Optimization of sulfuric acid leaching of roasted chalcopyrite concentrate with Box–Wilson experimental design

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Abstract

Chalcopyrite (CuFeS_2) is commonly used ore in production of copper, but leaching of this ore is very slow and inefficient due to “passivation” during leaching at atmospheric conditions. In this study, in order to overcome drawbacks of the passivation layers, the concentrate supplied from Eti Bakır A.Ş. Küre Plant in Turkey was roasted at 600 °C for 1 h and after leached. Box–Wilson procedure of statistical experimental design was utilized to identify the effects of significant leaching variables for instance leaching time (X_1 ; 10–120 min), solid/liquid ratio (X_2 ; 0.01–0.20), and H_2SO_4 concentration (X_3 ; 0.01–1.00 M) on Cu extraction (%) from roasted concentrate and was tried to be optimized. The coefficients of response functions have been calculated by regression analysis, and the estimates have been found to be well in line with the experimental outcomes. The optimal leaching parameters, time, solid/liquid rate and H_2SO_4 concentration were determined as 115 min, 0.116, and 0.71 M, respectively, and the highest Cu extraction (%) value was calculated as 92.45%.

Keywords Chalcopyrite concentrate · Sulfuric acid · Leaching · Box–Wilson experimental design · Optimization

1 Introduction

Copper, one of the most important metals for humanity for more than five thousand years [1, 2], is still among the most common metal used in the industry [3–5]. In nature, copper is generally found in the form of sulfide and oxide minerals such as azurite, malachite, tenorite, chrysocolla, bornite, brochantite, enargite, chalcopyrite, chalcocite, and covellite [3–8]. The most utilized mineral for the copper production [1, 2], chalcopyrite (CuFeS_2), is an important and plentiful source that accounts for about 70% of all copper in the world, and is one of the widest spread copper-bearing minerals [9–14].

The copper extraction from chalcopyrite (CuFeS_2) is performed by using hydrometallurgical and pyrometallurgical processes. About 80–85% of the copper production in the world is executed with the traditional pyrometallurgical

processes, which consist of concentration by flotation, smelting, fire refining, and electro-refining routes [1, 2, 11, 12, 15–19]. Recently, due to technical and economic reasons of the traditional pyrometallurgical process [20] such as high-grade ore requirement [21], high investment for smelting and refining plants, as well as undesirable environmental effects caused by the formation of sulfur oxides (SO_2 and/or SO_3) [17, 19, 21–23], the hydrometallurgical process becomes an alternative route to copper extraction from low grade and complex sulfide copper concentrates [17, 20, 24–29]. Copper extraction from chalcopyrite by hydrometallurgical methods can be classified according to used type of solvent such as chloride/chlorine systems, nitric acid, sulfuric acid, ammoniacal solution and biological systems [19, 30–32]. In many studies in the literature, sulfuric acid and hydrochloric acid are the most preferred for leaching in acidic environments [32–36]. It is stated in the literature

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that the consumption of sulfuric acid, which is the cheapest solvent for leaching of oxidized copper ores [37], varies between 0.4 and 0.7 tons H_2SO_4 per ton of copper recovered, depending on the nature of the ore [36].

Despite the advantages of the hydrometallurgical process such as short construction time, low cost, operation simplicity, typically less energy-intensive, more suitable for low grade and complex ore types, and lower environmental impacts [18, 38–42], the extraction of copper from chalcopyrite in acidic medium is both very slow and ineffective at low temperatures due to the stable passivation layers [11, 17, 19, 22, 33–35, 42–48]. It has been stated in the literature that grinding to a very fine particle size [49], pressure, temperature, powerful oxidizing agents [7, 19, 32, 36, 50–58], and roasting/calcination of the ore/concentrate [19, 30, 59] can be used to increase the dissolution kinetic and copper extraction recovery by eliminating the effect of this passivation layer forms, whose chemistry, nature, and formation mechanism are still poorly understood [11, 15, 32, 42, 60–62].

Roasting is the key unit operation in converting low solubility sulfide ores into high solubility oxides. During roasting, chalcopyrite reacts with air and decomposes to generate copper sulfate, sulfur dioxide, sulfur, copper-iron oxides, copper-oxy sulfate, and copper ferrite [63, 64]. In between 577 and 667 °C temperature range, it is stated that the roasting reactions Eq. (1) occurring as follows and CuSO_4 is formed, and above 745 °C, CuFe_2O_4 is formed according to the following reaction Eq. (2) [19, 30, 65–67]. It is stated that SO_2 , which is a problem in the roasting process as well as the pyrometallurgical processes and which can be converted into sulfuric acid normally [18, 19], can also be neutralized by using CaO according to the reaction Eq. (3) given below [68, 69]. In our study, our products obtained after roasting are in the form of CuFe_2O_4 (Cu Ferrite) and Cu_4O_5 . CuFe_2O_4 phase seen in the mineralogical analysis is $\text{CuO} \cdot \text{Fe}_2\text{O}_3$. Fe_2O_3 is not soluble in H_2SO_4 solutions. Cu_4O_5 is a metastable phase, and it comprises of CuO and Cu_2O . Possible dissolution reaction suggestions for CuFe_2O_4 (Cu Ferrite; $\text{CuO} \cdot \text{Fe}_2\text{O}_3$), CuO and Cu_2O in H_2SO_4 solution were added as Eqs. (4 and 5) [70–73].

Table 1 Average mineralogical analysis results of chalcopyrite concentrate

Component	Weight (%)
CuFeS_2	30
FeS_2	30
CuFe_2S_3	20
Fe_2O_3	15
FeS	5

Table 2 Average mineralogical analysis results of roasted chalcopyrite concentrate

Component	Weight (%)
FeS_2	30
Fe_2O_3	25
CuFe_2O_4 [Cu ferrite; $\text{CuO} \cdot \text{Fe}_2\text{O}_3$]	20
Cu_4O_5	15
Fe_3O_4	10

Significant copper resources in Turkey are scattered in the north of the country, and Küre copper ore deposit is one of the most important ones. Some studies have been carried out on leaching of Küre chalcopyrite concentrate using with some lixiviants [74–78]. However, it has not been used in roasted the concentrate leaching in previous studies. The aim of this study was to determine the suitability of the roasted Küre Chalcopyrite Concentrate for H_2SO_4 leaching after roasting and to produce data on the evaluation of domestic chalcopyrite ore/concentrate. For this purpose, the effects of leaching time, solid/liquid ratio, and H_2SO_4 concentration which are important parameters in roasted chalcopyrite leaching on Cu extraction (%) were examined by using Box–Wilson experimental design and optimum parameters were determined.

2 Materials and methods

2.1 Materials

Chalcopyrite concentrate samples were supplied from Küre Copper Concentrator Plant in Kastamonu, Turkey (Eti Bakır A.Ş.), flotation concentration plant. It was sieved to $-212 \mu\text{m}$ before dried at 105 °C for 12 h. The mineralogical analysis results of the chalcopyrite concentrate samples are given in Table 1, and the mineralogical analysis results of the roasted concentrate, which has been subjected to oxidizing roasting process at 600 °C for 1 h according to the data in the literature [6, 19, 20, 42, 63, 65, 67, 79–83], are given in Table 2.

The chalcopyrite concentrates samples were roasted by using Protherm brand MoS-B 180/8 Model (1.800 °C) Muffle Furnace in Hitit University Faculty of Engineering

Department of Metallurgical and Materials Engineering. X-Ray Diffraction (XRD) analysis was carried out by using the PANalytical brand X'Pert Pro model XRD Device in Istanbul Technical University Faculty of Engineering Department of Metallurgical and Materials Engineering Laboratories. XRF analysis was carried out by using Thermo Scientific brand Niton™ XL3t 950 GOLDD + model XRF Spectrometer in Cumhuriyet University Faculty of Engineering Department of Metallurgical and Materials Engineering. Solutions of H₂SO₄ (Sigma-Aldrich) were used as lixiviant. All chemicals used were at least analytical grade.

2.2 Methods

The experiments were performed within the scope of the study using the Box–Wilson experimental design, and optimization was made for the parameters effective in the extraction. In this context, independent parameters in the Box–Wilson experimental design method were used;

$$Y = 45.28 + 2.19(X_1) - 124.72(X_2) + 1.92(X_3) - 6.16(X_1 * X_2) - 4.52(X_1 * X_3) + 133.03(X_2 * X_3) - 0.021(X_1 * X_1) - 620.88(X_2 * X_2) + 103.50(X_3 * X_3) + 1.28(X_1 * X_2 * X_3) + 0.12(X_1 * X_1 * X_2) + 0.035(X_1 * X_1 * X_3) + 38.25(X_1 * X_2 * X_2) - 0.64(X_1 * X_1 * X_2 * X_2) \quad (7)$$

time: 10–120 min, solid/liquid ratio: 0.01–0.20, and H₂SO₄ concentration: 0.01–1.00 M.

The experiments were employed in a 400-mL beaker placed in a temperature-controlled water bath and sealed with a watch glass. Heidolph MR Hei-Tec model a magnetic stirrer having a digital controller unit, timer and thermostat was used for effective mixing and heating. A magnetic stirrer provided the agitation (400 rpm) required for homogeneity. Mono-distilled water (pH $\cong$ 6.5, approximately) was employed in the leaching experiments. After the required leaching temperature (60 °C) was achieved, the amount of chalcopyrite required for the calculated solid/liquid ratio (0.01–0.20) was added to the 200 mL solution containing water and H₂SO₄, required for calculated H₂SO₄ concentration (0.01–1.00 M). At the end of the desired leaching time (10–120 min), the suspension was filtered and the solid residues were thoroughly washed, dried, and the amount of copper in the filtrate was identified by XRF analysis. In this study, the Cu extraction (%) values, which are a measure of how much of the total copper is leached, were calculated using Eq. (6) given below:

$$\text{Cu Extraction (\%)} = \frac{\text{Amount of Dissolved Cu}}{\text{Amount of Cu in Feed}} * 100. \quad (6)$$

2.2.1 Box–Wilson experimental design

Details of the Box–Wilson statistical experimental design procedure can be found in the literature [84, 85]. Three working variables, i.e., time, solid/liquid ratio and the H₂SO₄ concentration, were chosen as the most significant independent variables. The time (X_1) was changed between 10 and 120 min; the solid/liquid ratio (X_2) between 0.01 and 0.20; and the H₂SO₄ concentration (X_3) between 0.01 and 1.00. The experimental design comprised of six axial points (A), eight factorial points (F), and three center points (C). For estimating the experimental error calculation, the center point was repeated three times. The experimental terms as coded values and real values utilized for the Box–Wilson statistical design are given in Table 3.

The Cu extraction (Y) was correlated with the other independent variables (X_1, X_2, X_3) using a quadratic regression. Design Expert 8.0 was used to determine Eq. (7) coefficients by regression analysis of the experimental data.

3 Results and discussion

A comparison of the values of empiric and predicted for the Cu extraction (%) is summarized in Table 4. The detected Cu extraction (%) values varied between 42.13% and 90.11%. The determination coefficient (R^2 values) between the observed and predicted value was 0.9959 for Cu extraction (%), indicating well in line between the values detected and those predicted.

3.1 The effects of time and solid/liquid ratio

The variation of the Cu extraction (%) in a fixed 0.505 M of H₂SO₄ concentration depending on time and solid/liquid ratio is given in Fig. 1.

As seen from Fig. 1, at the time rise up to 50 min, the Cu extraction (%) declined with increasing solid/liquid ratio, and reached a minimum value in the maximum solid/liquid ratio. In between 0.05 and 1.6 solid/liquid ratio range, the Cu extraction (%) values started to increase again with increasing time above 50 min and the Cu extraction (%) reached its maximum value in about 120 min. However, the Cu extraction (%) values rapidly decreased both at low (less than 0.5) and high

Table 3 Experimental conditions according to a Box–Wilson statistical design

Experiment no.	Coded values			Real values		
	X_1	X_2	X_3	Time (min)	Solid/liquid ratio	H ₂ SO ₄ concentration (M)
A1	1.73	0	0	120	0.105	0.505
A2	−1.73	0	0	10	0.105	0.505
A3	0	1.73	0	65	0.20	0.505
A4	0	−1.73	0	65	0.01	0.505
A5	0	0	1.73	65	0.105	1.00
A6	0	0	−1.73	65	0.105	0.01
F1	1	1	1	96.75	0.16	0.79
F2	1	1	−1	96.75	0.16	0.22
F3	1	−1	1	96.75	0.05	0.79
F4	1	−1	−1	96.75	0.05	0.22
F5	−1	1	1	33.25	0.16	0.79
F6	−1	1	−1	33.25	0.16	0.22
F7	−1	−1	1	33.25	0.05	0.79
F8	−1	−1	−1	33.25	0.05	0.22
C1	0	0	0	65	0.105	0.505
C2	0	0	0	65	0.105	0.505
C3	0	0	0	65	0.105	0.505
C (ave.)	0	0	0	65	0.105	0.505

Table 4 Observed and predicted Cu extraction (%) values

Experiment no.	Cu extraction (%)	
	Observed	Predicted
A1	73.96	73.96
A2	57.59	57.59
A3	42.13	42.13
A4	55.85	55.85
A5	73.75	73.75
A6	90.11	90.11
F1	75.21	72.08
F2	50.35	50.27
F3	69.71	69.60
F4	63.93	63.86
F5	63.37	63.29
F6	50.21	50.16
F7	70.68	70.64
F8	68.52	68.50
C (ave.)	56.57	56.57

(over than 1.6) solid/liquid ratio, at time above 50 min. At medium solid/liquid ratio values, increasing Cu extraction (%) due to the increase in time over 50 min can be attributed to the increased interaction of the particles with H₂SO₄ solutions [86]. At low leaching time (especially under 50 min), the decrease in Cu extraction (%)

Fig. 1 Effects of time and solid/liquid ratio on Cu extraction (%) (H₂SO₄ concentration: 0.505 M)

due to the increase in the solid/liquid ratio may be caused by the increase in the amount of particles per unit volume of the lixiviant [63, 69, 87, 88], worsening of mixing and increase in mass transfer resistance due to increased viscosity [89], and the worsening of the solid and liquid contact [88]. But, in industrial applications, it is desired to work at high solid/liquid ratios as much as possible due to economic factors.

Fig. 2 Effects of time and H_2SO_4 concentration on the Cu extraction (%) (solid/liquid ratio: 0.105)

3.2 Effects of time and H_2SO_4 concentration

The variation of the Cu extraction (%) at a constant solid/liquid ratio of 0.105, depending on the time and H_2SO_4 concentration, is given in Fig. 2.

Figure 2 shows that with the increase in time, the Cu extraction (%) increases and reaches its maximum values in the range of about 70–80 min at low H_2SO_4 concentration. At higher times, the Cu extraction (%) again decreased. In the range of 0.35–0.45 M H_2SO_4 concentration, the Cu extraction (%) did not change much depending on the time. At the higher H_2SO_4 concentration, the Cu extraction (%) values decreased rapidly to the minimum values in the range of approximately 70–80 min and reached the maximum values rapidly increasing again over 80 min. The highest Cu extraction (%) values were reached at the maximum values of the time and H_2SO_4 concentration. In other words, The Cu extraction (%) values increased due to the increase in the H_2SO_4 concentration in low and high times, whereas the Cu extraction (%) decreased as the H_2SO_4 concentration increased in the medium periods (in the range of 70–80 min).

Acid concentration in hydrometallurgical processes is one of the most significant variables to be controlled in terms of reaction kinetics and the economy [90]. It is known that increasing the acid concentration up to a certain value will increase leaching efficiency [91, 92]. At low H_2SO_4 concentration, with increasing the time up to 70 min, increasing Cu extraction (%) can be attributed to the increased interaction of the particles with H_2SO_4 concentration [86]. At low H_2SO_4 concentration, decreasing Cu extraction (%) due to the increase in time over 80 min can be attributed to the increase in pH value due to the dissolved oxygen in the solution [93, 94]. This

Fig. 3 The effects of H_2SO_4 concentration and solid/liquid ratio on the Cu extraction (%) (time: 65 min)

decrease may also have been due to the precipitation of dissolved Cu. The fact that Cu extraction (%) does not change much in the concentration range of 0.35–0.45 M H_2SO_4 at all times can be explained by the reduction of possible contact of H_2SO_4 solution with the particle surface [55], due to the precipitation of ferric sulfate forms on the surfaces and pores of the particles [11, 95–98]. Similar evaluations can be said in the explanation of low Cu extraction (%) at high H_2SO_4 concentrations in the range of 70–80 min.

3.3 Effects of H_2SO_4 concentration and solid/liquid ratio

The change in the Cu extraction (%) depending on the H_2SO_4 concentration and solid/liquid rate at 65 min constant time is given in Fig. 3.

As seen in Fig. 3, both at low and high H_2SO_4 concentrations, Cu extraction (%) values tend to increase at all solid/liquid ratios studied. The low Cu extraction (%) values were obtained at medium H_2SO_4 concentration (between 0.3 and 0.5 M). Also, regardless of the H_2SO_4 concentrations studied, the Cu extraction (%) values increased with increasing solid/liquid ratio up to 0.1 and it decreased partially afterward. The reasons for the increase/decrease in Cu extraction (%) depending on both H_2SO_4 concentration and solid/liquid ratio are discussed in the previous paragraphs.

3.4 Optimization

The roasted chalcopyrite concentrate was leached at Experiment No.: A6 both with a Cu extraction (%) of 90.11% and the lowest grade such as 1.42% Cu in solid residue. Optimum time (X_1 ; 10–120 min), solid/liquid ratio (X_2 ; 0.01–0.20), and H_2SO_4 concentration (X_3 ; 0.01–1.00 M) provided that

selected parameters which are the most important independent variables in the chalcopryite leaching, 115 min, 0.116 and 0.71 M, respectively, were determined, and the highest Cu extraction (%) value was calculated as 92.45%.

4 Conclusion

In this study, the suitability of Cu extraction (%) by using leaching after the roasting method from chalcopryite concentrate was identified by using the Box–Wilson statistical experimental design method. The Box–Wilson statistical experimental design method was found to be viable for modeling the effects of significant parameters on the Cu extraction (%) of roasted chalcopryite concentrates. Response function predictions based on regression analysis were well in line with the experimental results.

The effects of time, solid/liquid ratio and H_2SO_4 concentration on the Cu extraction (%), which are among the most important parameters effective in leaching of roasted chalcopryite concentrate, were examined and the optimum parameters were determined as 115 min, 0.116 and 0.71 M, respectively, and the highest Cu extraction (%) value was calculated as 92.45%. Copper in the roasted chalcopryite concentrate was leached with a 90.11% Cu extraction, and the copper grade in the solid residue was the lowest value as 1.42% Cu. It is seen that higher Cu extraction (%) values can be achieved with a study to be performed in the optimum parameters.

It may also be useful to examine parameters such as mixing speed, temperature and type of solvent that are effective in leaching. In addition, it will be useful to examine the behavior of some impurities such as Fe both in the leaching and in extraction from solution processes.

Compliance with ethical standards

Conflict of interest The authors do not have any conflicts of interest.

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