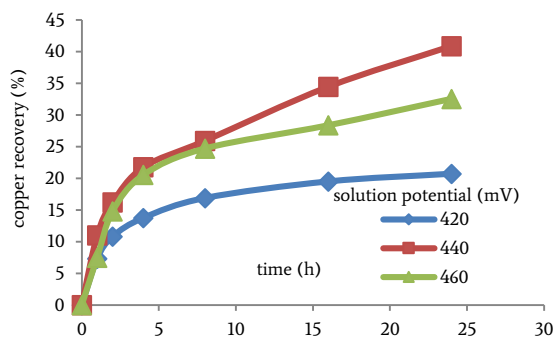
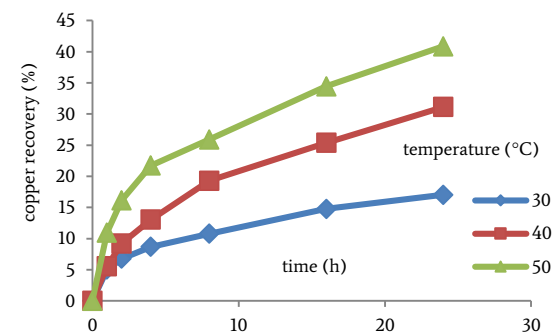
Results of other studies indicated that an increase in reaction rate was noted for each 10°C rise of temperature. Many authors pointed out that when the temperature increased, the dissolution of chalcopyrite increased rapidly [23]. Since the rest potential of sulfide minerals decreases with temperature increase, chalcopyrite at high temperature is more active, and its dissolution rate will accordingly increases [7, 19].

3.5. Effect of particle size

The other important factor which was studied was the effect of particle size. Determining the suitable particle size range is important for industrial application, because it is directly related to the power consumption, residence time in the reactor, and preparation stages prior to leaching [25]. The effect of particle size on copper recovery were studied at three size fractions (-74+53, -53+38, and -38 μm), under solution potential of 440mV, Py/Cp ratio of 4, temperature of 50°C, and stirring speed of 800rpm. Figure 6 shows increase in copper extraction with decreasing particle size. It was observed that in order to achieve the best copper extraction in a reasonable time, chalcopyrite would necessarily be grounded to below 75 μm .

Dreisinger and Abed (2002) have shown that the particle size plays an important role in the leaching process, under reducing conditions. In

addition, other researchers deduced that decreasing the particle size would cause an increase in the copper dissolution [10, 14, 26].

**Figure 3. Effect of stirring speed on the copper recovery.****Figure 4. Effect of the Py/Cp ratio on the copper recovery.****Figure 5. Effect of solution potential on the copper recovery.****Figure 6. Effect of temperature on the copper recovery.**

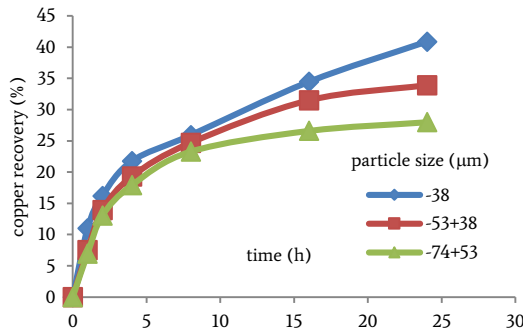


Figure 7. Effect of particle size on the copper recovery.

3.6. Kinetic Analysis

The most common model for the chalcopyrite dissolution is shrinking core model [8, 27-28]. The kinetics models and related equations are given in Table 4, where X is the fraction reacted, k_{cc} is the kinetics constant, M_B is the molecular weight of the solid, C_A is the concentration of the dissolved lixiviant A in the bulk of the solution, a is the stoichiometric coefficient of the reagent in the leaching reaction, r_0 is the initial radius of the solid particle, t is the reaction time, D_e is the diffusion coefficient in the porous product layer, ρ_b density of the solid and k_c , k_d and k_r are the rate constants which are respectively calculated from surface chemical reaction, diffusion through a product layer, and mixed control. Equations 6, 7 and 8 were applied to the results obtained from each temperature value. The results could be analyzed by the

values of correlation coefficient (R^2) which are presented in Table 5. Therefore, equation 6 was found to be well fitted by the data. The results in Figure 8 indicate that the linear relationship between $1-(1-X)^{1/3}$ and leaching time (t) is significant and suggests that the leaching rate of chalcopyrite is controlled by the surface reaction.

Table 4. Kinetic models and equations.

Surface chemical reaction $1 - (1 - X)^{\frac{1}{3}} = \frac{k_c M_B C_A}{\rho_b a r_0} t = k_r t$ Eq. 6

Diffusion through a product layer $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = \frac{2D_e M_B C_A}{\rho_b a r_0^2} t = k_d t$ Eq. 7

Mixed control $1 - (1 - X)^{\frac{1}{3}} + \frac{k_{cc} r_0}{\rho_b a} [1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}] = \frac{M_B C_A k_{cc}}{\rho_b a} = k_r t$ Eq. 8

Arrhenius law (equation 9) is used for activation energy calculation, where A is frequency factor, E_a is activation energy of the reaction, R is universal gas constant and T is the absolute temperature. The apparent rate constants (k) were calculated as slopes of the straight lines. Using the apparent rate constants obtained by application of equation 6, the Arrhenius plot ($\ln k$ vs $1/T$) was made (Figure 9), and the activation energy was accordingly calculated which was equal to 88 kJ/mol ($E_a = (-10.802) \times (-8.14) = 87.92$ kJ/mol). This value clearly confirms that this process is most likely controlled by the surface reaction model.

$$k = A \exp(-E_a/RT) \tag{9}$$

Table 5. The k_c , k_d and k_r values and correlation coefficients for each temperature.

Temperature (°C)	$K_c (\times 10^{-3} \text{ min}^{-1})$	R^2	$K_r (\times 10^{-3} \text{ min}^{-1})$	R^2	$K_d (\times 10^{-3} \text{ min}^{-1})$	R^2
30	0.001	0.8948	0.012	0.9909	0.004	0.9073
40	0.004	0.9161	0.023	0.9954	0.013	0.9224
50	0.011	0.9170	0.039	0.9933	0.034	0.9211

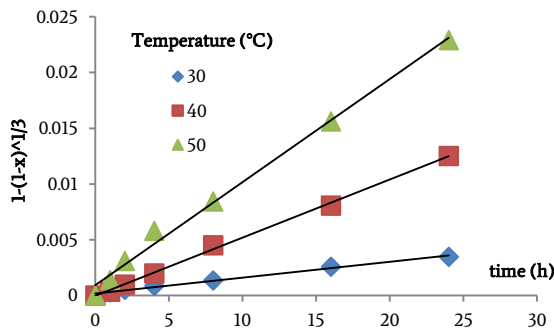


Figure 8. Plot of Eq. (6) vs. t for different temperatures.

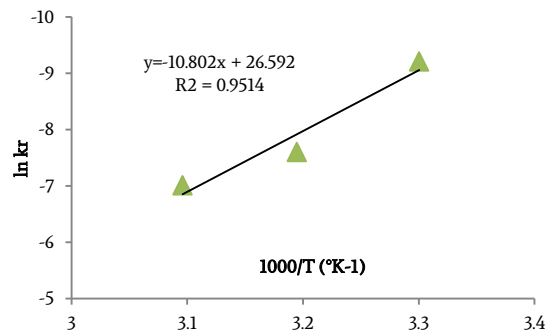


Figure 9. Arrhenius plot for chalcopyrite leaching.

4. Conclusions

Dissolution of chalcopyrite was studied using pyrite at low temperatures (30-50°C). The results of this study are as follow:

- It was shown that leaching in sulfate medium in the presence of pyrite is effective on the chalcopyrite leaching.
- Stirring speed has no significant effect on the copper recovery, but the Py/Cp ratio, solution potential, particle size and temperature have significant effects on copper recovery.
- Increasing the temperature and decreasing the particle size, considerably causes an increase on the chalcopyrite leaching rate.
- Moderate values of the Py/Cp ratio and solution potential were selected for this work.
- The optimum conditions was obtained at a stirring speed of 800rpm, Py/Cp ratio of 4, solution potential of 440mV, particle size of -38 and temperature of 50°C for 24 hours.

Kinetic investigation showed that chalcopyrite dissolution in the presence of pyrite met the shrinking core model, and the reaction was controlled by the surface reaction, and the activation energy (E_a) was calculated equal to 88 kJ/mol.

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