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Optimization of selective copper extraction from chalcopyrite concentrate in presence of ammonium persulfate and ammonium hydroxide

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Abstract: The dissolution of copper and iron from chalcopyrite concentrate in the presence of ammonium persulfate (APS) and ammonium hydroxide was investigated under atmospheric leaching conditions. Experiments were designed by central composite design (CCD). Under the optimum leaching conditions ($(NH_4)_2S_2O_8$ concentration = 328 g/L; NH_4OH addition = 16vol%; leaching temperature = 321 K (48°C); leaching time = 120 min; liquid-to-solid ratio = 16; stirring speed = 400 r/min), selective leaching was achieved. 98.14% of the copper was leached, whereas iron did not pass into the solution. X-ray diffraction analysis of the leaching residue showed that iron compounds were predominant. Given the leaching results, the fact that the leaching process does not include uneconomical leaching stages such as extended milling/mechanical activation or high pressures/temperatures, and the low copper dissolution conditions, the attained selective leaching yield may be remarkable.

Keywords: leaching; complex reaction; selectivity; copper; chalcopyrite

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1. Introduction

The production of certain base metals such as copper, zinc, and lead is based on sulfide ores and/or concentrates. Although copper exists as both oxide and sulfide ores in nature, a significant portion of its existing reserves are sulfide ores. Approximately 80% of the world's copper-from-ore originates from Cu–Fe–S ores. Cu–Fe–S minerals are not easily dissolved in aqueous solutions; thus, the vast majority of copper extraction from these minerals is pyrometallurgical [1]. Before the pyrometallurgical treatment, chalcopyrite (the most common Cu–Fe–S mineral, $CuFeS_2$), which is associated with pyrite (FeS_2), is enriched from other minerals via froth flotation. Flotation processes are associated with lower metal production costs. When the flotation technique is applied to chalcopyrite ore (average grade 0.5%–1.5% Cu), the copper grade in the concentrate reaches 15%–25% Cu.

The obtained concentrate is treated by conventional pyrometallurgical processes that involve melting, converting, refining, and electrolysis methods. Although pyrometallurgical methods remain a valid option for producing copper from chalcopyrite, researchers have recently focused on alternative methods, with the objectives of reducing costs, reducing the environmental impact, and achieving selective extraction. Hydrometallurgical processes for copper production appear to be appropriate alternative methods because of their numerous advantages [2–8]. Nevertheless, applying hydrometallurgical methods to chalcopyrite introduces problems such as nonselective leaching and low leachability due to the formation of a sulfur layer [9]. Popular methods that overcome these problems can be sorted as the mechanical activation/extended milling of chalcopyrite and roasting–leaching combined routes for the purpose of pretreatment [10–14].

In this study, response surface methodology (RSM) and an experimental layout design were used to evaluate the effectiveness of using ammonium persulfate (APS) and ammonium hydroxide for the selective leaching of chalcopyrite concentrate. APS was used as an oxidant (the decomposition product is oxygen), and ammonium hydroxide was used to complex copper ions and hydrolyze iron. The literature con-

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tains no articles about using APS and ammonium hydroxide together in this application, despite ammonium hydroxide and APS being widely used separately in numerous articles [15–20].

2. Experimental

Chalcopyrite concentrate was obtained from Karadeniz Copper Plant, Samsun, Turkey. The concentrate was sieved into five different fractions with a range of diameters: 297–1190 μm, 149–297 μm, 105–149 μm, 74–105 μm, and < 74 μm. All of fractions were dried at 323 K (50°C), and the samples were stored in a closed vessel for later use. Chemical analyses of the concentrate were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 2000DV); the samples were prepared as clear supernatants obtained via a microwave-assisted dissolution technique. A 0.100-g chalcopyrite sample was weighed with a precision of ± 0.001 g and placed in a Teflon bomb that could withstand high pressures. Two milliliters of HNO_3, 6 mL of HCl, and 2 mL of HF were added to the Teflon vessel. The resolution program was applied as 5 min at 250 W, 5 min at 400 W, and 10 min 500 W. The sulfur content of the concentrate was determined gravimetrically [21]. The results of the chemical analyses, which represent the average values for 25 samples, were as follows: Cu (22.02wt%), Fe (28.85wt%), Al (0.25wt%), Mn (0.44wt%), K (1.24wt%), Pb (1.44wt%), and S (28.01wt%).

Mineralogical analysis of the concentrate was conducted using an X-ray diffraction system and the powder diffraction technique. X-ray analyses (Rigaku RadB-DmaxII model) of the concentrate and residue were carried out using a Cu X-ray tube (λ = 15.405 nm). Mineralogical characteristics showed that the chalcopyrite concentrate was mainly composed of chalcopyrite ($CuFeS_2$) and pyrite (FeS_2).

According to results of the N_2 adsorption–desorption analysis of the surface area and particle size distribution of the less than 74 μm fraction using the Brunauer–Emmett–Teller (BET) method, the average particle size of the chalcopyrite concentrate was 14.56 μm; thus, this particle size represents the particle size of the flotation feeding material (Table 1).

Table 1. Particle size distribution and N_2-BET surface area of chalcopyrite concentrate

d = 10%	d = 50%	d = 90%	BET surface area / ($m^2 \cdot g^{-1}$)
3.68 μm	14.56 μm	32.27 μm	0.637

Note: d—rate of material passing through specified size.

All solutions used in the experiments were freshly prepared by dissolving the appropriate amount of APS and ammonium hydroxide into distilled water in a flask. All leaching experiments were performed under atmospheric conditions using a conventional magnetic multistirrer (Velp Scientifica MultiStirrer 15). Experiments were carried out in 200-mL flasks under reflux and with magnetic stirring.

Obtained leaching solutions were diluted with distilled water, and their Cu and Fe contents were analyzed by atomic absorption spectroscopy (AAS, Perkin-Elmer, AAnalyst 400). Experiments were designed with full-factorial-type modeling of the central composite design (CCD) using the State-Ease 6.0.10 software. Among parameters that affected the results, the APS concentration, leaching temperature, and ammonium hydroxide addition were screened as the three independent variables in the CCD layout. The parameter intervals were determined, and a total of 20 experiments including 6 replications for the central point were considered. During all of the leaching experiments, the liquid-to-solid ratio and stirring speed were kept constant at 16 and 400 r/min, respectively. The experimental variables and their corresponding levels are listed in Table 2.

Table 2. Experimental range and levels of the variables (advanced design point α = 1.68179)

Variables	Symbol	Unit	Range and levels				
			$-\alpha$	−1	0	+1	$+\alpha$
APS concentration	X_1	$g \cdot L^{-1}$	10.69	130	305	480	599.31
Ammonium hydroxide addition	X_2	vol%	2.41	6.50	12.50	18.50	22.59
Leaching temperature	X_3	K (°C)	292.82 (19.82)	301 (28)	313 (40)	325 (52)	333.18 (60.18)

3. Results and discussion

3.1. Results of preliminary experiments

The decomposition of APS results in the formation of active oxygen species in aqueous solutions. Active oxygen in the leaching solution is considered an oxidant for sulfide ores (Eqs. (1)–(3)):

$$(NH_4)_2S_2O_8 + H_2O \rightarrow 2NH_4(HSO_4) + 1/2O_2 \quad (1)$$

$$Me_xS_y \rightarrow xMe^{2+} + yS + 2xe^- \quad (2)$$

$$Me_xS_y + xS_2O_8^{2-} \rightarrow xMe^{2+} + yS + 2xSO_4^{2-} \quad (3)$$

where Me represents a metal.

The leaching temperature is an important parameter for metal extraction; increasing the temperature causes further decomposition of APS according to Eq. (1). To reveal effect of temperature on the leaching of metals, experiments were performed at different leaching temperatures (Fig. 1). As seen in Fig. 1, the copper extraction yields increased with increasing leaching temperatures until 333 K (60°C) and then decreased as the temperature was increased further. Because the leaching system was open, oxygen escaped the leaching medium via decomposition of APS. The escaped oxygen could then no longer be used effectively for oxidation of chalcopyrite. For this reason, the leaching temperature was investigated in the range 293–333 K (20–60°C) for the main experiments.

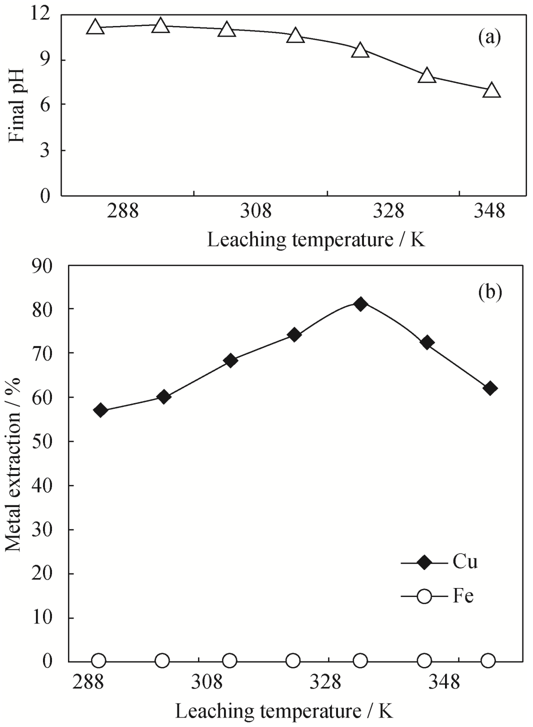

Fig. 1. Effect of (a) pH and (b) leaching temperature on metal extraction (APS concentration: 300 g/L; ammonium hydroxide: 22.5vol%; leaching temperature: 333 K (60°C); liquid-to-solid ratio: 10; leaching time: 45 min).

As shown in Fig. 2, the copper extraction yield tended to increase with decreasing particle size. Although the copper extraction was approximately 60% for the 297–1190 μm particle fraction, it reached 80% for the less than 74 μm under the same leaching conditions. Chalcopyrite was also ground into small particle fractions to obtain efficient mineral beneficiation during the flotation process. Therefore, the strategy of using small-particle-size fractions will provide representative approaches for processing.

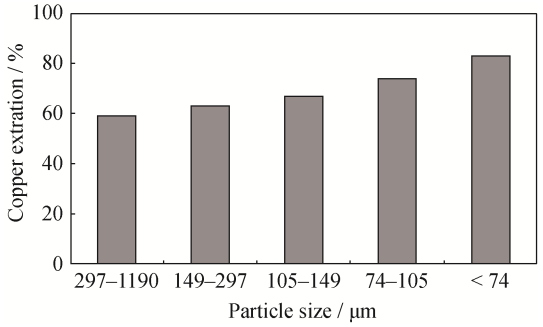

Fig. 2. Effect of particle size on copper extraction (APS concentration: 300 g/L; ammonium hydroxide: 22.5vol%; leaching temperature: 333 K (60°C); liquid-to-solid ratio: 10; leaching time: 45 min).

Notably, one of the biggest problems was nonselective leaching for the oxidative leaching of chalcopyrite. During copper leaching from chalcopyrite in the presence of an oxidant, a large quantity of iron ions passes into the solution, necessitating further purification. Nevertheless, the results of the preliminary experiments show that selective leaching of chalcopyrite concentrate in the presence of ammonium hydroxide is feasible. While the basic character of this reagent leads to complexation with copper ions, it causes iron to hydrolyze in the leaching solution.

3.2. Results of designed experiments

RSM aids in optimizing the process with respect to the number of operating parameters with a minimum number of experiments and in analyzing the interactions among the parameters. Moreover, CCD has some advantages in terms achieving a good fitting of a second-order model, and it contributes to a rotatable design by adding quadratic terms and an α value representing the distance of axial runs from the design center.

Rotatability is a reasonable basis for the selection of a response surface design. Because the purpose of RSM is optimization and because location of the optimum is unknown prior to running the experiment, it is reasonable to use a design that provides equal precision of estimation in all directions [22].

In the designed experiments, the APS concentration (X_1), ammonium hydroxide addition (X_2), and the leaching temperature (X_3) were defined as independent variables. All experiments were carried out under conditions of a leaching time of 120 min, a liquid-to-solid ratio of 16, and a stirring speed of 400 r/min. The results of the experiments under different experimental conditions are shown in Table 3.

Table 3. Experimental design with actual factors and obtained results

Run order	X_1 / $(g \cdot L^{-1})$	X_2 / vol%	X_3 / K	Y_1 (Cu extraction) / %	Y_2 (Fe extraction) / %
1	130.00	6.50	301.00	41.95	0
2	480.00	6.50	301.00	41.42	0
3	130.00	18.50	301.00	82.02	0
4	480.00	18.50	301.00	50.41	0
5	130.00	6.50	325.00	70.10	0
6	480.00	6.50	325.00	40.80	23.60
7	130.00	18.50	325.00	76.07	0.13
8	480.00	18.50	325.00	78.00	0
9	10.69	12.50	313.00	15.43	0.13
10	599.31	12.50	313.00	48.94	0
11	305.00	2.41	313.00	40.22	12.60
12	305.00	22.59	313.00	92.05	0.11
13	305.00	12.50	273.82	78.56	0
14	305.00	12.50	333.18	73.50	0
15	305.00	12.50	313.00	94.50	0
16	305.00	12.50	313.00	93.70	0
17	305.00	12.50	313.00	94.80	0
18	305.00	12.50	313.00	93.10	0
19	305.00	12.50	313.00	95.60	0
20	305.00	12.50	313.00	93.50	0

As shown in Table 3, Fe ions did not pass into the leaching solution when a sufficient quantity of ammonium hydroxide was added, offering good selectivity.

The experimental data obtained under the different conditions were evaluated using the software Stat-Ease Design Expert, and the parameters were evaluated statistically in the basis of the experimental data. A summary of the statistical analysis for two different responses is given in Table 4. While ammonium hydroxide was significant for copper and iron leaching, APS and ammonium hydroxide had a second-order effect on the copper leaching according to the obtained ($p < 0.05$) values.

Table 4. Summary of statistical results

Metals	Statistical data			
	R^2	Standard deviation	Adequate precision	Effective factors ($p < 0.05$)
Cu	0.85	13.39	6.329	X_2, X_1^2, X_2^2
Fe	0.67	4.07	9.053	X_2

The R^2 values of the metals are high, indicating a good fit to the model. The R^2 represents a measure of the variability of the response obtained using independent factor variables in the model. The adequate precision values for two metals are greater than 4 (desirable), indicating that the results provide an adequate approximation of the real system.

The final equations in terms of actual factors are shown in Eqs. (4) and (5) as

$$Y_1 = -109.19 + 0.41X_1 + 8.87X_2 + 3.37X_3 - 0.06871X_1^2 - 0.25X_2^2 - 0.04X_3^2 + 1.791 \times 10^{-3}X_1X_2 + 0.02841X_1X_3 - 0.01X_2X_3 \quad (4)$$

$$Y_2 = -14.25 - 0.01X_1 + 1.95X_2 + 0.23X_3 - 0.2831X_1X_2 + 0.1401X_1X_3 - 0.04X_2X_3 \quad (5)$$

where the unit for parameter X_3, temperature, is °C in Eqs. (4) and (5). These equations clearly show that copper leaching results, unlike the iron leaching results, fit the quadratic model equation.

The response surface graphs for metal extractions under the optimum conditions for copper are shown in Fig. 3. The use of APS and the use of ammonium hydroxide were significant for copper extraction from chalcopyrite concentrate. Although copper leaching was at minimum values under conditions of a low APS concentration and with ammonium hydroxide added, greater copper extraction could be achieved with increasing APS concentration. Notably, however, copper extraction decreased at high APS concentrations. This case can be explained by APS reaching the solubility limit in the leaching solution. In general, the increases in copper extraction with increasing APS concentration, with ammonium hydroxide added, and with increasing leaching temperature are represented as X_1, X_2, and X_3, respectively. Contour diagrams indicate the maximum values (metal extraction) in the case of the smallest elliptical lines. Elliptical contours are obtained when a perfect interaction occurs among the independent variables, as seen in the counter lines.

In Fig 4, the interaction of leaching parameters on the iron dissolution is shown. Iron dissolution reached maximum values under conditions of low ammonium hydroxide addition, high APS concentration, and high leaching temperature. Otherwise, iron dissolution could be kept at minimum because the ammonium hydroxide concentration was greater than 10vol% in the leaching solution. In view of these data, ammonium hydroxide might be used with APS for selective leaching of chalcopyrite concentrate so that hydroxide compounds could provide alkaline conditions for iron hydrolysis while simultaneously providing a complexing media for copper ions, as suggested in the following reaction, which is contrary to some reactions reported in the literature.

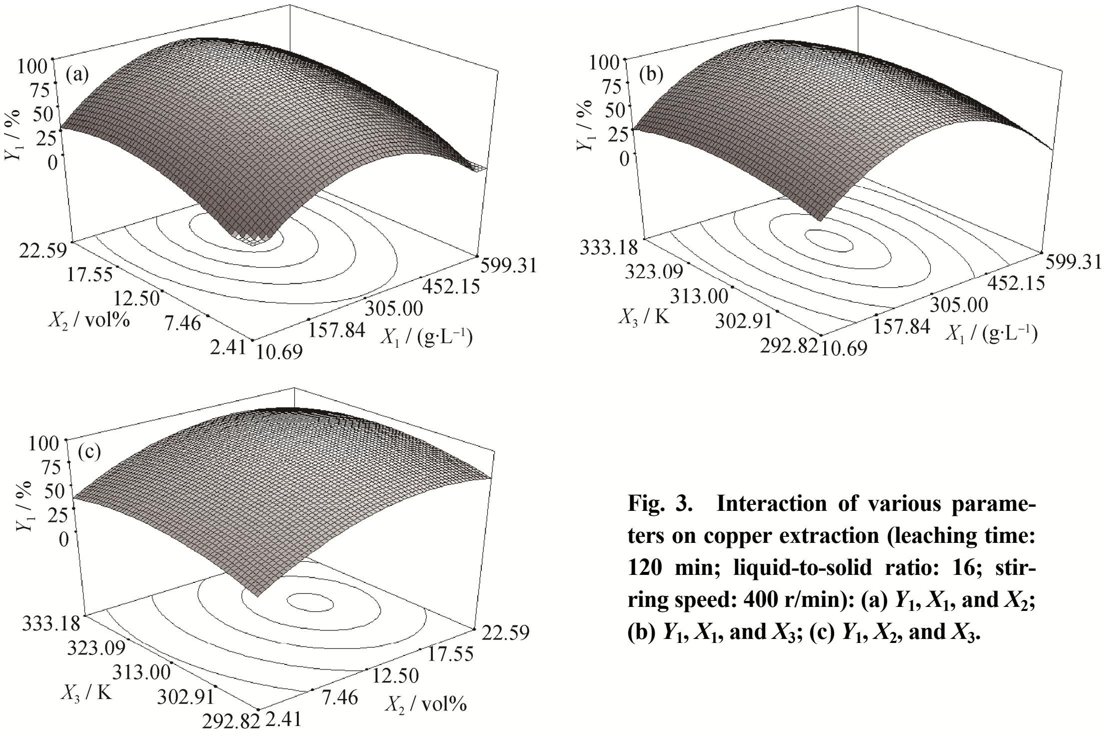

Fig. 3. Interaction of various parameters on copper extraction (leaching time: 120 min; liquid-to-solid ratio: 16; stirring speed: 400 r/min): (a) Y_1, X_1, and X_2; (b) Y_1, X_1, and X_3; (c) Y_1, X_2, and X_3.

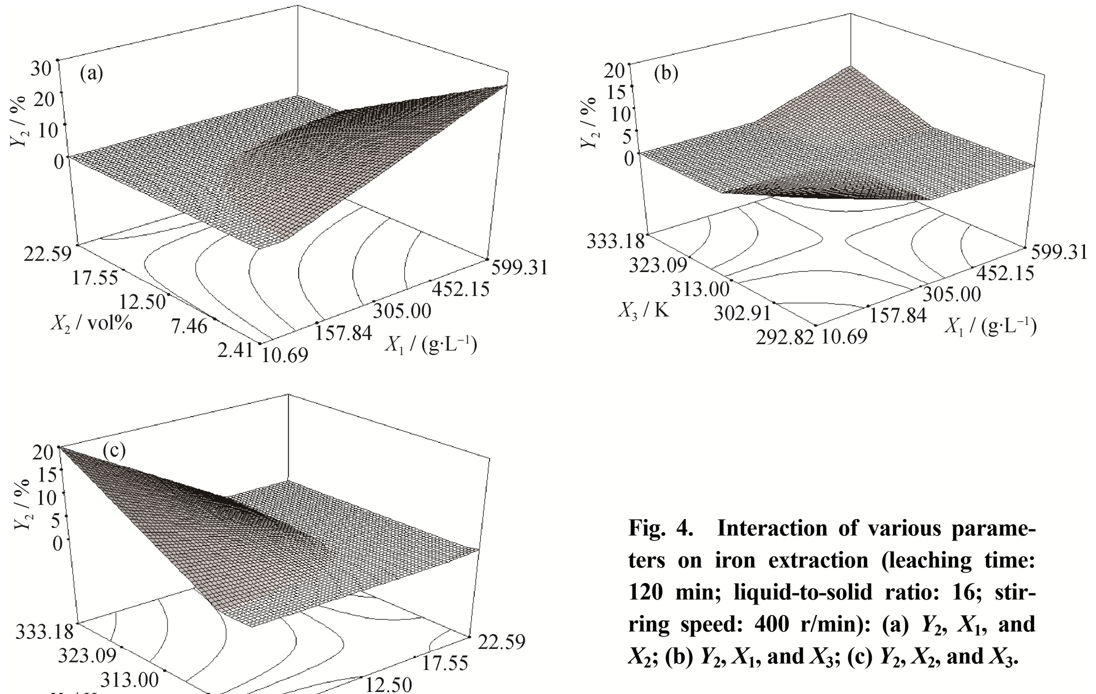

Fig. 4. Interaction of various parameters on iron extraction (leaching time: 120 min; liquid-to-solid ratio: 16; stirring speed: 400 r/min): (a) Y_2, X_1, and X_2; (b) Y_2, X_1, and X_3; (c) Y_2, X_2, and X_3.

$$2CuFeS_2 + 8NH_3 + 6OH^- + 3H_2O \rightarrow 2Cu(NH_3)_4^{2+} + S_2O_3^{2-} + 2S + 2Fe(OH)_3 + 3H_2 + 8e^- \quad (6)$$

The optimization criterion was defined to maximize the copper extraction while minimizing the iron extraction. The optimum point was selected, the experiment was run at this point, and the responses were determined (Table 5).

Table 5. Optimum leaching conditions with model validation

X_1 / (g·L^{-1})	X_2 / vol%	X_3 / K	Leaching rate / %			
			Predicted		Experimental	
			Cu	Fe	Cu	Fe
328.02	16.20	321	97.63	0.01	98.14	0

Similar to the results of previous studies, the results indicate that selective leaching can be obtained under conditions of using basic leach reactant together with APS [19]. However, the dissolution mechanism differs with respect to iron dissolution in an autoclave system [20].

Fig. 5 shows the XRD pattern of the leaching residue. The XRD pattern shows only minor chalcopyrite peaks and reveals that the iron compound was enriched in the residue as a result of the highly alkaline leaching conditions. Consequently, selective leaching and high copper extraction were achieved under the optimum leaching conditions.

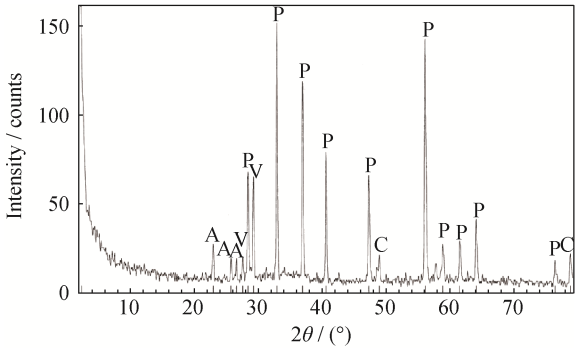

Fig. 5. XRD pattern of the leaching residue (A—S; C—chalcopyrite ($CuFeS_2$); P—pyrite (FeS_2); V—covellite (CuS)).

A proposed process flow sheet is illustrated in Fig. 6. The process proposed for selective copper leaching may be economically feasible if the APS can be recovered.

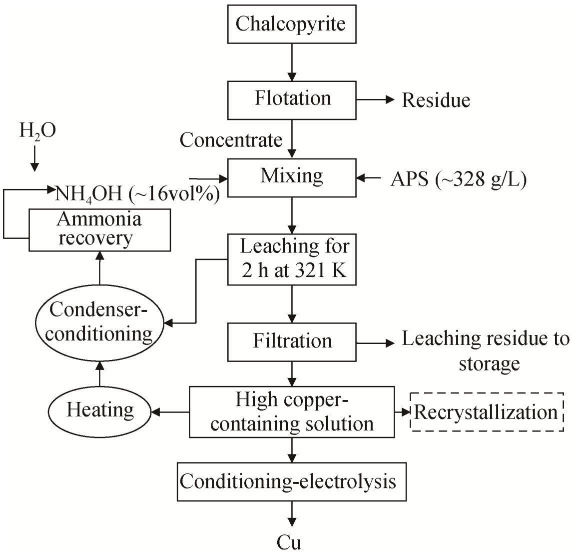

Fig. 6. Proposed flow sheet for selective copper leaching from chalcopyrite.

4. Conclusions

The effects of three parameters as independent factors in a model design (i.e., APS concentration, ammonium hydroxide addition, and leaching temperature) were investigated for leaching of chalcopyrite concentrate. The CCD was used to determine the optimum leaching conditions. The optimum conditions were defined as maximum copper extraction with minimal iron. Under the optimum leaching conditions, Cu and Fe extractions of 98.14% and 0% were obtained, respectively. These results suggest that the selective leaching of chalcopyrite concentrate is feasible, without the use of a conventional oxidizer. Also, XRD analysis of the residue revealed the present of iron compounds, supporting the feasibility of selective chalcopyrite leaching. The proposed model well fit the experimental data, as indicated by the obtained R^2 correlation coefficient.

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References

[1] W.G. Davenport, M.J. King, M.E. Schlesinger, and A.K. Biswas, *Extractive Metallurgy of Copper*, Pergamon, London, 2002.

[2] T.S. Qiu, G.H. Nie, J.F. Wang, and L.F. Cui, Kinetic process of oxidative leaching of chalcopyrite under low oxygen pressure and low temperature, *Trans. Nonferrous Met. Soc. China*, 17(2007), No. 2, p. 418.

[3] M. Al-Harahsheh, S. Kingman, and A. Al-Harahsheh, Ferric chloride leaching of chalcopyrite: Synergetic effect of $CuCl_2$, *Hydrometallurgy*, 91(2008), No. 1-4, p. 89.

[4] F. Carranza, N. Iglesias, A. Mazuelos, I. Palencia, and R. Romero, Treatment of copper concentrates containing chalcopyrite and non-ferrous sulphides by the BRISA process, *Hydrometallurgy*, 71(2004), No. 3-4, p. 413.

[5] R. Padilla, M. Rodriguez, and M.C Ruiz, Sulphidation of chalcopyrite with elemental sulphur, *Metall. Mater. Trans. B*, 34(2003), No. 1, p. 15.

[6] M.D. Turan, Z.A. Sarı, and J.D. Miller, Leaching of blended copper slag in microwave oven, *Trans. Nonferrous Met. Soc. China*, 27(2017), No. 6, p. 1404.

[7] M.D. Turan, M. Sarıkaya, Z.A. Sarı, A. Haxiaj, T. Depci, A. Demiraslan, and H. Nizamoğlu, Investigating and optimization of copper extraction from chalcopyrite concentrate with hydrogen peroxide in presence of acetic acid, *Curr. Phys. Chem.*, 7(2017), No. 4, p. 267.

[8] M.D. Turan, M. Boyrazlı, and H.S. Altundoğan, Improving of copper extraction from chalcopyrite by using NaCl, *J. Cent. South Univ.*, 25(2018), No. 1, p. 21.

[9] E.M. Córdoba, J.A. Muñoz, M.L. Blázquez, F. González, and

A. Ballester, Leaching of chalcopyrite with ferric ion. Part III: Effect of redox potential on the silver-catalyzed process, *Hydrometallurgy*, 93(2008), No. 3-4, p. 97.

[10] S. Vafaeian, M. Ahmadian, and B. Rezaei, Sulphuric acid leaching of mechanically activated copper sulphidic concentrate, *Miner. Eng.*, 24(2011), No. 15, p. 1713.

[11] M. Chakravorty and S. Srikanth, Kinetics of salt roasting of chalcopyrite using KCl, *Thermochim. Acta*, 362(2000), No. 1-2, p. 25.

[12] R. Padilla, E. Olivares, M.C. Ruiz, and H.Y. Sohn, Kinetics of the sulfidation of chalcopyrite with gaseous sulfur, *Metall. Mater. Trans. B*, 34(2003), No. 1, p. 61.

[13] K. Tkáčová and P. Baláž, Reactivity of mechanically activated chalcopyrite, *Int. J. Miner. Process.*, 44-45(1996), p. 197.

[14] M.S. Bafghi, A.H. Emami, A. Zakeri, and J.V. Khaki, Effect of mechanical activation on the kinetics of leaching of chalcopyrite in the ferric sulfate media, *Iran. J. Mater. Sci. Eng.*, 7(2010), No. 2, p. 30.

[15] A. Katsiapi, P.E. Tsakiridis, P. Oustadakis, and S. Agatzini-Leonardou, Cobalt recovery from mixed Co–Mn hydroxide precipitates by ammonia–ammonium carbonate leaching, *Miner. Eng.*, 23(2010), No. 8, p. 643.

[16] R.K. Nadirov, L.I. Syzdykova, A.K. Zhussupova, and M.T. Usserbaev, Recovery of value metals from copper smelter slag by ammonium chloride treatment, *Int. J. Miner. Process.*, 124(2013), p. 145.

[17] D. Feng and J.S.J. Van Deventer, Leaching behaviour of sulphides in ammoniacal thiosulphate systems, *Hydrometallurgy*, 63(2002), No. 2, p. 189.

[18] M.D. Turan and H.S. Altundoğan, Leaching of a copper flotation concentrate with ammonium persulfate in an autoclave system, *Int. J. Miner. Metall. Mater.*, 21(2014), No. 9, p. 862.

[19] M.D. Turan, Direct selective leaching of chalcopyrite concentrate, *Can. Metall. Q.*, 53(2014), No. 4, p. 444.

[20] M.D. Turan, H. Arslanoğlu, and H.S. Altundoğan, Optimization of the leaching conditions of chalcopyrite concentrate using ammonium persulfate in an autoclave system, *J. Taiwan Inst. Chem. Eng.*, 50(2015), p. 49.

[21] G.H. Jeffery, J. Bassett, J. Mendham, and R.C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, Addison-Wesley Longman, London, 1989.

[22] D.C. Montgomery, *Design and Analysis of Experiments*, John Wiley & Sons, USA, 2001.