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Leaching of Flotation Concentrate of Oxide Copper Ore from Sepon Mine, Lao PDR

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Abstract**—**Acid leaching of flotation concentrate of oxide copper ore containing mainly of malachite was performed in a standard agitation tank with various parameters. The effects of solid to liquid ratio, sulfuric acid concentration, agitation speed, leaching temperature and time were examined to get proper conditions. The best conditions are 1:8 solid to liquid ratio, 10% concentration by weight, 250 rev/min, 30 °C and 5-min leaching time in respect. About 20% Cu grade assayed by atomic absorption technique with 98% copper recovery was obtained from these combined optimum conditions. Dissolution kinetics of the concentrate was approximated as a logarithmic function. As a result, the first-order reaction rate is suggested from this leaching study.

Keywords**—**Agitation leaching, dissolution kinetics, flotation concentrate, oxide copper ore, sulfuric acid.

I. Introduction

The demand of high-grade copper metal makes it necessary to extract copper ores using hydrometallurgical processing method. In recent years, copper cathode is mostly produced by acid leaching, solvent extraction and electro-winning (L-SX-EW) technology [1]-[4]. This technology is already proved to be a successful process for copper recovery, especially for low grade copper ores.

Copper ores can be broadly classified into two groups: sulfide and oxide [5]. Chalcopyrite is a major sulfide ore processed using flotation technique in Phubia mine located in the northern part of Lao PDR. On the other hand, malachite and other oxide ores are processed using hydrometallurgical extraction in Sepon mine located in the southern part of the country. Leaching of oxide copper ore contained mainly of malachite with sulfuric acid (H_2SO_4) can be given as:

$$CuCO_3Cu(OH)_2 + 2H_2SO_4 \rightarrow 2Cu^{2+} + 2SO_4^{2-} + CO_2 + 3H_2O \quad (1)$$

Bingöl and Canbazoğlu [6] noted that H_2SO_4 is the cheapest leaching agent for oxidized copper ores. However, its increasing dosage and cost are also important economic factors for leaching of complex oxide ores. Malachite is normally associated with carbonate rock e.g. limestone ($CaCO_3$) and dolomite [$(Ca,Mg(CO_3)_2$] and iron-bearing minerals such as hematite (Fe_2O_3). These gangue minerals consume large amounts of H_2SO_4, as shown in chemical reactions [7]-[10]:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \quad (2)$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \quad (3)$$

In order to reduce the large amount of sulfuric acid used, the combined flotation and L-SX-EW technologies are very interesting to process that kind of oxide ore. Rattanakawin and Varsailora [11] have shown that flotation of oxide copper ore from Sepon mine, Lao PDR with sodium oleate has a successful outcome. The floated copper concentrate has copper content more than 25% compiled with the market standard. Therefore, it is very promising to further study about processing of that concentrate by using L-SX-EW technology to yield high-grade cathode copper. The objective of this research was to study the effects of various parameters: leaching time, sulfuric acid concentration, agitation speed, solid to liquid ratio, and leaching temperature on the leaching performance. The percent copper recovery was used as a criterion to measure the performance. Also, kinetics of copper dissolution at the optimal leaching conditions was examined.

II. Materials and Method

A. Materials

The sample used in this study obtained from flotation concentrate of oxide copper ore collected from Sepon mine, Savannakhet, Lao PDR. Mineralogical analysis using x-ray diffraction (XRD) showed that malachite is a major mineral while quartz, kaolinite and marcasite are gangue minerals. Therefore, this sample was floated with sodium oleate and other flotation reagents at 65% passing size of 75 μm successfully [11]. Leaching of the flotation concentrate was carried out in a 400 ml standard agitation tank. The tank was equipped with a six flat blade turbine driven by a controllable stirrer. The agitation speed of stirrer was monitored by a tachometer. Moreover, hot water bath with a thermometer was utilized to control the tank temperature for this agitation leaching.

Analytical grade chemicals were used in this leaching study. Sulfuric acid is a main chemical lixiviant. Besides, nitric acid (HNO_3) was used to digest and/or dilute the leaching products (feed, leachate and tailing), and copper standard solution prior to do chemical analysis. Moreover, 1000 mg copper standard ($CuCl_2$ in H_2O; Merck KgaA, Darmstadt, Germany) was used to make various standard solutions to generate a calibration curve for an atomic

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absorption spectrometry.

B. Analysis

Chemical composition of the flotation concentrate sample was analyzed using x-ray fluorescence (XRF) technique by Vanta handheld XRF analyzer, as described by Rattanakawin and Varsailor [11]. Measuring conditions were set in Geochem2 mode. There are two x-ray beams: beam number 1 radiating at 40 KV, while beam number 2 at 10 KV with measuring time of 30 min/beam in this mode. The sample was filled into a cup covered by 4 micron Prolene® Film. Then the sample in the filled cup was x-rayed with the above-mentioned conditions.

All leaching products were analyzed using Perkin Elmer, Model 3310 atomic absorption spectrometry (AAS) at the wavelength of 324.8 nm with two replications. The AAS measuring condition was set at the lamp current of 15 mA with 3 sec delay readings.

Firstly, the 1000 mg copper standard was diluted with 1% HNO_3 solution into different concentrations of 0.5 ppm, 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm. Secondly, the dilution was done in a 100 ml volumetric flask from 1000 ppm to 100 ppm. After that, the 100 ppm solution was further diluted separately into 0.5 ppm, 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm with 99.5 ml, 99 ml, 98 ml, 97 ml, 96 ml and 95 ml of that dilute acid in respect. Finally, these diluted solutions were used to make a calibration curve for the AAS measurement using the above-commented condition.

The leachates from all experiments were diluted with the dilute HNO_3 solution to facilitate the AAS measurement. In order to prepare sample solutions of feed and tailing, 0.1 g of feed and 0.5 g of tailing were separately digested with 50 ml of 65% HNO_3 solution in 100 ml beaker placed on a hot plate with temperature of 80ºC for 1 hour. After that, it was added 20 ml of 1% HNO_3 solution to the beaker before making any filtration. Then, filter the dissolved solution into a 400 ml Erlenmeyer flask by using Whatman #41 filter. Next, the filtrated residue was triple-washed with the dilute acid. Finally, the acid was added and made up the dissolved solution to 400 ml of the flask. This stock solution was further pipetted into 100 ml volumetric flask and diluted with 1% HNO_3 solution to a desired concentration which is appropriate for the AAS measurement.

C. Agitation Leaching

Agitation leaching of flotation concentrate of oxide copper ore contained mainly of malachite was performed as follows:

1. Sample the flotation concentrate using a Jones Riffle Splitter.
2. Put the sample into the standard agitation tank together with dilute sulfuric acid with desired concentration.
3. Investigate the effect of leaching times of 1 min, 2 min, 3 min, 4 min, 5 min, 10 , min 15 min and 30 min with H_2SO_4 (10% w/w), agitation speed (250 rev/min or rpm), solid to liquid ratio (1:8), leaching temperature (30°C) on leaching performance.
4. Examine the effect of H_2SO_4 concentrations of 2.5%, 5%, 7.5%, 10% and 12.5% (w/w) with agitation speed (250 rpm), solid to liquid ratio (1:8) and leaching temperature (30°C) on the performance at the proper leaching times considered above.
5. Study the effect of agitation speed of 0 rpm, 50 rpm, 100 rpm, 125 rpm, 250 rpm and 500 rpm with solid to liquid ratio (1:8) and leaching temperature (30ºC) on the performance at the appropriate leaching time and acid concentration.
6. Test the effect of solid to liquid ratio of 1:2, 1:4, 1:6, 1:8 and 1:10 with leaching temperature (30ºC) on the performance at the selected leaching time, acid concentration and agitation speed.
7. Check the effect of leaching temperatures at 30°C, 45°C, 60°C, 75°C and 90°C with the best leaching time, acid concentration, agitation speed and solid to liquid ratio on the performance to extract the flotation concentrate.
8. Explore an initial dissolution rate of the concentrate with H_2SO_4 (10% w/w concentration), agitation speed (250 rpm), solid to liquid ratio (1:8) and leaching temperature (30°C) from lap times 1-5 min.
9. Filter the leachate into 400 ml volumetric flask by using a funnel with the dampened filter paper.
10. Dilute the leachate at the proper copper concentration prior to assaying by using the AAS instrument.
11. Digest and then dilute the feed and tailing solution before analyzing with the AAS.
12. Evaluate the agitation leaching performance by using copper recovery (%R) as the criterion. Calculate %R using the two-product formula on the basic of product weights as:

$$R = \frac{W_l}{W_l \, x \, W_r} \, x \, 100\% \quad (4)$$

where W_l and W_r are weights of copper in the leachate and tailing in respect [4].

TABLE I
CHEMICAL COMPOSITION OF COPPER CONCENTRATE

Elements	(%)
Cu	20.5
Si	17.3
Mg	10.2
Fe	4.30
Al	1.97
Ca	1.83
Mn	0.50
S	0.25
K	0.23
Ti	0.13
Zn	0.11
Light elements	42.5

III. Results and Discussion

A. Chemical Composition

Chemical composition of the flotation concentrate analyzed using Vanta Handheld XRF Analyzer is shown in Table I. The results show that Cu (20.53%) is a major element. Other constituents are 17.31% Si, 10.18% Mg, 4.3% Fe, 1.97% Al, 1.83% Ca, 0.5% Mn, 0.25% S, 0.23% K, 0.13% Ti, 0.11% Zn and 42.54% light elements. This result is corresponding well with the above-indicated mineralogical analysis [11].

B. Effect of Leaching Time

The effect of leaching time on copper grade and recovery of the leachate is shown in Table II and Fig. 1, respectively. It was found that the grade slightly increases with the leaching time up to 10 min. However, the recovery increases sharply with the time especially in the initial stage of leaching from 0-5 min.

At 5 min, 98.6% of copper recovery was obtained. After this time, the recovery slightly increases and reaches the plateau after 10 min with about 99.0% recovery. Therefore, 5 min leaching time was expected to be an optimum time. This time was chosen as the best condition for further leaching studies.

C. Effect of Sulfuric Acid Concentration

Fig. 2 shows the effect of sulfuric acid concentration on leaching performance of the flotation concentrate in term of copper recovery.

TABLE II
CHEMICAL ANALYSES OF LEACHING PRODUCTS AND COPPER RECOVERY AS A FUNCTION OF LEACHING TIMES

Leaching Time (min)	Product	Grade (% Cu)	Recovery (%)
	Feed	19.0	
1	Leachate	16.2	89.1
	Tailing	2.00	
	Feed	19.5	
2	Leachate	17.0	89.7
	Tailing	1.95	
	Feed	19.5	
3	Leachate	17.8	91.5
	Tailing	1.65	
	Feed	20.4	
4	Leachate	19.4	95.8
	Tailing	0.85	
	Feed	19.9	
5	Leachate	19.4	98.6
	Tailing	0.27	
	Feed	20.4	
10	Leachate	20.2	98.8
	Tailing	0.24	
	Feed	19.5	
15	Leachate	19.4	99.0
	Tailing	0.20	
	Feed	19.7	
30	Leachate	19.5	99.0
	Tailing	0.19	

Typically, hydrometallurgical extraction of copper ores has a direct relationship with the sulfuric acid concentration [5]. As a result, copper recovery increases with the increase of H_2SO_4 concentration up to 10% (w/w), and the recovery remains almost constant after this concentration. Therefore, this concentration was considered as the appropriate condition for further leaching studies.

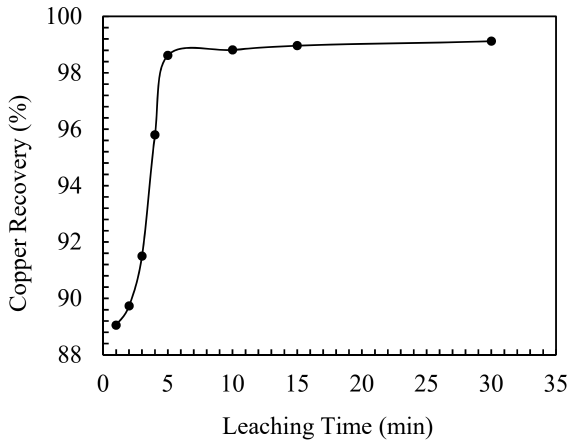

Fig. 1 Copper recovery as a function of leaching time with H_2SO_4 concentration (10% w/w), solid to liquid ratio (1:8), agitation speed (250 rpm) and leaching temperature (30^{o}C)

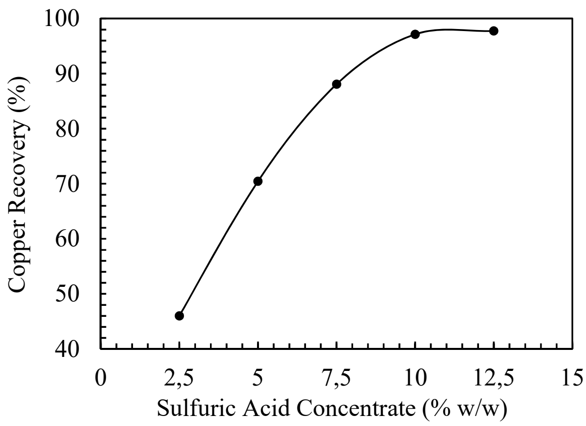

Fig. 2 Copper recovery as a function of H_2SO_4 concentration with leaching time (5 min), solid to liquid ratio (1:8), agitation speed (250 rpm) and leaching temperature (30^{o}C)

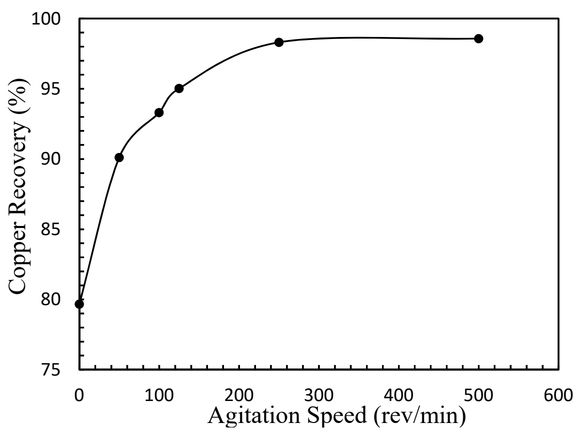

Fig. 3 Copper recovery as a function of agitation speed with leaching time (5 min), H_2SO_4 concentration (10% w/w), solid to liquid ratio (1:8) and leaching temperature (30^{o}C)

D.Effect of Agitation Speed

The effect of agitation speed on copper recovery from the flotation concentrate is illustrated in Fig. 3.

E. Effect of Solid to Liquid Ratio

Fig. 4 illustrates the effect of solid to liquid ratio on the leaching performance. It was found that the copper recovery increases until the ratio is 1:8 where about 98% of copper is recovered. At the ratio higher than 1:8, there is no significant increasing of the recovery.

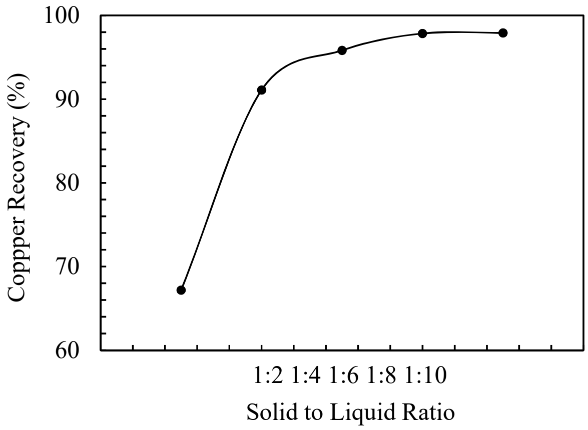

Fig. 4 Copper recovery as a function of solid to liquid ratio with leaching time (5 min), H_2SO_4 concentration (10% w/w), agitation speed (250 rpm) and leaching temperature (30°C).

Shabani et al. [5] also indicated that the copper dissolving is increased by increasing the liquid amount. On the other hand, it is decreased while increasing the amount of solid. Therefore, the solid to liquid ratio of 1:8 was selected as the proper ratio for next studies.

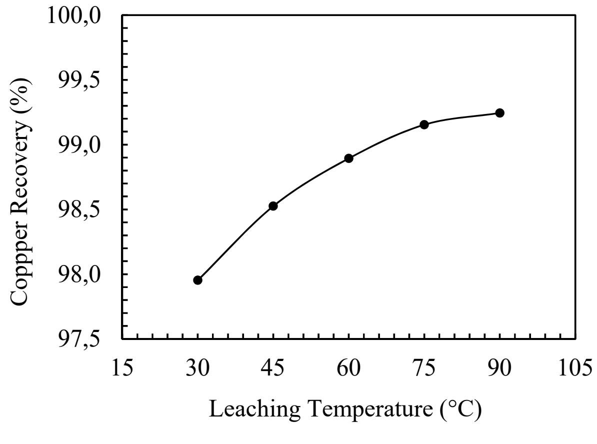

Fig. 5 Copper recovery as a function of leaching temperature with leaching time (5 min), H_2SO_4 concentration (10% w/w), agitation speed (250 rev/min) and solid to liquid ratio (1:8)

F. Effect of Leaching Temperature

The effect of leaching temperature on copper recovery is shown in Fig. 5. As seen from Fig. 5, almost 98% of copper recovery is acquired at 30°C. Further increasing of the temperature from 30°C to 90°C results in less significant amount on the recovery. Only 1.29% of copper can be further recovered. It was implied that most of the copper metal in flotation concentrate is leached out at 30°C. Then 30°C is used as the best leaching temperature in this research.

G.Kinetics of Copper Dissolution

Copper dissolution kinetics can be studied by using integral method suggested by Han [12]. Natural logarithmic of copper concentration (C) and leaching time of the flotation concentrate was plotted in Fig. 6. It can be seen that the first order rate law is quite valid for this leaching process with rate constant of 1.45 mg/L-sec. The initial dissolution of this concentrate may be a diffusion-controlled reaction as described at length by Bingöl and Canbazoğlu [6].

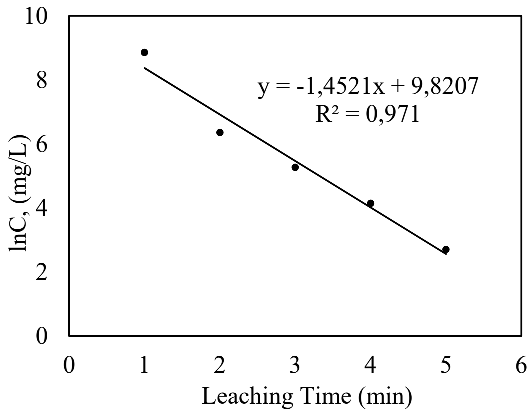

Fig. 6 ln C - time plot of a batch leaching of the flotation concentrate at agitation speed (250 rpm), H_2SO_4 concentration (10% w/w), solid to liquid ratio (1:8), and leaching temperature (30°C)

IV. CONCLUSIONS

The effect of various parameters on the leaching performance of the flotation concentrate in sulfuric acid solution has been determined. Key conclusions obtained from this study are:

1. The most important variable affecting agitation leaching of the concentrate in terms of percentage copper recovery is sulfuric acid concentration.
2. Leaching of the concentrate is also increased with time, agitation speed, and solid to liquid ratio. However, the increase of leaching temperature has no significant effect on copper recovery.
3. The best conditions are 5-min leaching time, 10% (w/w) sulfuric acid, 250 rev/min agitation speed, 1:8 solid to liquid ratio, and 30°C leaching temperature in respect. Under these optimum conditions, leaching of the concentrate in sulfuric acid solution yields about 98% recovery with 20% Cu grade.

4. Copper dissolution kinetics of the concentrate was approximated as a logarithmic function. As a result, the first-order reaction rate is suggested from this leaching study.

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